



▲ The energy produced by this fuel cell can power an entire house.

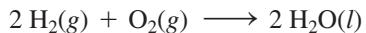


▲ The B-Class F-Cell vehicle from Mercedes Benz is a four passenger sedan that accelerates from 0 to 60 mph in about 9 seconds. The car runs on hydrogen and its only emission is water.

Review Section 4.9 on assigning oxidation states.

heater or a furnace. Similar fuel cells can also power cars. Fuel cells are highly efficient and, although some obstacles to their development and use must yet be overcome, one day they may supply a majority of our power while producing less pollution than fossil fuel combustion.

Fuel cells are based on oxidation–reduction reactions (see Section 4.9). The most common type of fuel cell—called the hydrogen–oxygen fuel cell—is based on the reaction between hydrogen and oxygen:

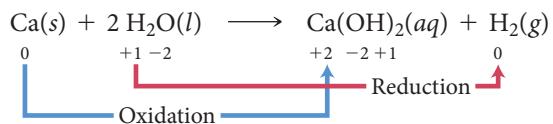


In this reaction, hydrogen and oxygen form covalent bonds with one another. Recall that, according to Lewis theory, a single covalent bond is a shared electron pair. However, since oxygen is more electronegative than hydrogen, the electron pair in a hydrogen–oxygen bond is not *equally* shared: oxygen gets the larger portion (see Section 9.6). In effect, oxygen has more electrons in H_2O than it does in elemental O_2 —it has gained electrons in the reaction and has therefore been reduced.

In a reaction between hydrogen and oxygen, oxygen atoms gain electrons directly from hydrogen atoms. In a hydrogen–oxygen fuel cell, this same redox reaction occurs, but the hydrogen and oxygen are separated, forcing electrons to travel through an external wire to get from hydrogen to oxygen. The moving electrons constitute an electrical current. In this way, fuel cells employ the electron-gaining tendency of oxygen and the electron-losing tendency of hydrogen to force electrons to move through a wire to create the electricity that can provide power for a home or an electric automobile. Smaller fuel cells can also replace batteries and be used to power consumer electronics such as laptop computers, smart phones, and MP3 players. The generation of electricity from spontaneous redox reactions (such as those that occur in a fuel cell) and the use of electricity to drive nonspontaneous redox reactions (such as those that occur in gold or silver plating) are examples of electrochemistry, the subject of this chapter.

18.2 Balancing Oxidation–Reduction Equations

Recall from Section 4.9 that *oxidation* is the loss of electrons, and *reduction* is the gain of electrons. Recall also that we can identify oxidation–reduction reactions through changes in oxidation states: *oxidation corresponds to an increase in oxidation state and reduction corresponds to a decrease in oxidation state*. For example, consider the following reaction between calcium and water:



Because calcium increases in oxidation state from 0 to +2, it is oxidized. Because hydrogen decreases in oxidation state from +1 to 0, it is reduced.

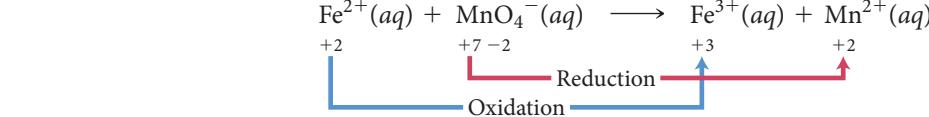
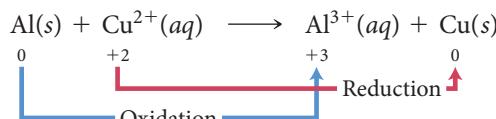
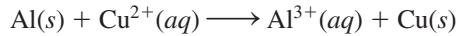
Balancing redox reactions can be more complicated than balancing other types of reactions because both the mass (or number of each type of atom) and the charge must be balanced. We can balance redox reactions occurring in aqueous solutions with a special procedure called the *half-reaction method of balancing*. In this procedure, we break down the overall equation into two half-reactions: one for oxidation and one for reduction. We then balance the half-reactions individually and add them together. The steps differ slightly for reactions occurring in acidic and in basic solution. Examples 18.1 and 18.2 demonstrate the method for an acidic solution, and Example 18.3 demonstrates the method for a basic solution.

PROCEDURE FOR...**Half-Reaction Method of Balancing Aqueous Redox Equations in Acidic Solution****GENERAL PROCEDURE**

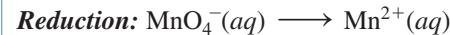
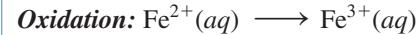
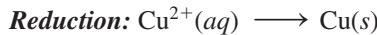
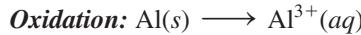
Step 1 Assign oxidation states to all atoms and identify the substances being oxidized and reduced.

EXAMPLE 18.1**Half-Reaction Method of Balancing Aqueous Redox Equations in Acidic Solution**

Balance the redox equation:



Step 2 Separate the overall reaction into two half-reactions: one for oxidation and one for reduction.

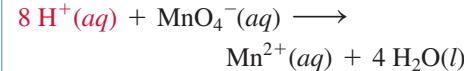
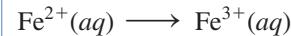


Step 3 Balance each half-reaction with respect to mass in the following order:

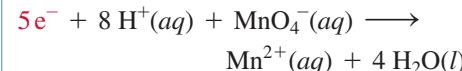
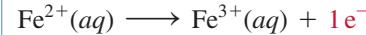
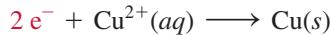
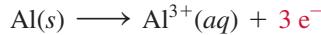
- Balance all elements other than H and O.
- Balance O by adding H_2O .
- Balance H by adding H^+ .

All elements are balanced, so proceed to the next step.

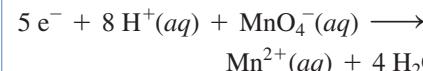
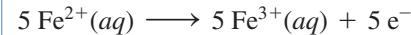
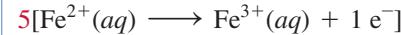
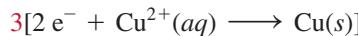
All elements other than H and O are balanced so proceed to balance H and O.



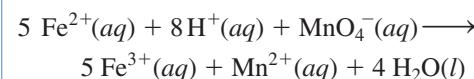
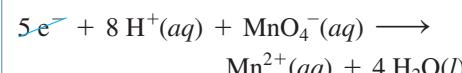
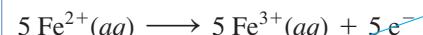
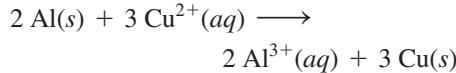
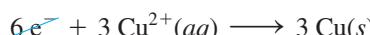
Step 4 Balance each half-reaction with respect to charge by adding electrons. (Make the sum of the charges on both sides of the equation equal by adding as many electrons as necessary.)



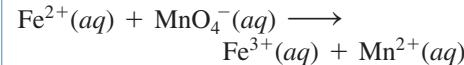
Step 5 Make the number of electrons in both half-reactions equal by multiplying one or both half-reactions by a small whole number.



Step 6 Add the two half-reactions together, canceling electrons and other species as necessary.

**EXAMPLE 18.2****Half-Reaction Method of Balancing Aqueous Redox Equations in Acidic Solution**

Balance the redox equation:



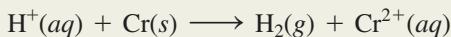
Step 7 Verify that the reaction is balanced both with respect to mass and with respect to charge.

Reactants	Products
2 Al	2 Al
3 Cu	3 Cu
+6 charge	+6 charge

Reactants	Products
5 Fe	5 Fe
8 H	8 H
1 Mn	1 Mn
4 O	4 O
+17 charge	+17 charge

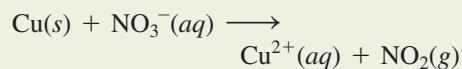
FOR PRACTICE 18.1

Balance the redox reaction in acidic solution:



FOR PRACTICE 18.2

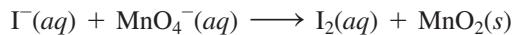
Balance the redox reaction in acidic solution:



When a redox reaction occurs in basic solution, we balance the reaction in a similar manner, except that we add an additional step to neutralize any H^+ with OH^- . The H^+ and the OH^- combine to form H_2O as shown in Example 18.3.

EXAMPLE 18.3 Balancing Redox Reactions Occurring in Basic Solution

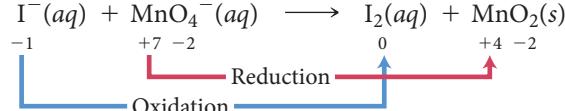
Balance the equation occurring in basic solution:



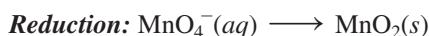
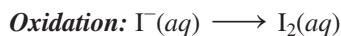
SOLUTION

To balance redox reactions occurring in basic solution, follow the half-reaction method outlined in Examples 18.1 and 18.2, but add an extra step to neutralize the acid with OH^- as shown in step 3.

1. Assign oxidation states.

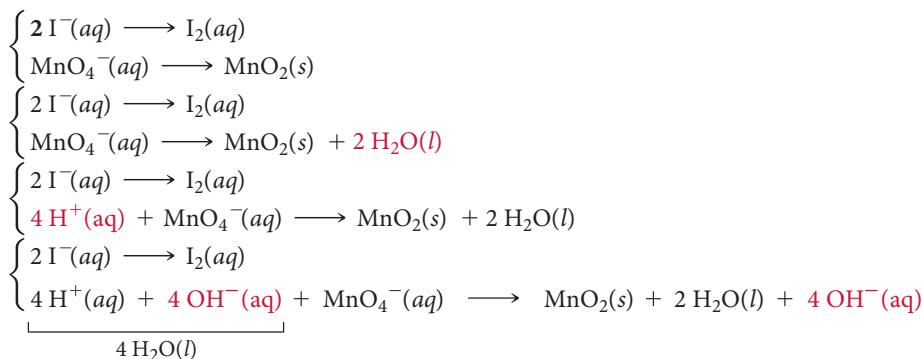


2. Separate the overall reaction into two half-reactions.



3. Balance each half-reaction with respect to mass.

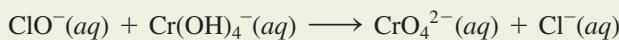
- Balance all elements other than H and O.
- Balance O by adding H_2O .
- Balance H by adding H^+ .
- Neutralize H^+ by adding enough OH^- to neutralize each H^+ . Add the same number of OH^- ions to each side of the equation.



4. Balance each half-reaction with respect to charge.	$2 \text{I}^-(\text{aq}) \longrightarrow \text{I}_2(\text{aq}) + 2 \text{e}^-$ $4 \text{H}_2\text{O}(\text{l}) + \text{MnO}_4^-(\text{aq}) + 3 \text{e}^- \longrightarrow \text{MnO}_2(\text{s}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{OH}^-(\text{aq})$												
5. Make the number of electrons in both half-reactions equal.	$3[2 \text{I}^-(\text{aq}) \longrightarrow \text{I}_2(\text{aq}) + 2 \text{e}^-]$ $6 \text{I}^-(\text{aq}) \longrightarrow 3 \text{I}_2(\text{aq}) + 6 \text{e}^-$ $2[4 \text{H}_2\text{O}(\text{l}) + \text{MnO}_4^-(\text{aq}) + 3 \text{e}^- \longrightarrow \text{MnO}_2(\text{s}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{OH}^-(\text{aq})]$ $8 \text{H}_2\text{O}(\text{l}) + 2 \text{MnO}_4^-(\text{aq}) + 6 \text{e}^- \longrightarrow 2 \text{MnO}_2(\text{s}) + 4 \text{H}_2\text{O}(\text{l}) + 8 \text{OH}^-(\text{aq})$												
6. Add the half-reactions together.	$6 \text{I}^-(\text{aq}) \longrightarrow 3 \text{I}_2(\text{aq}) + 6 \text{e}^-$ $48 \text{H}_2\text{O}(\text{l}) + 2 \text{MnO}_4^-(\text{aq}) + 6 \text{e}^- \longrightarrow 2 \text{MnO}_2(\text{s}) + 4 \cancel{\text{H}_2\text{O}(\text{l})} + 8 \text{OH}^-(\text{aq})$ <hr/> $6 \text{I}^-(\text{aq}) + 4 \text{H}_2\text{O}(\text{l}) + 2 \text{MnO}_4^-(\text{aq}) \longrightarrow 3 \text{I}_2(\text{aq}) + 2 \text{MnO}_2(\text{s}) + 8 \text{OH}^-(\text{aq})$												
7. Verify that the reaction is balanced.	<table border="1"> <thead> <tr> <th>Reactants</th> <th>Products</th> </tr> </thead> <tbody> <tr> <td>6 I</td> <td>6 I</td> </tr> <tr> <td>8 H</td> <td>8 H</td> </tr> <tr> <td>2 Mn</td> <td>2 Mn</td> </tr> <tr> <td>12 O</td> <td>12 O</td> </tr> <tr> <td>-8 charge</td> <td>-8 charge</td> </tr> </tbody> </table>	Reactants	Products	6 I	6 I	8 H	8 H	2 Mn	2 Mn	12 O	12 O	-8 charge	-8 charge
Reactants	Products												
6 I	6 I												
8 H	8 H												
2 Mn	2 Mn												
12 O	12 O												
-8 charge	-8 charge												

FOR PRACTICE 18.3

Balance the following redox reaction occurring in basic solution.



18.3 Voltaic (or Galvanic) Cells: Generating Electricity from Spontaneous Chemical Reactions

Electrical current is the flow of electric charge. Electrons flowing through a wire or ions flowing through a solution both constitute electrical current. Since redox reactions involve the transfer of electrons from one substance to another, they have the potential to generate electrical current as we discussed in Section 18.1. For example, consider the spontaneous redox reaction:

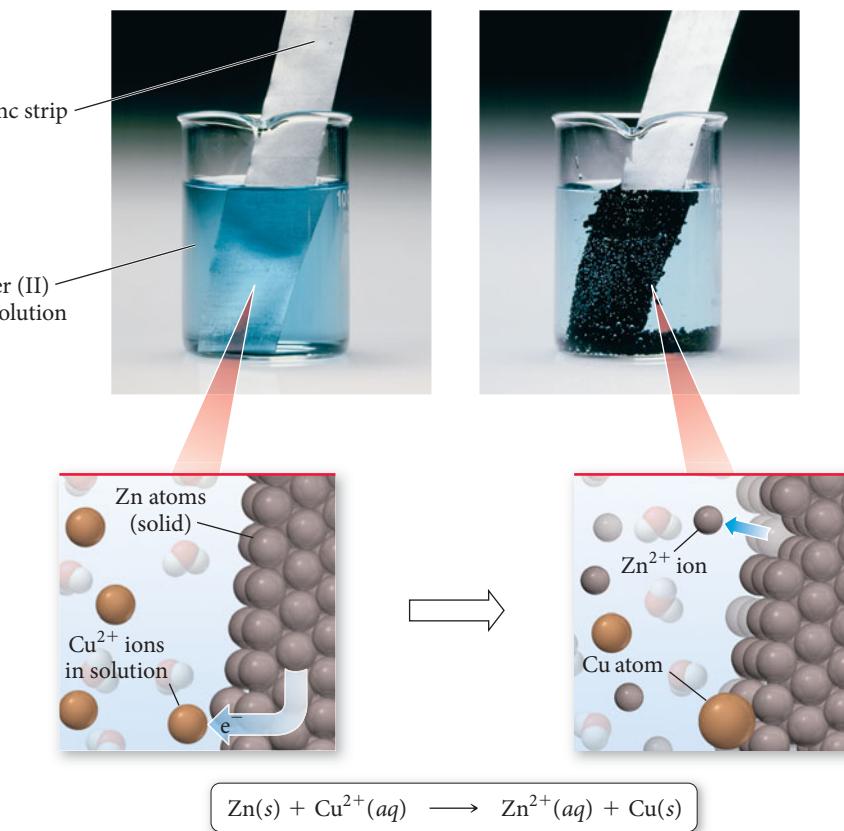


When Zn metal is placed in a Cu^{2+} solution, the greater tendency of zinc to lose electrons results in Zn being oxidized and Cu^{2+} being reduced. Electrons are transferred directly from the Zn to the Cu^{2+} (Figure 18.1 ▶). Although the actual process is more complicated, we can imagine that—on the atomic scale—a zinc atom within the zinc metal transfers two electrons to a copper ion in solution. The zinc atom then becomes a zinc ion dissolved in the solution. The copper ion accepts the two electrons and is deposited on the zinc as solid copper.

Suppose we could separate the zinc atoms and copper ions and force the electron transfer to occur another way—not directly from the zinc atom to the copper ion, but through a wire connecting the two half-reactions. The flowing electrons would constitute an electrical current and could be used to do electrical work.

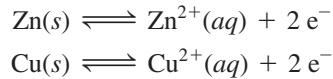
► FIGURE 18.1 A Spontaneous Oxidation-Reduction Reaction When zinc is immersed in a solution containing copper ions, the zinc atoms transfer electrons to the copper ions. The zinc atoms are oxidized and dissolve in the solution. The copper ions are reduced and are deposited on the electrode.

A Spontaneous Redox Reaction: Zn + Cu²⁺



The generation of electricity through redox reactions is normally carried out in a device called an **electrochemical cell**. A **voltaic (or galvanic) cell**, is an electrochemical cell that *produces* electrical current from a *spontaneous* chemical reaction. A second type of electrochemical cell, called an **electrolytic cell**, *consumes* electrical current to drive a *nonspontaneous* chemical reaction. We discuss voltaic cells in this section and electrolytic cells in Section 18.8.

In the voltaic cell in Figure 18.2 ►, a solid strip of zinc is placed in a Zn(NO₃)₂ solution to form a **half-cell**. A solid strip of copper placed in a Cu(NO₃)₂ solution forms a second half-cell. The strips act as **electrodes**, conductive surfaces through which electrons can enter or leave the half-cells. Each metal strip reaches equilibrium with its ions in solution according to these half-reactions:



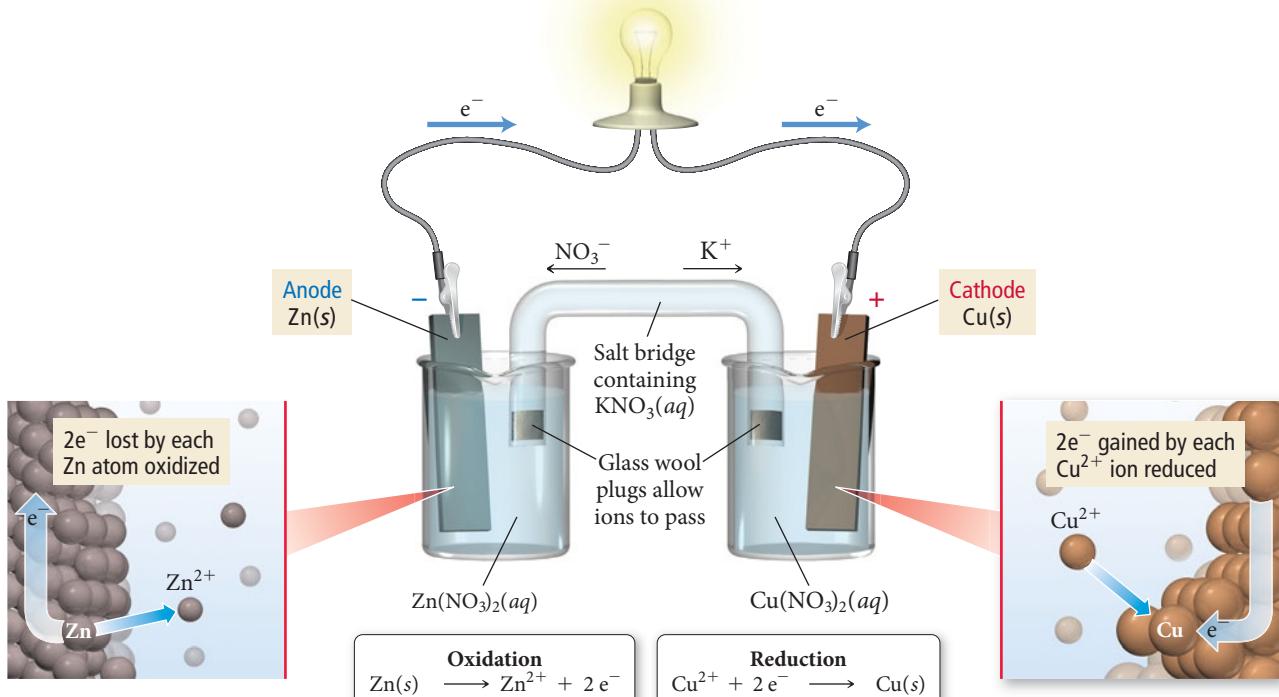
However, the position of these equilibria is not the same for both metals. As we have just seen, the zinc has a greater tendency to ionize than the copper, so the zinc half-reaction lies further to the right. As a result, the zinc electrode becomes negatively charged relative to the copper electrode.

If the two half-cells are connected by a wire running from the zinc—through a lightbulb or other electrical device—to the copper, electrons spontaneously flow from the zinc electrode (which is more negatively charged and therefore repels electrons) to the copper electrode. As the electrons flow away from the zinc electrode, the Zn/Zn²⁺ equilibrium shifts to the right (according to Le Châtelier's principle) and oxidation occurs. As electrons flow to the copper electrode, the Cu/Cu²⁺ equilibrium shifts to the left, and reduction occurs. The flowing electrons constitute an electrical current that lights the bulb.

The continual flow of electrical current in a voltaic cell requires a pathway by which counterions can flow to neutralize charge build-up; this is discussed later.

The idea that one electrode in a voltaic cell becomes more negatively charged relative to the other electrode due to differences in ionization tendencies is central to understanding how a voltaic cell works.

A Voltaic Cell



▲ FIGURE 18.2 A Voltaic Cell The tendency of zinc to transfer electrons to copper results in a flow of electrons through the wire that lights the bulb. The movement of electrons from the zinc anode to the copper cathode creates a positive charge buildup at the zinc half-cell and a negative charge buildup at the copper half-cell. The flow of ions within the salt bridge neutralizes this charge buildup, allowing the reaction to continue.

We can understand electrical current and why it flows by analogy with water current in a stream (Figure 18.3 ▶). The *rate of electrons flowing* through a wire is analogous to the *rate of water moving* through a stream. Electrical current is measured in units of **ampères (A)**, also called *amps*. One ampere represents the flow of one coulomb (a measure of electrical charge) per second.

The ampere is often abbreviated as *amp*.

$$1 \text{ A} = 1 \text{ C/s}$$

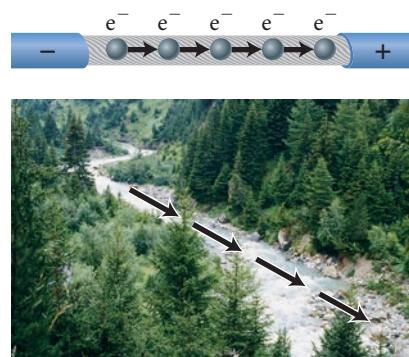
Because an electron has a charge of $1.602 \times 10^{-19} \text{ C}$, 1 A corresponds to the flow of 6.242×10^{18} electrons per second.

The *driving force* for electrical current is analogous to the driving force for water current. Water current is driven by a difference in gravitational potential energy (caused by a gravitational field). Streams flow downhill, from higher to lower potential energy. Electrical current is also driven by a difference in potential energy (caused by an electric field resulting from the charge difference on the two electrodes) called **potential difference**. *Potential difference is a measure of the difference in potential energy (usually in joules) per unit of charge (coulombs)*. The SI unit of potential difference is the **volt (V)**, which is equal to one joule per coulomb.

$$1 \text{ V} = 1 \text{ J/C}$$

In other words, a potential difference of one volt indicates that a charge of one coulomb experiences an energy difference of one joule between the two electrodes.

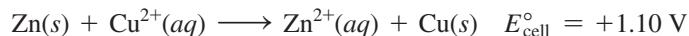
A large potential difference corresponds to a large difference in charge between the two electrodes and therefore a strong tendency for electron flow (analogous to a steeply descending streambed). Potential difference, since it gives rise to the force that results in the motion of electrons, is also referred to as **electromotive force (emf)**.



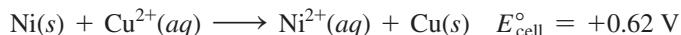
▲ FIGURE 18.3 An Analogy for Electrical Current Just as water flows downhill in response to a difference in gravitational potential energy, electrons flow through a conductor in response to an electrical potential difference, creating an electrical current.

In a voltaic cell, the potential difference between the two electrodes is the **cell potential (E_{cell})** or **cell emf**. The cell potential depends on the relative tendencies of the reactants to undergo oxidation and reduction. Combining the oxidation of a substance with a strong tendency to undergo oxidation and the reduction of a substance with a strong tendency to undergo reduction produces a large difference in charge between the two electrodes and therefore a high positive cell potential.

In general, the cell potential also depends on the concentrations of the reactants and products in the cell and the temperature (which we will assume to be 25 °C unless otherwise noted). Under standard conditions (1 M concentration for reactants in solution and 1 atm pressure for gaseous reactants), the cell potential is called the **standard cell potential (E_{cell}°)** or **standard emf**. For example, the standard cell potential in the zinc and copper cell described previously is 1.10 volts.



If the zinc is replaced with nickel (which has a lower tendency to be oxidized) the cell potential is lower.



The cell potential is a measure of the overall tendency of the redox reaction to occur spontaneously—the lower the cell potential, the lower the tendency to occur. A negative cell potential indicates that the forward reaction is not spontaneous.

In all electrochemical cells, we call the electrode where oxidation occurs the **anode** and the electrode where reduction occurs the **cathode**. In a voltaic cell, the anode is the more negatively charged electrode and we label it with a negative (−) sign. The cathode of a voltaic cell is the more positively charged electrode and we label it with a (+) sign. Electrons flow from the anode to the cathode (from negative to positive) through the wires connecting the electrodes.

As electrons flow out of the anode, positive ions (Zn^{2+} in the preceding example) form in the oxidation half-cell, resulting in a buildup of *positive charge* in the *solution*. As electrons flow into the cathode, positive ions (Cu^{2+} in the preceding example) are reduced at the reduction half-cell, resulting in a buildup of *negative charge* in the *solution*.

If the movement of electrons from anode to cathode were the only flow of charge, the build up of the opposite charge in the solution would stop electron flow almost immediately. The cell needs a pathway by which counterions can flow between the half-cells without the solutions in the half-cells totally mixing. One such pathway is a **salt bridge**, an inverted, U-shaped tube that contains a strong electrolyte such as KNO_3 and connects the two half-cells (see Figure 18.2). The electrolyte is usually suspended in a gel and held within the tube by permeable stoppers. The salt bridge allows a flow of ions that neutralizes the charge buildup in the solution. *The negative ions within the salt bridge flow to neutralize the accumulation of positive charge at the anode, and the positive ions flow to neutralize the accumulation of negative charge at the cathode.* In other words, the salt bridge completes the circuit, allowing electrical current to flow.

Conceptual Connection 18.1 Voltaic Cells

In a voltaic cell, electrons flow

- (a) from the more negatively charged electrode to the more positively charged electrode.
- (b) from the more positively charged electrode to the more negatively charged electrode.
- (c) from lower potential energy to higher potential energy.

Electrochemical Cell Notation

We can represent electrochemical cells with a compact notation called a *cell diagram* or *line notation*. For example, we can represent the electrochemical cell discussed previously in which Zn is oxidized to Zn^{2+} and Cu^{2+} is reduced to Cu as follows:



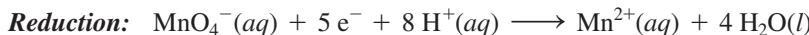
In this representation,

- we write the oxidation half-reaction on the left and the reduction on the right. A double vertical line, indicating the salt bridge, separates the two half-reactions.
- substances in different phases are separated by a single vertical line, which represents the boundary between the phases.
- for some redox reactions, the reactants and products of one or both of the half-reactions may be in the same phase. In these cases (which are explained further next), we separate the reactants and products from each other with a comma in the line diagram. Such cells use an inert electrode, such as platinum (Pt) or graphite, as the anode or cathode (or both).

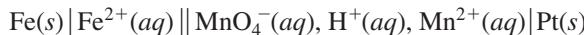
Consider the redox reaction in which $\text{Fe}(s)$ is oxidized and $\text{MnO}_4^-(aq)$ is reduced:



The half-reactions for this overall reaction are:

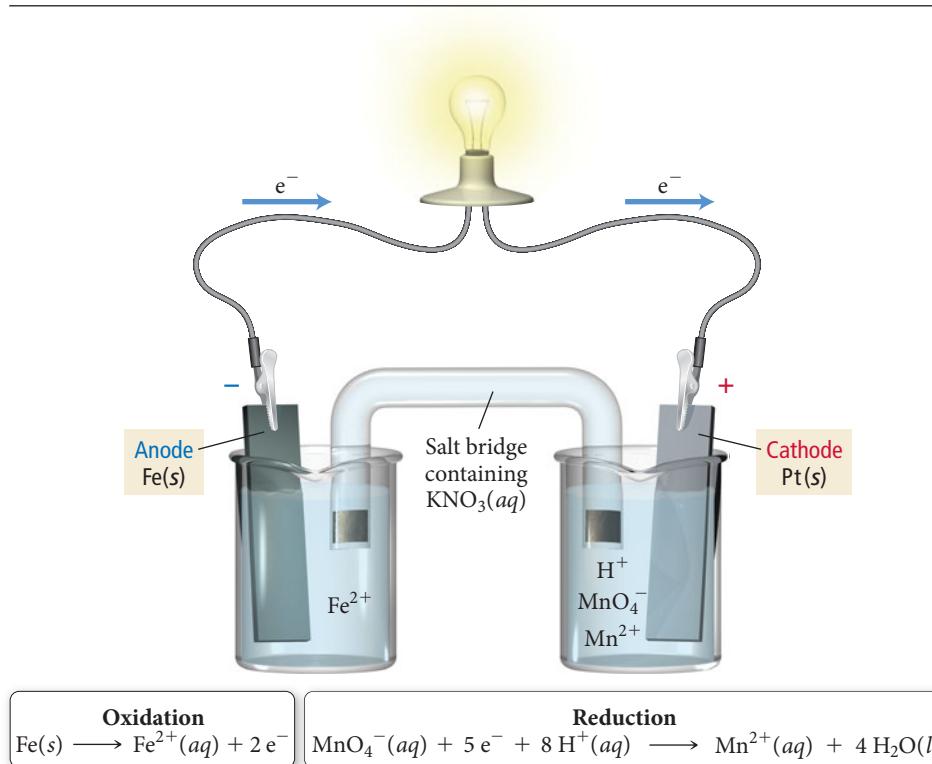


Notice that in the reduction half-reaction the principal species are all in the aqueous phase. In this case, the electron transfer needs an electrode on which to occur. An inert platinum electrode is employed, and the electron transfer takes place at its surface. Using line notation, we represent the electrochemical cell corresponding to the above reaction as:

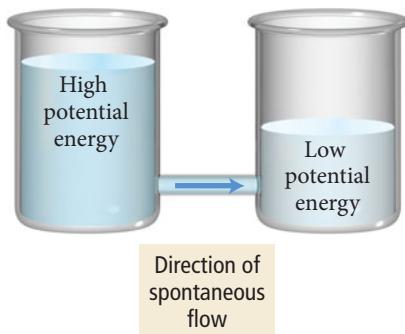


The $\text{Pt}(s)$ on the far right indicates that an inert platinum electrode acts as the cathode in this reaction, as depicted in Figure 18.4 ▼.

Inert Platinum Electrode



◀ FIGURE 18.4 Inert Platinum Electrode
When the participants in a half-reaction are all in the aqueous phase, a conductive surface is needed for electron transfer to take place. In such cases an inert electrode of graphite or platinum is often used. In this electrochemical cell, an iron strip acts as the anode and a platinum strip acts as the cathode. Iron is oxidized at the anode and MnO_4^- is reduced at the cathode.



▲ FIGURE 18.5 An Analogy for Electrode Potential

18.4 Standard Electrode Potentials

As we have just seen, the standard cell potential (E_{cell}°) for an electrochemical cell depends on the specific half-reactions occurring in the half-cells and is a measure of the potential energy difference (per unit charge) between the two electrodes. We can think of the electrode in each half-cell as having its own individual potential, called the **standard electrode potential**. The overall standard cell potential (E_{cell}°) is the difference between the two standard electrode potentials.

We can better understand this idea with an analogy. Consider two water tanks with different water levels connected by a common pipe, as shown in Figure 18.5 ▲. The water in each tank has its own level and corresponding potential energy. When the tanks are connected, water flows from the tank with the higher level (higher potential energy) to the tank with a lower water level (lower potential energy). Similarly, each half-cell in an electrochemical cell has its own charge and corresponding electrode potential. *When the cells are connected, electrons flow from the electrode with more negative charge (greater potential energy) to the electrode with more positive charge (less potential energy).*

One limitation to this analogy is that, unlike the water level in a tank, we cannot measure the electrode potential in a half-cell directly—we can only measure the overall potential that occurs when two half-cells are combined in a whole cell. However, we can arbitrarily assign a potential of zero to the electrode in a *particular* type of half-cell and then measure all other electrode potentials relative to that zero.

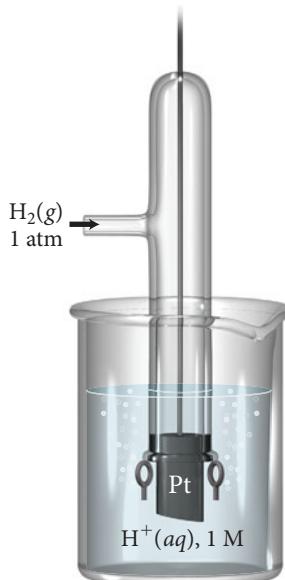
The half-cell electrode that is normally chosen to have a potential of zero is the **standard hydrogen electrode (SHE)**. This half-cell consists of an inert platinum electrode immersed in 1 M HCl with hydrogen gas at 1 atm bubbling through the solution, as shown in Figure 18.6 ▼. When the SHE acts as the cathode, the following half-reaction occurs:



If we connect the standard hydrogen electrode to an electrode in another half-cell of interest, we can measure the potential difference (or voltage) between the two electrodes. Since we assigned the standard hydrogen electrode zero voltage, we can now determine the electrode potential of the other half-cell.

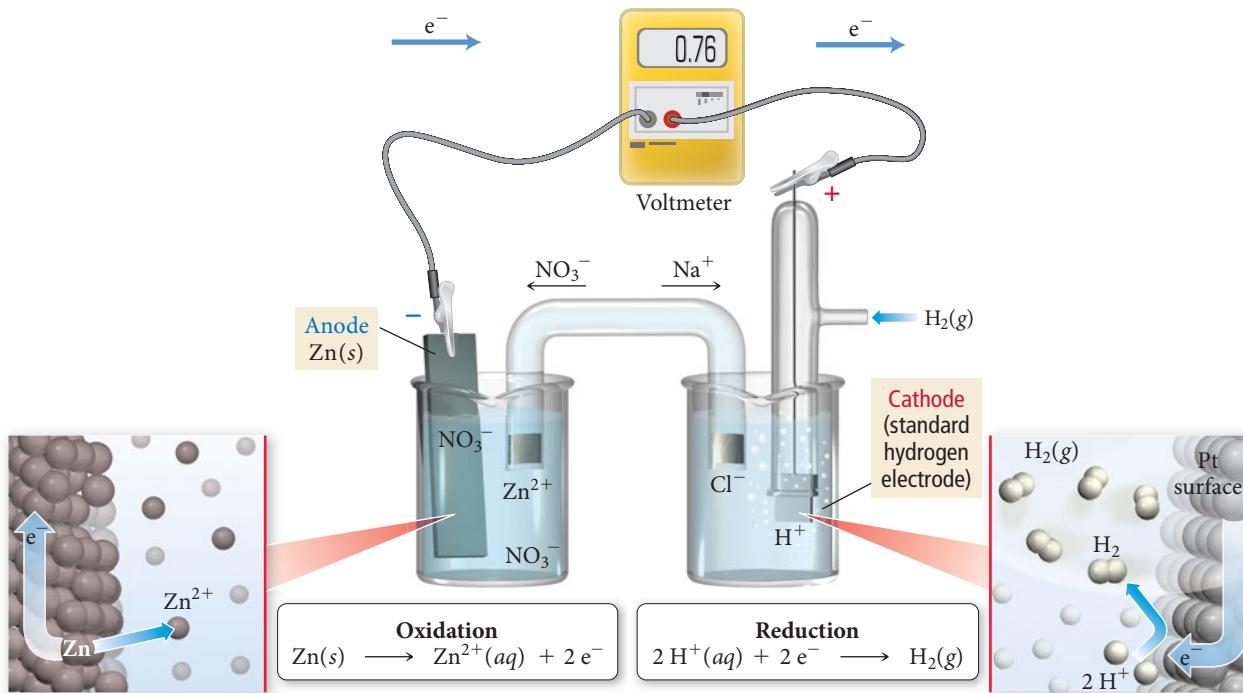
For example, consider the electrochemical cell shown in Figure 18.7 ▷. In this electrochemical cell, Zn is oxidized to Zn^{2+} and H^{+} is reduced to H_2 under standard conditions (all solutions are 1 M in concentration and all gases are 1 atm in pressure) and

Standard Hydrogen Electrode (SHE)



► FIGURE 18.6 The Standard Hydrogen Electrode The standard hydrogen electrode (SHE) is arbitrarily assigned an electrode potential of zero. All other electrode potentials are then measured relative to the SHE.

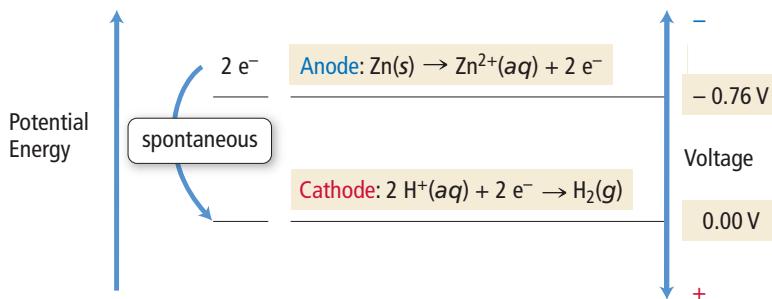
Measuring Half-Cell Potential with the SHE



at 25 °C. Electrons travel from the anode (where oxidation occurs) to the cathode (where reduction occurs), so we define E_{cell}° as *the difference in voltage between the cathode (final state) and the anode (initial state)*.

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{final}}^{\circ} - E_{\text{initial}}^{\circ} \\ &= E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} \end{aligned}$$

The measured cell potential for this cell is +0.76 V. The anode (in this case, Zn/Zn²⁺) is at a more negative voltage (higher potential energy) than the cathode (in this case, the SHE). Therefore, electrons spontaneously flow from the anode to the cathode. We can diagram the potential energy and the voltage as follows:



Referring back to our water tank analogy, the zinc half-cell is like the water tank with the higher water level, and electrons therefore flow from the zinc electrode to the standard hydrogen electrode.

Because we assigned the SHE a potential of zero (0.00 V), we can determine the electrode potential for the Zn/Zn²⁺ half-cell (the anode) from the measured cell potential (E_{cell}°).

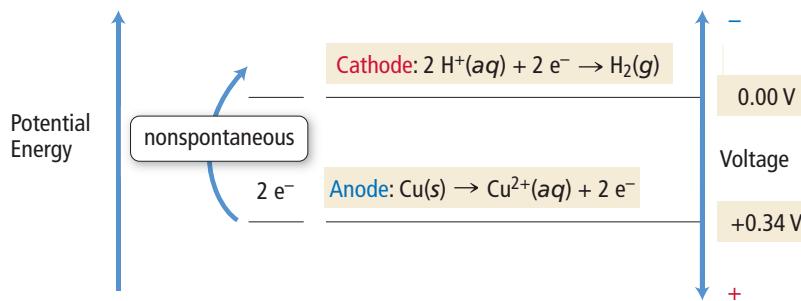
$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} \\ 0.76 \text{ V} &= 0.00 \text{ V} - E_{\text{anode}}^{\circ} \\ E_{\text{anode}}^{\circ} &= -0.76 \text{ V} \end{aligned}$$

The potential for the Zn/Zn²⁺ electrode is *negative*. The negative potential indicates that an electron at the Zn/Zn²⁺ electrode has greater potential energy than it does at the SHE. Remember that the more negative the electrode potential is, the greater the potential energy of an electron at that electrode (because negative charge repels electrons).

▲ **FIGURE 18.7** Measuring Electrode Potential Because the electrode potential of the SHE is zero, the electrode potential for the oxidation of Zn is equal to the cell potential.

What would happen if we connected an electrode in which the electron has *more positive* potential (than the standard hydrogen electrode) to the standard hydrogen electrode? That electrode would then have a more *positive* voltage (lower potential energy for an electron).

For example, suppose we connect the standard hydrogen electrode to a Cu electrode immersed in a 1 M Cu^{2+} solution. The measured cell potential for this cell is -0.34 V . The anode (defined as Cu/Cu^{2+}) is at a more positive voltage (lower potential energy) than the cathode (the SHE). Therefore, electrons will *not* spontaneously flow from the anode to the cathode. We can diagram the potential energy and the voltage of this cell as follows:



The copper half-cell is like the water tank with the lower water level and electrons *do not* spontaneously flow from the copper electrode to the standard hydrogen electrode.

We can again determine the electrode potential for the Cu/Cu^{2+} half-cell (the anode) from the measured cell potential.

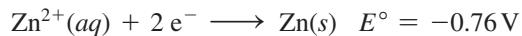
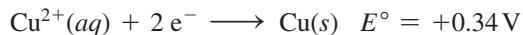
$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

$$-0.34 \text{ V} = 0.00 \text{ V} - E_{\text{anode}}^{\circ}$$

$$E_{\text{anode}}^{\circ} = +0.34 \text{ V}$$

The potential for the Cu/Cu^{2+} electrode is *positive*. The positive potential indicates that an electron at the Cu/Cu^{2+} electrode has *lower* potential energy than it does at the SHE. The more positive the electrode potential, the lower the potential energy of an electron at that electrode (because positive charge attracts electrons).

By convention, standard electrode potentials are written for *reduction* half-reactions. We write the standard electrode potentials for the two half-reactions just discussed as:



We can see that the Cu/Cu^{2+} electrode is positive relative to the SHE (and will therefore tend to draw electrons *away* from the SHE), and that the Zn/Zn^{2+} electrode is negative relative to the SHE (and will therefore tend to repel electrons towards the SHE). The standard electrode potentials for a number of common half-reactions are listed in Table 18.1.

Summarizing Standard Electrode Potentials:

- ▶ The electrode potential of the standard hydrogen electrode (SHE) is exactly zero.
- ▶ The electrode in any half-cell with a greater tendency to undergo reduction is positively charged relative to the SHE and therefore has a positive E° .
- ▶ The electrode in any half-cell with a lesser tendency to undergo reduction (or greater tendency to undergo oxidation) is negatively charged relative to the SHE and therefore has a negative E° .
- ▶ The cell potential of any electrochemical cell (E_{cell}°) is the difference between the electrode potentials of the cathode and the anode ($E_{\text{cell}}^{\circ} = E_{\text{cat}}^{\circ} - E_{\text{an}}^{\circ}$).
- ▶ E_{cell}° is positive for spontaneous reactions and negative for nonspontaneous reactions.

TABLE 18.1 Standard Electrode Potentials at 25 °C

Reduction Half-Reaction		$E^\circ(V)$
Stronger oxidizing agent		
$F_2(g) + 2 e^- \longrightarrow 2 F^-(aq)$	2.87	
$H_2O_2(aq) + 2 H^+(aq) + 2 e^- \longrightarrow 2 H_2O(l)$	1.78	
$PbO_2(s) + 4 H^+(aq) + SO_4^{2-}(aq) + 2 e^- \longrightarrow PbSO_4(s) + 2 H_2O(l)$	1.69	
$MnO_4^-(aq) + 4 H^+(aq) + 3 e^- \longrightarrow MnO_2(s) + 2 H_2O(l)$	1.68	
$MnO_4^-(aq) + 8 H^+(aq) + 5 e^- \longrightarrow Mn^{2+}(aq) + 4 H_2O(l)$	1.51	
$Au^{3+}(aq) + 3 e^- \longrightarrow Au(s)$	1.50	
$PbO_2(s) + 4 H^+(aq) + 2 e^- \longrightarrow Pb^{2+}(aq) + 2 H_2O(l)$	1.46	
$Cl_2(g) + 2 e^- \longrightarrow 2 Cl^-(aq)$	1.36	
$Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e^- \longrightarrow 2 Cr^{3+}(aq) + 7 H_2O(l)$	1.33	
$O_2(g) + 4 H^+(aq) + 4 e^- \longrightarrow 2 H_2O(l)$	1.23	
$MnO_2(s) + 4 H^+(aq) + 2 e^- \longrightarrow Mn^{2+}(aq) + 2 H_2O(l)$	1.21	
$I_2O_3^-(aq) + 6 H^+(aq) + 5 e^- \longrightarrow \frac{1}{2}I_2(aq) + 3 H_2O(l)$	1.20	
$Br_2(l) + 2 e^- \longrightarrow 2 Br^-(aq)$	1.09	
$VO_2^+(aq) + 2 H^+(aq) + e^- \longrightarrow VO^{2+}(aq) + H_2O(l)$	1.00	
$NO_3^-(aq) + 4 H^+(aq) + 3 e^- \longrightarrow NO(g) + 2 H_2O(l)$	0.96	
$ClO_2(g) + e^- \longrightarrow ClO_2^-(aq)$	0.95	
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	0.80	
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	0.77	
$O_2(g) + 2 H^+(aq) + 2 e^- \longrightarrow H_2O_2(aq)$	0.70	
$MnO_4^-(aq) + e^- \longrightarrow MnO_4^{2-}(aq)$	0.56	
$I_2(s) + 2 e^- \longrightarrow 2 I^-(aq)$	0.54	
$Cu^+(aq) + e^- \longrightarrow Cu(s)$	0.52	
$O_2(g) + 2 H_2O(l) + 4 e^- \longrightarrow 4 OH^-(aq)$	0.40	
$Cu^{2+}(aq) + 2 e^- \longrightarrow Cu(s)$	0.34	
$SO_4^{2-}(aq) + 4 H^+(aq) + 2 e^- \longrightarrow H_2SO_3(aq) + H_2O(l)$	0.20	
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	0.16	
$Sn^{4+}(aq) + 2 e^- \longrightarrow Sn^{2+}(aq)$	0.15	
$2 H^+(aq) + 2 e^- \longrightarrow H_2(g)$	0	
Weak reducing agent		
$Fe^{3+}(aq) + 3 e^- \longrightarrow Fe(s)$	-0.036	
$Pb^{2+}(aq) + 2 e^- \longrightarrow Pb(s)$	-0.13	
$Sn^{2+}(aq) + 2 e^- \longrightarrow Sn(s)$	-0.14	
$Ni^{2+}(aq) + 2 e^- \longrightarrow Ni(s)$	-0.23	
$Cd^{2+}(aq) + 2 e^- \longrightarrow Cd(s)$	-0.40	
$Fe^{2+}(aq) + 2 e^- \longrightarrow Fe(s)$	-0.45	
$Cr^{3+}(aq) + e^- \longrightarrow Cr^{2+}(aq)$	-0.50	
$Cr^{3+}(aq) + 3 e^- \longrightarrow Cr(s)$	-0.73	
$Zn^{2+}(aq) + 2 e^- \longrightarrow Zn(s)$	-0.76	
$2 H_2O(l) + 2 e^- \longrightarrow H_2(g) + 2 OH^-(aq)$	-0.83	
$Mn^{2+}(aq) + 2 e^- \longrightarrow Mn(s)$	-1.18	
$Al^{3+}(aq) + 3 e^- \longrightarrow Al(s)$	-1.66	
$Mg^{2+}(aq) + 2 e^- \longrightarrow Mg(s)$	-2.37	
$Na^+(aq) + e^- \longrightarrow Na(s)$	-2.71	
$Ca^{2+}(aq) + 2 e^- \longrightarrow Ca(s)$	-2.76	
$Ba^{2+}(aq) + 2 e^- \longrightarrow Ba(s)$	-2.90	
$K^+(aq) + e^- \longrightarrow K(s)$	-2.92	
$Li^+(aq) + e^- \longrightarrow Li(s)$	-3.04	

Example 18.4 shows how to calculate the potential of an electrochemical cell from the standard electrode potentials of the half-reactions.

EXAMPLE 18.4 Calculating Standard Potentials for Electrochemical Cells from Standard Electrode Potentials of the Half-Reactions

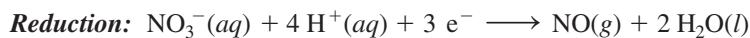
Use tabulated standard electrode potentials to calculate the standard cell potential for the following reaction occurring in an electrochemical cell at 25 °C. (The equation is balanced.)



SOLUTION

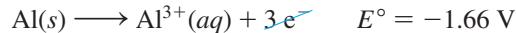
Begin by separating the reaction into oxidation and reduction half-reactions. (In this case, you can readily see that $\text{Al}(s)$ is oxidized. In cases where it is not so apparent, you may want to assign oxidation states to determine the correct half-reactions.)

Look up the standard electrode potentials for each half-reaction in Table 18.1. Add the half-cell reactions together to obtain the overall redox equation. Calculate the standard cell potential by subtracting the electrode potential of the anode from the electrode potential of the cathode.

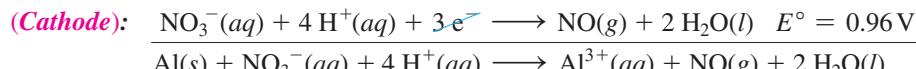


Oxidation

(Anode):



Reduction



$$\begin{aligned} E_{\text{cell}}^\circ &= E_{\text{cat}}^\circ - E_{\text{an}}^\circ \\ &= 0.96 \text{ V} - (-1.66 \text{ V}) \\ &= 2.62 \text{ V} \end{aligned}$$

FOR PRACTICE 18.4

Use tabulated standard electrode potentials to calculate the standard cell potential for the following reaction occurring in an electrochemical cell at 25 °C. (The equation is balanced.)



Conceptual Connection 18.2 Standard Electrode Potentials

An electrode has a negative electrode potential. Which statement is correct regarding the potential energy of an electron at this electrode?

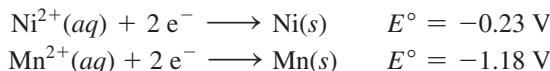
- (a) An electron at this electrode has a lower potential energy than it has at a standard hydrogen electrode.
- (b) An electron at this electrode has a higher potential energy than it has at a standard hydrogen electrode.
- (c) An electron at this electrode has the same potential energy as it has at a standard hydrogen electrode.

Predicting the Spontaneous Direction of an Oxidation–Reduction Reaction

To determine the spontaneous direction of an oxidation–reduction reaction, examine the electrode potentials of the two relevant half-reactions in Table 18.1. The half-reaction with the more *negative* electrode potential tends to lose electrons and therefore undergo

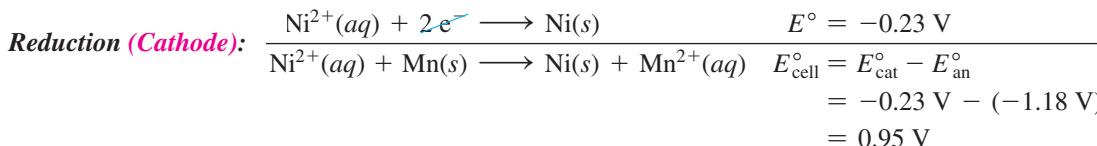
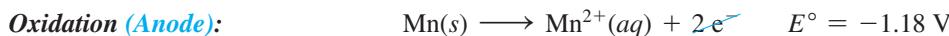
oxidation. (Remember that negative charge repels electrons.) The half-reaction having the more *positive* electrode potential tends to gain electrons and therefore undergo reduction. (Remember that positive charge attracts electrons.)

For example, consider the two reduction half-reactions:



Because the manganese half-reaction has a more negative electrode potential, it repels electrons and proceeds in the reverse direction (oxidation). Because the nickel half-reaction has the more positive (or least negative) electrode potential, it attracts electrons and proceeds in the forward direction.

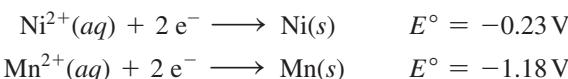
We can confirm this by calculating the standard electrode potential for manganese acting as the anode (oxidation) and nickel acting as the cathode (reduction).



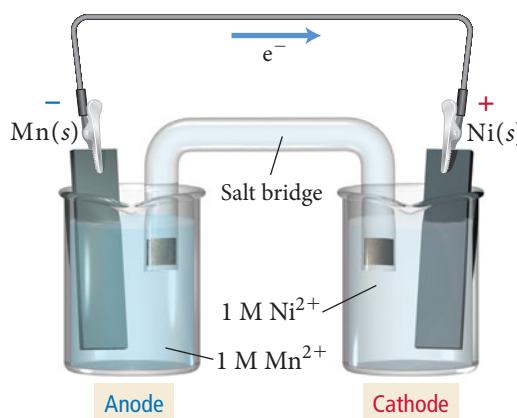
The overall cell potential is positive, indicating a spontaneous reaction. Consider the electrochemical cell corresponding to this spontaneous redox reaction in Figure 18.8 ▶. We draw the manganese half-cell on the left as the anode and the nickel half-cell on the right as the cathode. Electrons flow from the anode to the cathode.

Another way to predict the spontaneity of a redox reaction is to note the relative positions of the two half-reactions in Table 18.1. Since the table lists half-reactions in order of *decreasing* electrode potential, the half-reactions near the top of the table—those having large *positive* electrode potentials—attract electrons and therefore tend to occur in the forward direction. Half-reactions near the bottom of the table—those having large *negative* electrode potentials—repel electrons and therefore tend to occur in the reverse direction. In other words, as you move down Table 18.1, the half-reactions become less likely to occur in the forward direction and more likely to occur in the reverse direction. As a result, *any reduction half-reaction listed is spontaneous when paired with the reverse of a half-reaction that appears below it in Table 18.1.*

For example, if we return to our two previous half-reactions involving manganese and nickel we can see that the manganese half-reaction is listed below the nickel half-reaction in Table 18.1.



Therefore, the nickel reaction occurs in the forward direction (reduction) and the manganese reaction occurs in the reverse direction (oxidation).



The following mnemonics (NIO and PIR) can help you predict the spontaneous direction of redox reactions:
N.I.O.—More Negative Is Oxidation
P.I.R.—More Positive Is Reduction

◀ **FIGURE 18.8** Mn/Ni²⁺ Electrochemical Cell Since the reduction of Mn²⁺ is listed below the reduction of Ni²⁺ in Table 18.1, the reduction of Ni²⁺ is spontaneous when paired with the oxidation of Mn.

Recall from Section 4.9 that an **oxidizing agent** causes the oxidation of another substance (and is itself reduced) and that a **reducing agent** causes the reduction of another substance (and is itself oxidized).

Summarizing the Prediction of Spontaneous Direction for Redox Reactions:

- ▶ The half-reaction with the more *positive* electrode potential attracts electrons more strongly and will undergo reduction. (Substances listed at the top of Table 18.1 tend to undergo reduction; they are good oxidizing agents.)
- ▶ The half-reaction with the more *negative* electrode potential repels electrons more strongly and will undergo oxidation. (Substances listed near the bottom of Table 18.1 tend to undergo oxidation; they are good reducing agents.)
- ▶ Any reduction reaction in Table 18.1 is spontaneous when paired with the *reverse* of any of the reactions listed below it on the table.

EXAMPLE 18.5 Predicting Spontaneous Redox Reactions and Sketching Electrochemical Cells

Without calculating E_{cell}° , predict whether each of the following redox reactions is spontaneous. If the reaction is spontaneous as written, make a sketch of the electrochemical cell in which the reaction could occur. If the reaction is not spontaneous as written, write an equation for the spontaneous direction in which the reaction would occur and sketch the electrochemical cell in which the spontaneous reaction would occur. In your sketches, make sure to label the anode (which should be drawn on the left), the cathode, and the direction of electron flow.

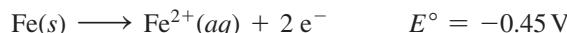
- (a) $\text{Fe}(s) + \text{Mg}^{2+}(aq) \longrightarrow \text{Fe}^{2+}(aq) + \text{Mg}(s)$
 (b) $\text{Fe}(s) + \text{Pb}^{2+}(aq) \longrightarrow \text{Fe}^{2+}(aq) + \text{Pb}(s)$

SOLUTION

- (a) $\text{Fe}(s) + \text{Mg}^{2+}(aq) \longrightarrow \text{Fe}^{2+}(aq) + \text{Mg}(s)$
 This reaction involves the reduction of Mg^{2+} :



and the oxidation of Fe:



However, the magnesium half-reaction has the more negative electrode potential and therefore repels electrons more strongly and undergoes oxidation. The iron half-reaction has the more positive electrode potential and therefore attracts electrons more strongly and undergoes reduction. So the reaction as written is *not* spontaneous. (The reaction pairs the reduction of Mg^{2+} with the reverse of a half-reaction *above it* in Table 18.1—such pairings are not spontaneous.)

However, the reverse reaction is spontaneous.



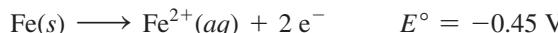
The corresponding electrochemical cell is shown in Figure 18.9 ◀.

- (b) $\text{Fe}(s) + \text{Pb}^{2+}(aq) \longrightarrow \text{Fe}^{2+}(aq) + \text{Pb}(s)$

This reaction involves the reduction of Pb^{2+} :



and the oxidation of iron:

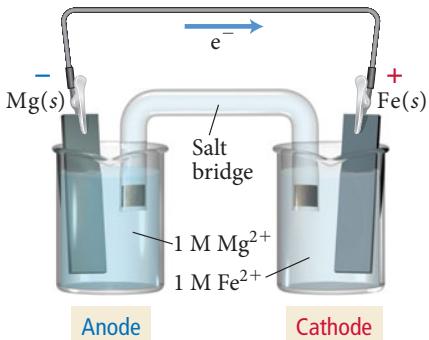


The iron half-reaction has the more negative electrode potential and therefore repels electrons and undergoes oxidation. The lead half-reaction has the more positive electrode potential and therefore attracts electrons and undergoes reduction. Therefore, the reaction *is* spontaneous as written. (The reaction pairs the reduction of Pb^{2+} with the reverse of a half-reaction *below it* in Table 18.1—such pairings are always spontaneous.) The corresponding electrochemical cell is shown in Figure 18.10 ◀.

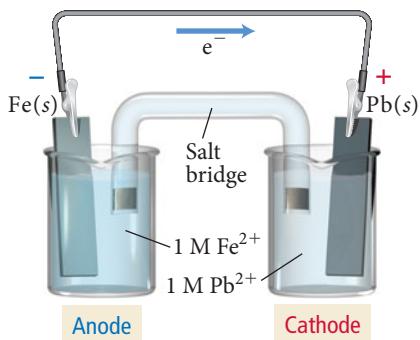
FOR PRACTICE 18.5

Are the following redox reactions spontaneous under standard conditions?

- (a) $\text{Zn}(s) + \text{Ni}^{2+}(aq) \longrightarrow \text{Zn}^{2+}(aq) + \text{Ni}(s)$
 (b) $\text{Zn}(s) + \text{Ca}^{2+}(aq) \longrightarrow \text{Zn}^{2+}(aq) + \text{Ca}(s)$



▲ FIGURE 18.9 Mg/Fe²⁺ Electrochemical Cell



▲ FIGURE 18.10 Fe/Pb²⁺ Electrochemical Cell

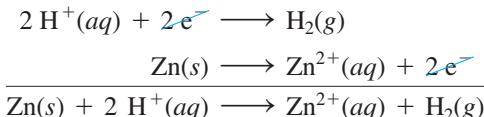
Conceptual Connection 18.3 Selective Oxidation

A solution contains both NaI and NaBr. Which oxidizing agent could you add to the solution to selectively oxidize $\text{I}^-(aq)$ but not $\text{Br}^-(aq)$?

- (a) Cl_2 (b) H_2O_2 (c) CuCl_2 (d) HNO_3

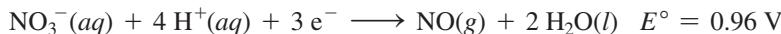
Predicting Whether a Metal Will Dissolve in Acid

In Chapter 15, we learned that acids dissolve metals. Most acids dissolve metals by the reduction of H^+ ions to hydrogen gas and the corresponding oxidation of the metal to its ion. For example, if solid Zn is dropped into hydrochloric acid, the following reaction occurs:

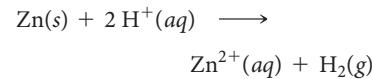


We observe the reaction as the dissolving of the zinc and the bubbling of hydrogen gas. The zinc is oxidized and the H^+ ions are reduced. Notice that this reaction involves the pairing of a reduction half-reaction (the reduction of H^+) with the reverse of a half-reaction that falls below it in Table 18.1. Therefore, this reaction is spontaneous. What happens, however, if we pair the reduction of H^+ with the oxidation of Cu? The reaction is not spontaneous, because it involves pairing the reduction of H^+ with the reverse of a half-reaction that is listed *above it* in the table. Consequently, copper does not react with H^+ and does not dissolve in acids such as HCl. In general, *metals whose reduction half-reactions are listed below the reduction of H^+ to H_2 in Table 18.1 dissolve in acids, while metals listed above it do not.*

An important exception to this rule is nitric acid (HNO_3), which can oxidize metals through the reduction half-reaction:



Since this half-reaction is above the reduction of H^+ in Table 18.1, HNO_3 can oxidize metals (such as copper) that can't be oxidized by HCl.



▲ When zinc is immersed in hydrochloric acid, the zinc is oxidized, forming ions that become solvated in the solution. Hydrogen ions are reduced, forming bubbles of hydrogen gas.

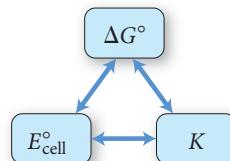
Conceptual Connection 18.4 Metals Dissolving in Acids

Which metal dissolves in HNO_3 but not in HCl?

- (a) Fe (b) Au (c) Ag

18.5 Cell Potential, Free Energy, and the Equilibrium Constant

We have seen that a positive standard cell potential (E_{cell}°) corresponds to a spontaneous oxidation-reduction reaction. And we know (from Chapter 17) that the spontaneity of a reaction is determined by the sign of ΔG° . Therefore, E_{cell}° and ΔG° must be related. We also know from Section 17.9 that ΔG° for a reaction is related to the equilibrium constant (K) for the reaction. Since E_{cell}° and ΔG° are related, then E_{cell}° and K must also be related.



Before we look at the nature of each of these relationships in detail, let's consider the following generalizations.

For a spontaneous redox reaction (one that will proceed in the forward direction when all reactants and products are in their standard states):

- ΔG° is negative (<0)
- E_{cell}° is positive (>0)
- $K > 1$

For a nonspontaneous reaction (one that will proceed in the reverse direction when all reactants and products are in their standard states):

- ΔG° is positive (>0)
- E_{cell}° is negative (<0)
- $K < 1$

The Relationship between ΔG° and E_{cell}°

We can derive a relationship between ΔG° and E_{cell}° by briefly returning to the definition of potential difference from Section 18.3—a potential difference is a measure of the difference of potential energy per unit charge (q):

$$E = \frac{\text{potential energy difference (in J)}}{\text{charge (in C)}}$$

Since the potential energy difference represents the maximum amount of work that can be done by the system on the surroundings, we can write:

$$w_{\text{max}} = -qE_{\text{cell}}^\circ \quad [18.1]$$

The negative sign follows the convention used throughout this book that work done by the system on the surroundings is negative.

We can quantify the charge (q) that flows in an electrochemical reaction by using **Faraday's constant (F)**, which represents the charge in coulombs of 1 mol of electrons.

$$F = \frac{96,485 \text{ C}}{\text{mol e}^-}$$

The total charge is $q = nF$, where n is the number of moles of electrons from the balanced chemical equation and F is Faraday's constant. Substituting $q = nF$ into Equation 18.1:

$$\begin{aligned} w_{\text{max}} &= -qE_{\text{cell}}^\circ \\ &= -nFE_{\text{cell}}^\circ \end{aligned} \quad [18.2]$$

Finally, recall from Chapter 17 that the standard change in free energy for a chemical reaction (ΔG°) represents the maximum amount of work that can be done by the reaction. Therefore, $w_{\text{max}} = \Delta G^\circ$. Making this substitution into Equation 18.2, we arrive at the following important result:

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ \quad [18.3]$$

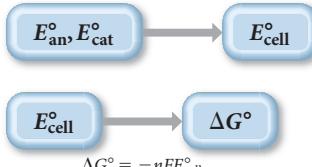
where ΔG° is the standard change in free energy for an electrochemical reaction, n is the number of moles of electrons transferred in the balanced equation, F is Faraday's constant, and E_{cell}° is the standard cell potential. Example 18.6 shows how to apply this equation to calculate the standard free energy change for an electrochemical cell.

EXAMPLE 18.6 Relating ΔG° and E_{cell}° 

Use the tabulated electrode potentials to calculate ΔG° for the reaction.



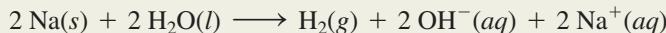
Is the reaction spontaneous?

SORT You are given a redox reaction and asked to find ΔG° .	GIVEN: $\text{I}_2(s) + 2 \text{Br}^-(aq) \longrightarrow 2 \text{I}^-(aq) + \text{Br}_2(l)$ FIND: ΔG°
STRATEGIZE Refer to the values of electrode potentials in Table 18.1 to calculate E_{cell}° . Then use Equation 18.3 to calculate ΔG° from E_{cell}° .	CONCEPTUAL PLAN  $\Delta G^\circ = -nFE_{\text{cell}}^\circ$
SOLVE Separate the reaction into oxidation and reduction half-reactions and find the standard electrode potentials for each. Determine E_{cell}° by subtracting E_{an} from E_{cat} .	SOLUTION <i>Oxidation (Anode):</i> $2 \text{Br}^-(aq) \longrightarrow \text{Br}_2(l) + 2e^- \quad E^\circ = 1.09 \text{ V}$ <i>Reduction (Cathode):</i> $\text{I}_2(s) + 2e^- \longrightarrow 2 \text{I}^-(aq) \quad E^\circ = 0.54 \text{ V}$ $\begin{array}{rcl} \text{I}_2(s) + 2 \text{Br}^-(aq) \longrightarrow 2 \text{I}^-(aq) + \text{Br}_2(l) & E_{\text{cell}}^\circ = E_{\text{cat}}^\circ - E_{\text{an}}^\circ \\ & = -0.55 \text{ V} \end{array}$
Calculate ΔG° from E_{cell}° . The value of n (the number of moles of electrons) corresponds to the number of electrons that are canceled in the half-reactions. Remember that $1 \text{ V} = 1 \text{ J/C}$.	$\begin{aligned} \Delta G^\circ &= -nFE_{\text{cell}}^\circ \\ &= -2 \text{ mole}^- \left(\frac{96,485 \text{ C}}{\text{mole}^-} \right) \left(-0.55 \frac{\text{J}}{\text{C}} \right) \\ &= +1.1 \times 10^5 \text{ J} \end{aligned}$ <p>Since ΔG° is positive, the reaction is not spontaneous under standard conditions.</p>

CHECK The answer is in the correct units (joules) and seems reasonable in magnitude ($\approx 110 \text{ kJ}$). You have seen (in Chapter 17) that values of ΔG° typically range from plus or minus tens to hundreds of kilojoules. The sign is positive, as expected for a reaction in which E_{cell}° is negative.

FOR PRACTICE 18.6

Use tabulated electrode potentials to calculate ΔG° for the reaction.



Is the reaction spontaneous?

**Connection 18.5** Periodic Trends and the Direction of Spontaneity for Redox Reactions

Consider the result of Example 18.6. The calculation revealed that the reaction is not spontaneous. Based on conceptual reasoning, which of the following best explains why I_2 does not oxidize Br^- ?

- (a) Br is more electronegative than I; therefore, we do not expect Br^- to give up an electron to I_2 .
- (b) I is more electronegative than Br; therefore, we do not expect I_2 to give up an electron to Br^- .
- (c) Br^- is in solution and I_2 is a solid. Solids do not gain electrons from substances in solution.

The Relationship between E°_{cell} and K

We can derive a relationship between the standard cell potential (E_{cell}°) and the equilibrium constant for the redox reaction occurring in the cell (K) by returning to the relationship between ΔG° and K that we learned in Chapter 17. Recall from Section 17.9 that:

$$\Delta G^\circ = -RT \ln K \quad [18.4]$$

By setting Equations 18.3 and 18.4 equal to each other, we get:

$$E_{\text{cell}}^{\circ} = \frac{RT}{nF} \ln K \quad [18.5]$$

Equation 18.5 is usually simplified for use at 25 °C by making the following substitutions:

$$R = 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}; T = 298.15 \text{ K}; F = \left(\frac{96,485 \text{ C}}{\text{mol e}^-} \right); \text{and } \ln K = 2.303 \log K$$

Substituting into Equation 18.5, we get the following important result:

$$E_{\text{cell}}^{\circ} = \frac{0.0592 \text{ V}}{n} \log K \quad [18.6]$$

where E_{cell}° is the standard cell potential, n is the number of moles of electrons transferred in the redox reaction, and K is the equilibrium constant for the balanced redox reaction at 25 °C. Example 18.7 demonstrates how to use Equation 18.6.

EXAMPLE 18.7 Relating E_{cell}° and K

Use the tabulated electrode potentials to calculate K for the oxidation of copper by H^+ (at 25 °C).



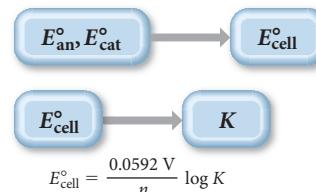
SORT You are given a redox reaction and asked to find K .

GIVEN: Cu(s) + 2 H⁺(aq) → Cu²⁺(aq) + H₂(g)

FIND: K

STRATEGIZE Refer to the values of electrode potentials in Table 18.1 to calculate E_{cell}° . Then use Equation 18.6 to calculate K from E_{cell}° .

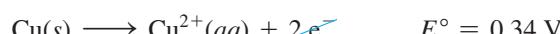
CONCEPTUAL PLAN



SOLVE Separate the reaction into oxidation and reduction half-reactions and find the standard electrode potentials for each. Find E_{cell}° by subtracting E_{an} from E_{cat} .

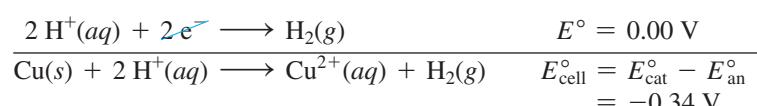
SOLUTION

Oxidation



Reduction

Reduction (Cathode)



Calculate K from E_{cell}° . The value of n (the number of moles of electrons) corresponds to the number of electrons that are canceled in the half-reactions.

$$E_{\text{cell}}^{\circ} = \frac{0.0592 \text{ V}}{n} \log K$$

$$\log K = E_{\text{cell}}^{\circ} \frac{n}{0.0592 \text{ V}}$$

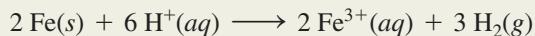
$$\log K = -0.34 \frac{2}{0.0592} = -11.48$$

$$K = 10^{-11.48} = 3.3 \times 10^{-12}$$

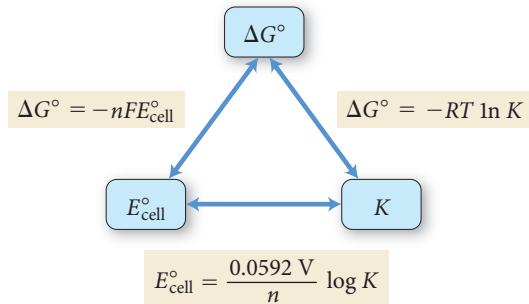
CHECK The answer has no units, as expected for an equilibrium constant. The magnitude of the answer is small, indicating that the reaction lies far to the left at equilibrium, as expected for a reaction in which E_{cell}° is negative.

FOR PRACTICE 18.7

Use the tabulated electrode potentials to calculate K for the oxidation of iron by H^+ (at 25 °C).



Notice that the fundamental quantity in the given relationships is the standard change in free energy for a chemical reaction ($\Delta G_{\text{rxn}}^{\circ}$). From that quantity, we can calculate both E_{cell}° and K . The relationships between these three quantities is summarized with the following diagram:



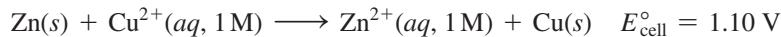
Conceptual Connection 18.6 Relating K , $\Delta G_{\text{rxn}}^{\circ}$, and E_{cell}°

A redox reaction has an equilibrium constant of $K = 1.2 \times 10^3$. Which statement is true regarding $\Delta G_{\text{rxn}}^{\circ}$ and E_{cell}° for this reaction?

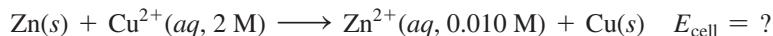
- (a) E_{cell}° is positive and $\Delta G_{\text{rxn}}^{\circ}$ is positive.
- (b) E_{cell}° is negative and $\Delta G_{\text{rxn}}^{\circ}$ is negative.
- (c) E_{cell}° is positive and $\Delta G_{\text{rxn}}^{\circ}$ is negative.
- (d) E_{cell}° is negative and $\Delta G_{\text{rxn}}^{\circ}$ is positive.

18.6 Cell Potential and Concentration

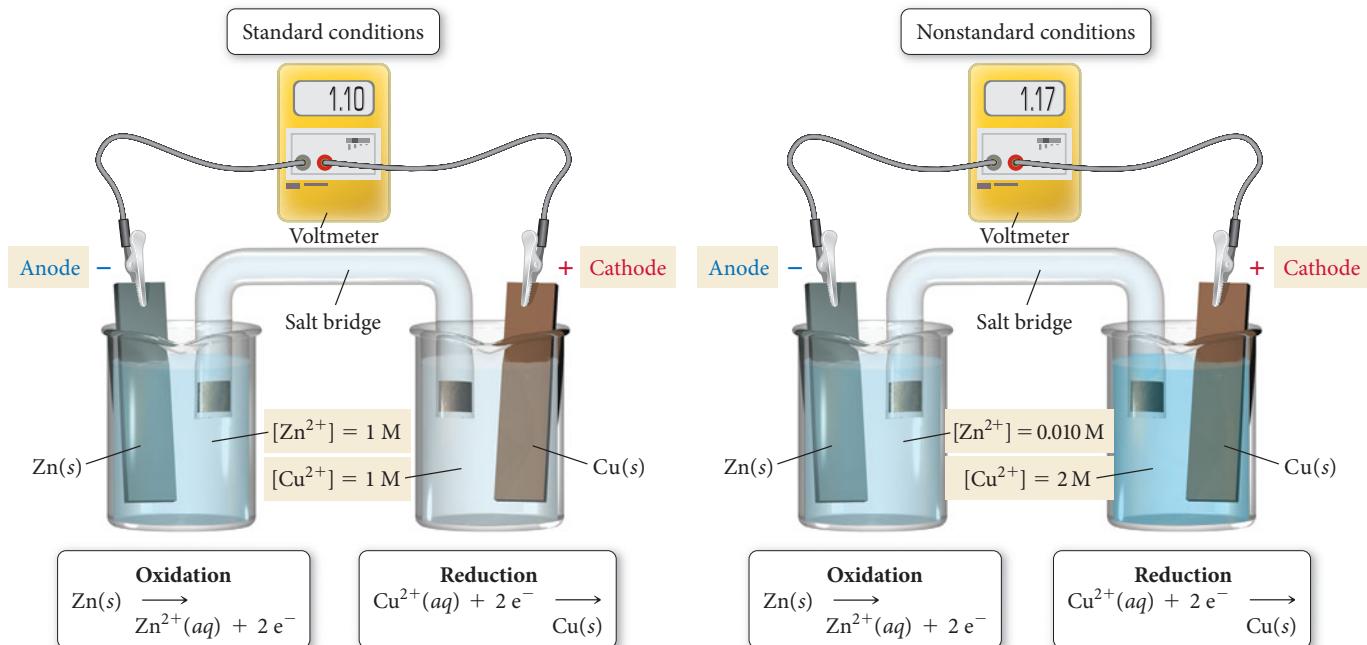
We have learned how to find E_{cell}° under standard conditions. For example, we know that when $[\text{Cu}^{2+}] = 1 \text{ M}$ and $[\text{Zn}^{2+}] = 1 \text{ M}$, the following reaction produces a potential of 1.10 V.



However, what if $[\text{Cu}^{2+}] > 1 \text{ M}$ and $[\text{Zn}^{2+}] < 1 \text{ M}$? For example, how would the cell potential for the following conditions be different from the potential under standard conditions?



Since the concentration of a reactant is greater than standard conditions, and since the concentration of product is less than standard conditions, we can use Le Châtelier's principle to predict that the reaction has an even stronger tendency to occur in the forward direction and that E_{cell} is therefore greater than +1.10 V (Figure 18.11 ►).



▲ FIGURE 18.11 Cell Potential and Concentration This figure compares the Zn/Cu²⁺ electrochemical cell under standard and nonstandard conditions. In this case, the nonstandard conditions consist of a higher Cu²⁺ concentration ([Cu²⁺] > 1 M) at the cathode and a lower Zn²⁺ concentration at the anode ([Zn²⁺] < 1 M). According to Le Châtelier's principle, the forward reaction has a greater tendency to occur, resulting in a greater overall cell potential than the potential under standard conditions.

We can derive an exact relationship between E_{cell} (under nonstandard conditions) and E_{cell}° by considering the relationship between the change in free energy (ΔG) and the *standard* change in free energy (ΔG°) from Section 17.8:

$$\Delta G = \Delta G^{\circ} + RT \ln Q \quad [18.7]$$

where R is the gas constant (8.314 J/mol · K), T is the temperature in kelvins, and Q is the reaction quotient corresponding to the nonstandard conditions. Since we know the relationship between ΔG and E_{cell} (Equation 18.3), we can substitute into Equation 18.7:

$$\begin{aligned} \Delta G &= \Delta G^{\circ} + RT \ln Q \\ -nFE_{\text{cell}} &= -nFE_{\text{cell}}^{\circ} + RT \ln Q \end{aligned}$$

We can then divide each side by $-nF$ to arrive at:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln Q \quad [18.8]$$

As we have seen, R and F are constants; at $T = 25^\circ\text{C}$, $\frac{RT}{nF} \ln Q = \frac{0.0592 \text{ V}}{n} \log Q$.

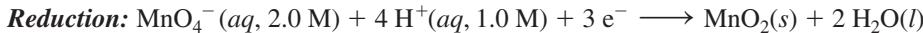
Substituting into Equation 18.8, we arrive at the **Nernst equation**:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log Q \quad [18.9]$$

where E_{cell} is the cell potential in volts, E_{cell}° is the *standard* cell potential in volts, n is the number of moles of electrons transferred in the redox reaction, and Q is the reaction quotient. Notice that, under standard conditions, $Q = 1$, and (since $\log 1 = 0$) $E_{\text{cell}} = E_{\text{cell}}^{\circ}$, as expected. Example 18.8 shows how to calculate the cell potential under nonstandard conditions.

EXAMPLE 18.8 Calculating E_{cell} under Nonstandard Conditions

Determine the cell potential for an electrochemical cell based on the following two half-reactions:



SORT You are given the half-reactions for a redox reaction and the concentrations of the aqueous reactants and products. You are asked to find the cell potential.

STRATEGIZE Use the tabulated values of electrode potentials to calculate E_{cell}° . Then use Equation 18.9 to calculate E_{cell} .

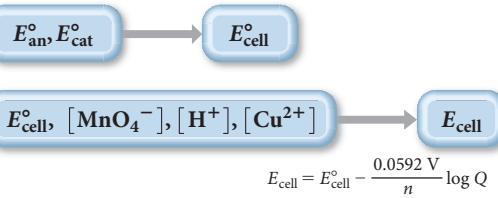
SOLVE Write the oxidation and reduction half-reactions, multiplying by the appropriate coefficients to cancel the electrons. Find the standard electrode potentials for each. Find E_{cell}° .

Calculate E_{cell} from E_{cell}° . The value of n (the number of moles of electrons) corresponds to the number of electrons (6 in this case) canceled in the half-reactions. Determine Q based on the overall balanced equation and the given concentrations of the reactants and products. (Note that pure liquid water, solid MnO_2 , and solid copper are omitted from the expression for Q .)

GIVEN: $[\text{MnO}_4^-] = 2.0 \text{ M}$; $[\text{H}^+] = 1.0 \text{ M}$; $[\text{Cu}^{2+}] = 0.010 \text{ M}$

FIND: E_{cell}

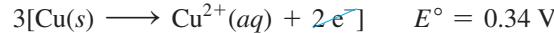
CONCEPTUAL PLAN



SOLUTION

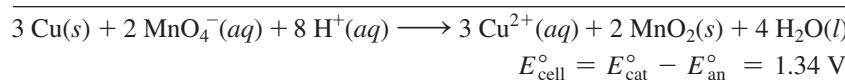
Oxidation

(Anode):



Reduction

(Cathode): $2[\text{MnO}_4^-(aq) + 4 \text{ H}^+(aq) + 3 \text{ e}^- \longrightarrow \text{MnO}_2(s) + 2 \text{ H}_2\text{O}(l)] \quad E^\circ = 1.68 \text{ V}$



$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^\circ - \frac{0.0592 \text{ V}}{n} \log Q \\ &= E_{\text{cell}}^\circ - \frac{0.0592 \text{ V}}{n} \log \frac{[\text{Cu}^{2+}]^3}{[\text{MnO}_4^-]^2 [\text{H}^+]^8} \\ &= 1.34 \text{ V} - \frac{0.0592 \text{ V}}{6} \log \frac{(0.010)^3}{(2.0)^2 (1.0)^8} \\ &= 1.34 \text{ V} - (-0.065 \text{ V}) \\ &= 1.41 \text{ V} \end{aligned}$$

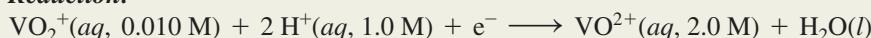
CHECK The answer has the correct units (V). The value of E_{cell} is larger than E_{cell}° , as expected based on Le Châtelier's principle because one of the aqueous reactants has a concentration greater than standard conditions and the one aqueous product has a concentration less than standard conditions. Therefore, the reaction has a greater tendency to proceed toward products and has a greater cell potential.

FOR PRACTICE 18.8

Determine the cell potential of an electrochemical cell based on the following two half-reactions:



Reduction:



From Equation 18.9, we can conclude the following:

- When a redox reaction within a voltaic cell occurs under standard conditions $Q = 1$; therefore, $E_{\text{cell}} = E_{\text{cell}}^{\circ}$.

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log Q \\ &= E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log 1 \quad \text{log } 1 = 0 \\ &= E_{\text{cell}}^{\circ} \end{aligned}$$

- When a redox reaction within a voltaic cell occurs under conditions in which $Q < 1$, the greater concentration of reactants relative to products drives the reaction to the right, resulting in $E_{\text{cell}} > E_{\text{cell}}^{\circ}$.
- When a redox reaction within an electrochemical cell occurs under conditions in which $Q > 1$, the greater concentration of products relative to reactants drives the reaction to the left, resulting in $E_{\text{cell}} < E_{\text{cell}}^{\circ}$.
- When a redox reaction reaches equilibrium, $Q = K$. The redox reaction has no tendency to occur in either direction and $E_{\text{cell}} = 0$.

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log Q \quad E_{\text{cell}}^{\circ} \quad (\text{see Equation 18.6}) \\ &= E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log K \\ &= E_{\text{cell}}^{\circ} - E_{\text{cell}}^{\circ} \\ &= 0 \end{aligned}$$

This last point explains why batteries do not last forever—as the reactants are depleted, the reaction proceeds toward equilibrium and the potential tends toward zero.

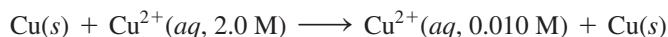
Conceptual Connection 18.7 Relating Q , K , E_{cell} , and E_{cell}°

In an electrochemical cell, $Q = 0.0010$ and $K = 0.10$. What can you conclude about E_{cell} and E_{cell}° ?

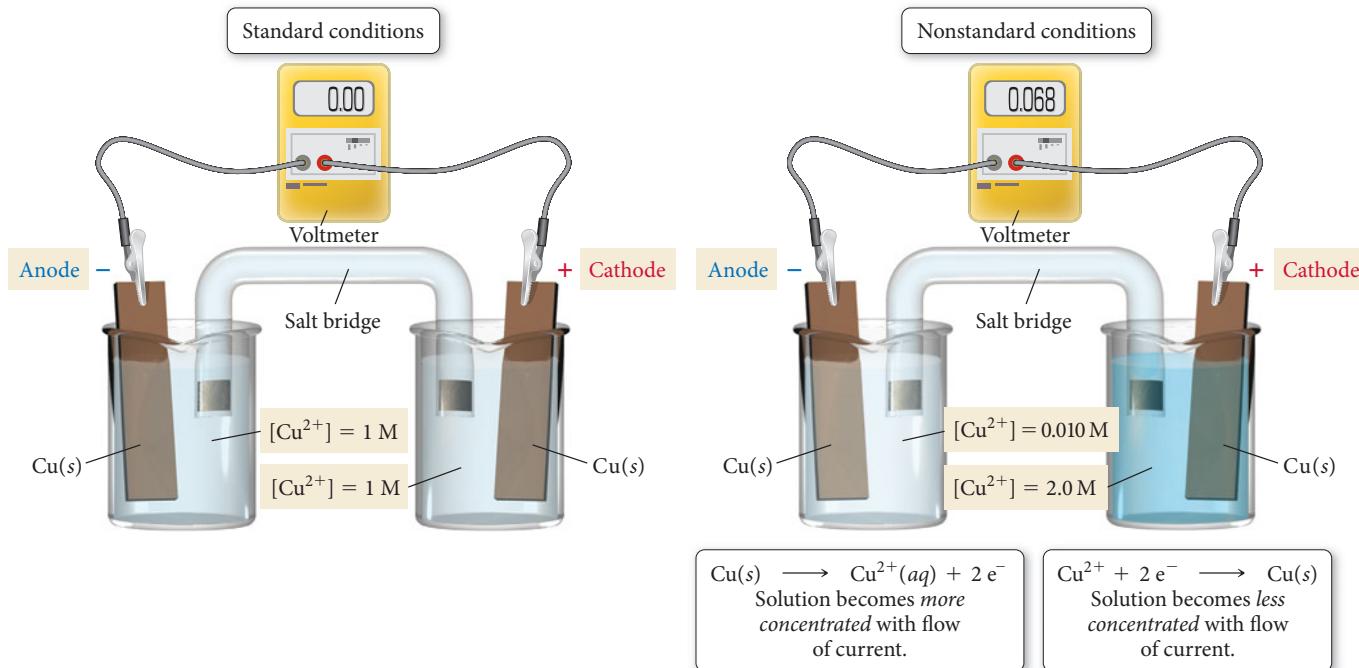
- E_{cell} is positive and E_{cell}° is negative.
- E_{cell} is negative and E_{cell}° is positive.
- Both E_{cell} and E_{cell}° are positive.
- Both E_{cell} and E_{cell}° are negative.

Concentration Cells

Since cell potential depends not only on the half-reactions occurring in the cell, but also on the *concentrations* of the reactants and products in those half-reactions, we can construct a voltaic cell in which both half-reactions are the same, but in which *a difference in concentration drives the current flow*. For example, consider the electrochemical cell shown in Figure 18.12 ►, in which copper is oxidized at the anode and copper ions are reduced at the cathode. The second part of Figure 18.12 depicts this cell under nonstandard conditions, with $[\text{Cu}^{2+}] = 2.0 \text{ M}$ in one half-cell and $[\text{Cu}^{2+}] = 0.010 \text{ M}$ in the other:

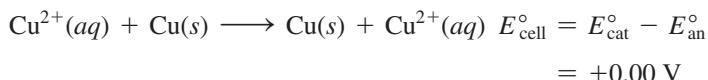
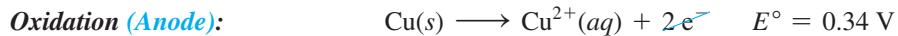


A Concentration Cell



▲ FIGURE 18.12 Cu/Cu²⁺ Concentration Cell If two half-cells have the same Cu²⁺ concentration, the cell potential is zero. If one half-cell has a greater Cu²⁺ concentration than the other, a spontaneous reaction occurs. In the reaction, Cu²⁺ ions in the more concentrated cell are reduced (to solid copper), while Cu²⁺ ions in the more dilute cell are formed (from solid copper). The concentration of copper ions in the two half-cells tends toward equality.

The half-reactions are identical and the *standard* cell potential is therefore zero.



Because of the different concentrations in the two half-cells, the cell potential must be calculated using the Nernst equation.

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592 \text{ V}}{2} \log \frac{0.010}{2.0} \\ = 0.000 \text{ V} + 0.068 \text{ V} \\ = 0.068 \text{ V}$$

The cell produces a potential of 0.068 V. Electrons spontaneously flow from the half-cell with the lower copper ion concentration to the half-cell with the higher copper ion concentration. You can imagine a concentration cell in the same way you think about any concentration gradient. If you mix a concentrated solution of Cu²⁺ with a dilute solution, the Cu²⁺ ions flow from the concentrated solution to the dilute one. Similarly, in a concentration cell, the transfer of electrons from the dilute half-cell results in the formation of Cu²⁺ ions in the dilute half-cell. The electrons flow to the concentrated cell, where they react with Cu²⁺ ions and reduce them to Cu(s). Therefore, the flow of electrons has the effect of increasing the concentration of Cu²⁺ in the dilute cell and decreasing the concentration of Cu²⁺ in the concentrated half-cell.

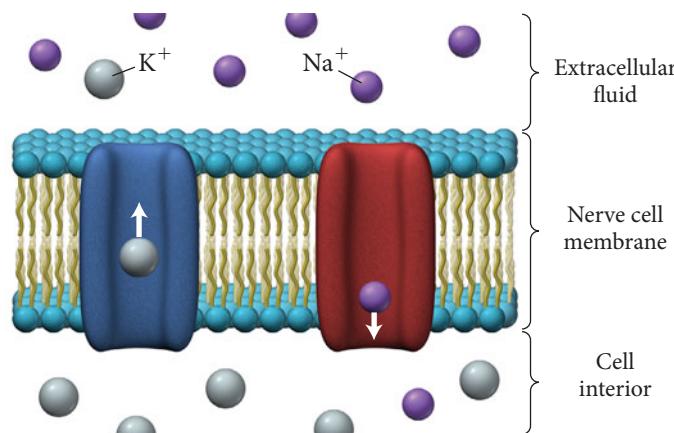


Chemistry and Medicine

Concentration Cells in Human Nerve Cells

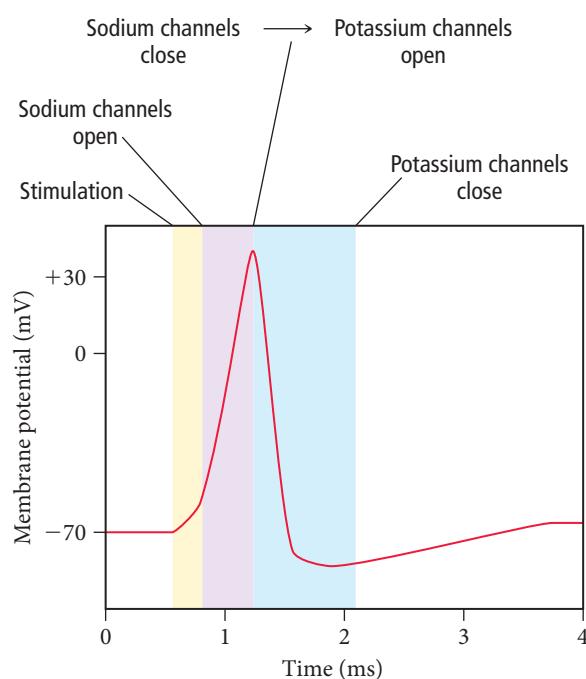
Recall from Section 8.1 that tiny pumps in the membranes of human nerve cells pump ions—especially sodium (Na^+) and potassium (K^+)—through those membranes, establishing a concentration gradient for each type of ion: the concentration of sodium ions is higher outside the cell than within, while exactly the opposite is true for potassium ions. These concentration gradients result in an electrical potential across the cell membrane, called the resting potential, of about -70 mV . (The interior of the cell is negative with respect to the exterior.)

When the nerve cell is stimulated, certain channels in the membrane open, allowing Na^+ ions to rush into the cell and causing the potential to temporarily rise to about $+30\text{ mV}$ (Figure 18.13 ▶). Other channels that allow K^+ ions to rush out of the cell open in turn, bringing the potential back down to near its resting potential. The result is a spike in the electrochemical potential across the membrane, which provides the



▲ FIGURE 18.13 Concentration Changes in Nerve Cells

stimulus for a similar spike in the neighboring segment of the membrane (Figure 18.14 ▷). In this way, an electrical signal moves down the length of a nerve cell.



▲ FIGURE 18.14 Potential Changes across the Nerve Cell Membrane The changes in ion concentrations that take place when a nerve cell is stimulated result in a spike in the electrochemical potential across the membrane.

In a nerve cell at rest, the concentration of sodium ions is higher outside the cell than inside. The reverse is true for potassium ions. When a nerve cell is stimulated, sodium channels open and Na^+ ions flood into the cell. A fraction of a second later, the sodium channels close and potassium channels open, allowing K^+ ions to leave the cell.

When the electrical signal reaches the end of the nerve cell, it triggers the release of a chemical neurotransmitter, which travels to the neighboring nerve cell and stimulates the same kind of electrochemical spike. In this way, neural signals travel throughout the brain and nervous system.

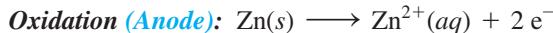
18.7 Batteries: Using Chemistry to Generate Electricity

We have seen that we can combine the electron-losing tendency of one substance with the electron-gaining tendency of another to create electrical current in a voltaic cell. Batteries are voltaic cells conveniently packaged to act as portable sources of electricity. The actual oxidation and reduction reactions depend on the particular type of battery. In this section, we examine several different types.

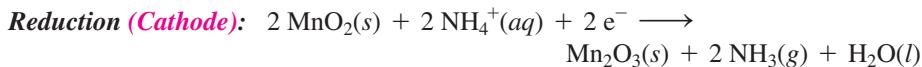
Dry-Cell Batteries

Common batteries, such as the kind you find in a flashlight, are called **dry-cell batteries** because they do not contain large amounts of liquid water. There are several familiar

types of dry-cell batteries. The most inexpensive are composed of a zinc case that acts as the anode (Figure 18.15(a) ▶). The zinc is oxidized according to the reaction:

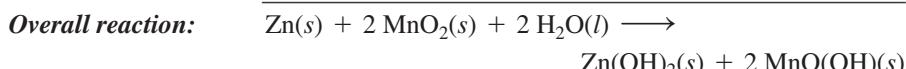
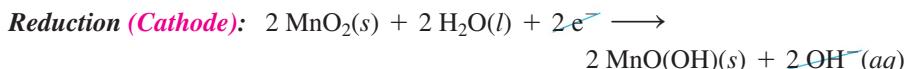


The cathode is a carbon rod immersed in a moist paste of MnO_2 that also contains NH_4Cl . The MnO_2 is reduced to Mn_2O_3 according to the reaction:



These two half-reactions produce a voltage of about 1.5 V. Two or more of these batteries can be connected in series (cathode-to-anode connection) to produce higher voltages.

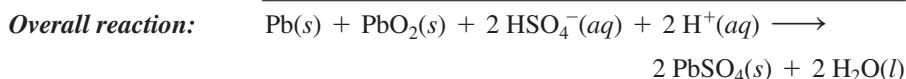
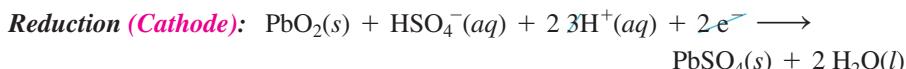
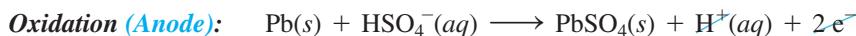
The more common **alkaline batteries** (Figure 18.15(b)) employ slightly different half-reactions in a basic medium (therefore the name alkaline). In an alkaline battery, the zinc is oxidized in a basic environment:



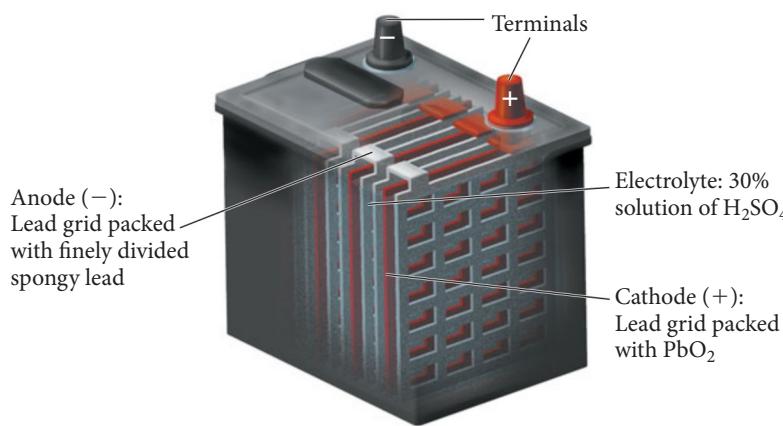
Alkaline batteries have a longer working life and a longer shelf life than their nonalkaline counterparts.

Lead-Acid Storage Batteries

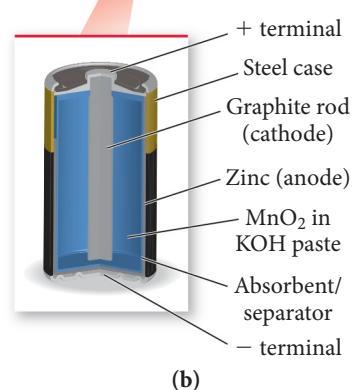
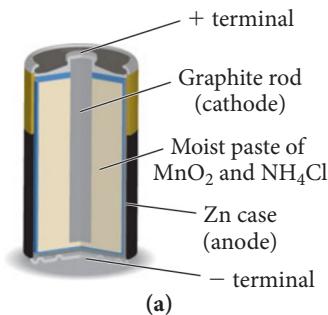
The batteries in most automobiles are **lead-acid storage batteries**. These batteries consist of six electrochemical cells wired in series (Figure 18.16 ▶). Each cell produces 2 V for a total of 12 V. Each cell contains a porous lead anode where oxidation occurs and a lead(IV) oxide cathode where reduction occurs according to the reactions:



Both the anode and the cathode are immersed in sulfuric acid (H_2SO_4). As electrical current is drawn from the battery, both electrodes become coated with $\text{PbSO}_4(s)$. If the battery is run for a long time without recharging, too much $\text{PbSO}_4(s)$ develops on the surface of the electrodes and the battery goes dead. The lead-acid storage battery can be recharged by an electrical current (which must come from an external source such as an alternator in a car). The current causes the preceding reaction to occur in reverse, converting the $\text{PbSO}_4(s)$ back to $\text{Pb}(s)$ and $\text{PbO}_2(s)$.



◀ FIGURE 18.16 Lead-Acid Storage Battery A lead-acid storage battery consists of six cells wired in series. Each cell contains a porous lead anode and a lead oxide cathode, both immersed in sulfuric acid.

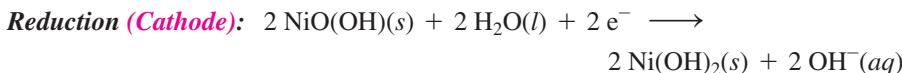


▲ FIGURE 18.15 Dry-Cell Battery (a) In a common dry-cell battery, the zinc case acts as the anode and a graphite rod immersed in a moist, slightly acidic paste of MnO_2 and NH_4Cl acts as the cathode. (b) The longer-lived alkaline batteries employ a graphite cathode immersed in a paste of MnO_2 and a base.

Other Rechargeable Batteries

The ubiquity of power electronic products such as laptops, cell phones, and digital cameras, as well as the growth in popularity of hybrid electric vehicles, drive the need for efficient, long-lasting, rechargeable batteries. The most common types include the **nickel–cadmium (NiCad) battery**, the **nickel–metal hydride (NiMH) battery**, and the **lithium ion battery**.

The Nickel–Cadmium (NiCad) Battery Nickel–cadmium batteries consist of an anode composed of solid cadmium and a cathode composed of $\text{NiO(OH)}(s)$. The electrolyte is usually $\text{KOH}(aq)$. During operation, the cadmium is oxidized and the NiO(OH) is reduced according to the equations:



▲ Several types of batteries, including NiCad, NiMH, and lithium ion batteries, are recharged by chargers that use household current.

The overall reaction produces about 1.30 V. As current is drawn from the NiCad battery, solid cadmium hydroxide accumulates on the anode and solid nickel(II) hydroxide accumulates on the cathode. But by running current in the opposite direction, the reactants can be regenerated from the products. A common problem in recharging NiCad and other rechargeable batteries is knowing when to stop. Once all of the products of the reaction are converted back to reactants, the charging process should ideally terminate—otherwise the electrical current will drive other, usually unwanted, reactions such as the electrolysis of water to form hydrogen and oxygen gas. These reactions typically damage the battery and may sometimes even cause an explosion. Consequently, most commercial battery chargers have sensors that measure when the charging is complete. These sensors rely on the small changes in voltage or increases in temperature that occur once the products have all been converted back to reactants.

The Nickel–Metal Hydride (NiMH) Battery Although NiCad batteries were the standard rechargeable battery for many years, they are being replaced by other types of rechargeable batteries, in part because of the toxicity of cadmium and the resulting disposal problems. One of these replacements is the nickel–metal hydride or NiMH battery. The NiMH battery employs the same cathode reaction as the NiCad battery but a different anode reaction. In the anode of a NiMH battery, hydrogen atoms held in a metal alloy are oxidized. If we let M represent the metal alloy, we can write the half-reactions as follows:



In addition to being more environmentally friendly than NiCad batteries, NiMH batteries also have a greater energy density (energy content per unit battery mass), as we can see in Table 18.2. In some cases, a NiMH battery can carry twice the energy of a NiCad battery of the same mass, making NiMH batteries the most common choice for hybrid electric vehicles.

The Lithium Ion Battery The newest and most expensive common type of rechargeable battery is the lithium ion battery. Since lithium is the least dense metal (0.53 g/cm^3), lithium batteries have high energy densities (see Table 18.2). The lithium battery works differently than the other batteries we have examined so far, and the details of its operation are beyond the scope

TABLE 18.2 Energy Density and Overcharge Tolerance of Several Rechargeable Batteries

Battery Type	Energy Density (W · h/kg)	Overcharge Tolerance
NiCad	45-80	Moderate
NiMH	60-120	Low
Li ion	110-160	Low
Pb storage	30-50	High

of our current discussion. Briefly, you can think of the operation of the lithium battery as being due primarily to the motion of lithium ions from the anode to the cathode. The anode is composed of graphite into which lithium ions are incorporated between layers of carbon atoms. Upon discharge, the lithium ions spontaneously migrate to the cathode, which consists of a lithium transition metal oxide such as LiCoO_2 or LiMn_2O_4 . The transition metal is reduced during this process. Upon recharging, the transition metal is oxidized, forcing the lithium to migrate back into the graphite (Figure 18.17 ▶). The flow of lithium ions from the anode to the cathode causes a corresponding flow of electrons in the external circuit. Lithium ion batteries are commonly used in applications where light weight and high energy density are important. These include cell phones, laptop computers, and digital cameras.

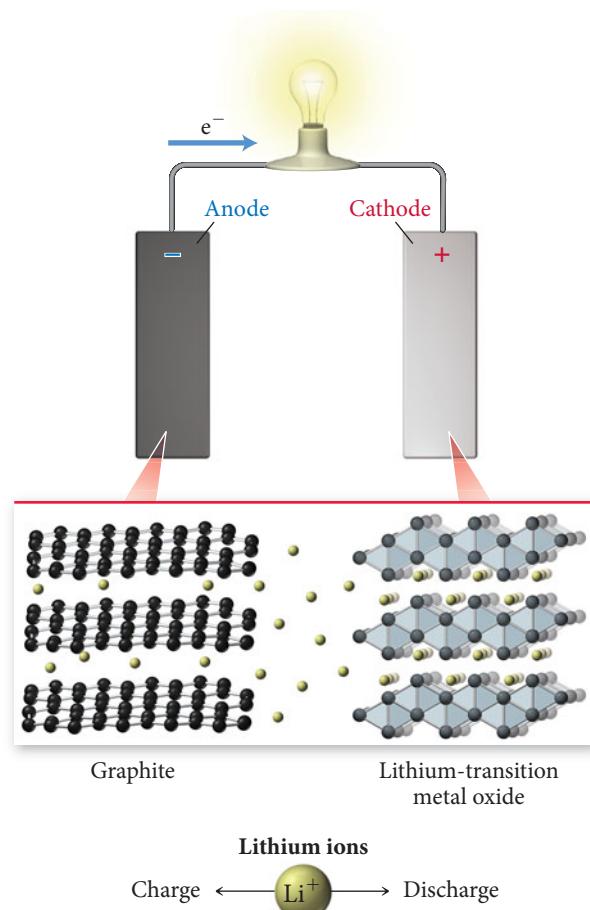
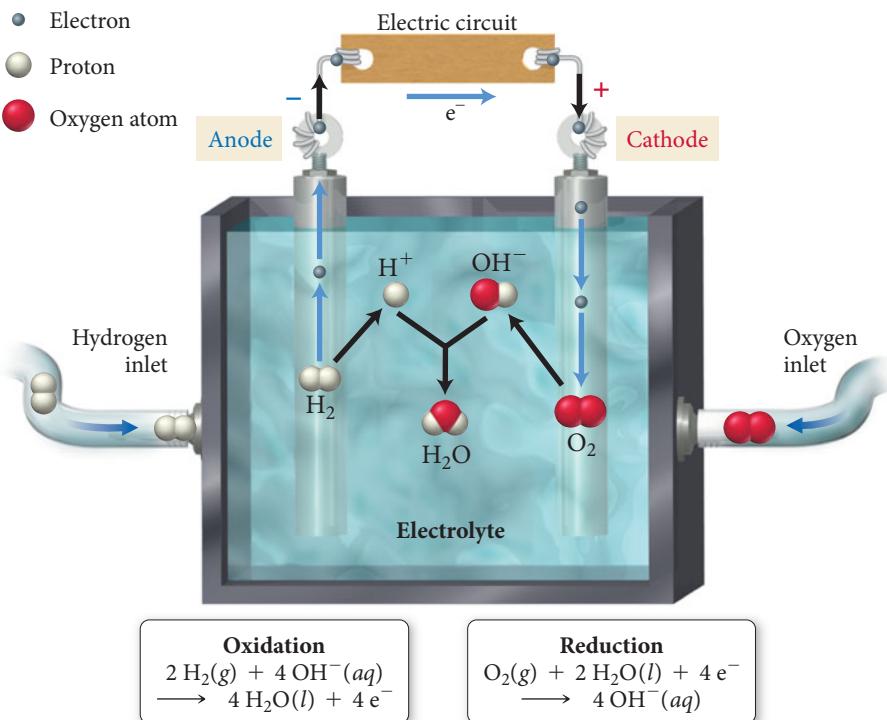
Fuel Cells

We discussed the potential for *fuel cells* in the opening section of this chapter. Fuel cells may one day replace—or at least work in combination with—centralized power grid electricity. In addition, vehicles powered by fuel cells may one day usurp vehicles powered by internal combustion engines. Fuel cells are like batteries; the key difference is that a battery is self-contained, while in a fuel cell the reactants need to be constantly replenished from an external source. With use, normal batteries lose their ability to generate voltage because the reactants become depleted as electrical current is drawn from the battery. In a **fuel cell**, the reactants—the fuel provided from an external source—constantly flow through the battery, generating electrical current as they undergo a redox reaction.

The most common fuel cell is the hydrogen–oxygen fuel cell (Figure 18.18 ▼). In this cell, hydrogen gas flows past the anode (a screen coated with platinum catalyst) and undergoes oxidation.



Hydrogen–Oxygen Fuel Cell



▲ FIGURE 18.17 Lithium Ion Battery

In the lithium ion battery, the spontaneous flow of lithium ions from the graphite anode to the lithium transition metal oxide cathode causes a corresponding flow of electrons in the external circuit.

◀ FIGURE 18.18 Hydrogen–Oxygen Fuel Cell

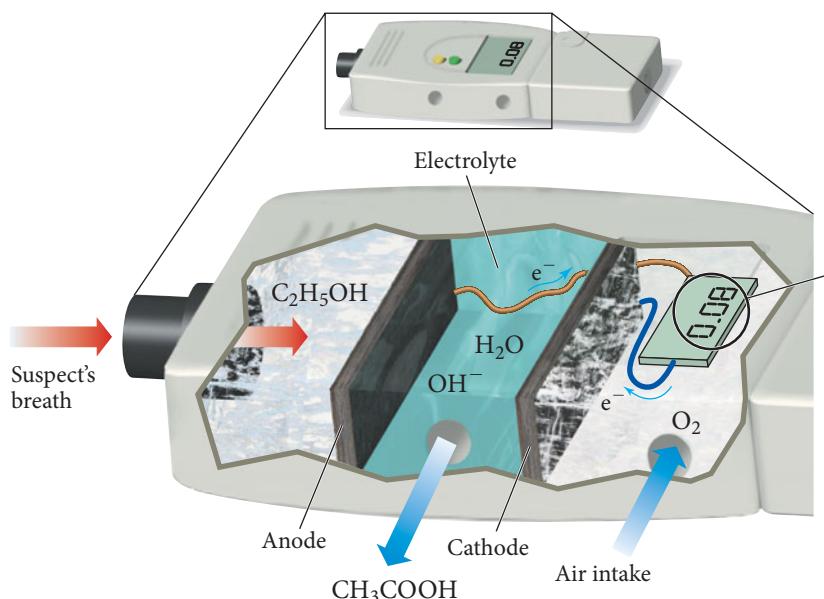
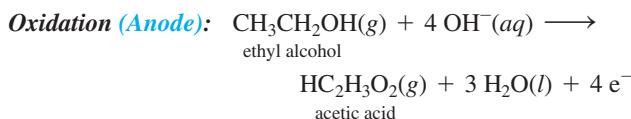
In this fuel cell, hydrogen and oxygen combine to form water.



Chemistry in Your Day

The Fuel-Cell Breathalyzer

Police often use a device called a breathalyzer to measure the amount of ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) in the bloodstream of a person suspected of driving under the influence of alcohol (Figure 18.19 ▶). Breathalyzers work because the quantity of ethyl alcohol in the breath is proportional to the quantity of ethyl alcohol in the bloodstream. One type of breathalyzer employs a fuel cell to measure the quantity of alcohol in the breath. When a suspect blows into the breathalyzer, ethyl alcohol is oxidized to acetic acid at the anode:

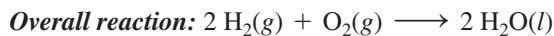


▲ FIGURE 18.19 Fuel-Cell Breathalyzer The fuel-cell breathalyzer works by oxidizing ethyl alcohol in the breath to acetic acid. The electrical current that is produced is proportional to the concentration of ethyl alcohol in the breath.

Oxygen gas flows past the cathode (a similar screen) and undergoes reduction:



The half-reactions sum to the following overall reaction:

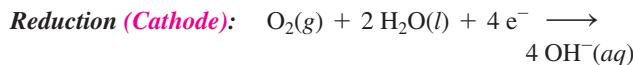


Notice that the only product is water. In the space shuttle program, hydrogen–oxygen fuel cells consume hydrogen to provide electricity and astronauts drink the water that is produced by the reaction. In order for hydrogen-powered fuel cells to become more widely used, a more readily available source of hydrogen must be developed.

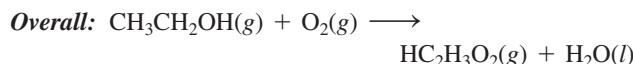
18.8 Electrolysis: Driving Nonspontaneous Chemical Reactions with Electricity

In a voltaic cell, a spontaneous redox reaction produces electrical current. In an *electrolytic cell*, electrical current drives an otherwise nonspontaneous redox reaction through a process called **electrolysis**. We have seen that the reaction of hydrogen with

At the cathode, oxygen is reduced:

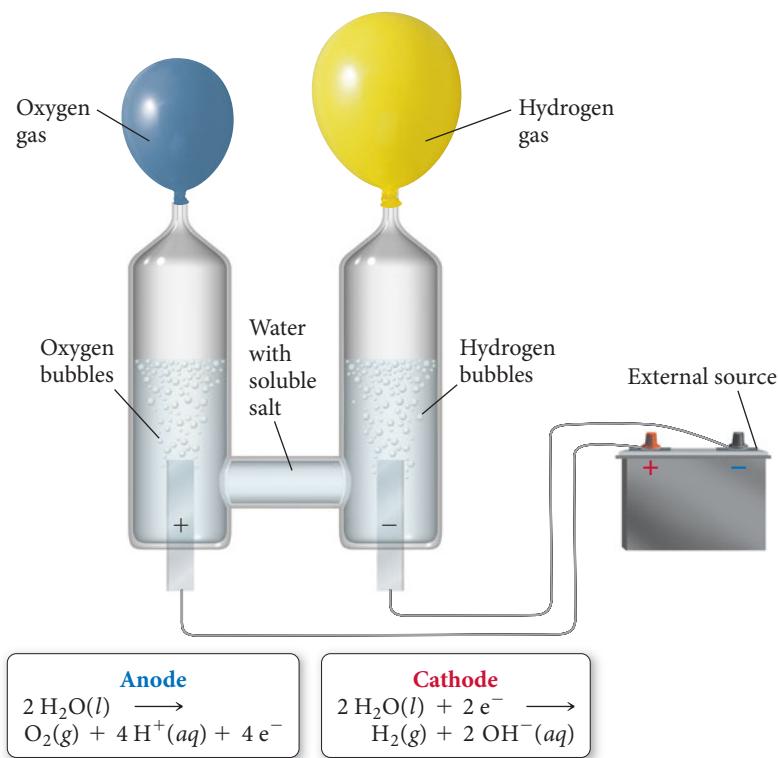


The overall reaction is the oxidation of ethyl alcohol to acetic acid and water:



The magnitude of electrical current produced depends on the quantity of alcohol in the breath. A higher current results from a higher blood alcohol level. When calibrated correctly, the fuel-cell breathalyzer can precisely measure the blood alcohol level of a suspected drunk driver.

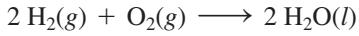
Electrolysis of Water



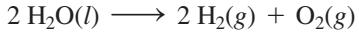
◀ FIGURE 18.20 Electrolysis of Water

Electrical current can decompose water into hydrogen and oxygen gas.

oxygen to form water is spontaneous and can be used to produce an electrical current in a fuel cell. Conversely, by *supplying* electrical current, we can cause the reverse reaction to occur, separating water into hydrogen and oxygen (Figure 18.20 ▲).



(spontaneous—produces electrical current; occurs in a voltaic cell)



(nonspontaneous—consumes electrical current; occurs in an electrolytic cell)

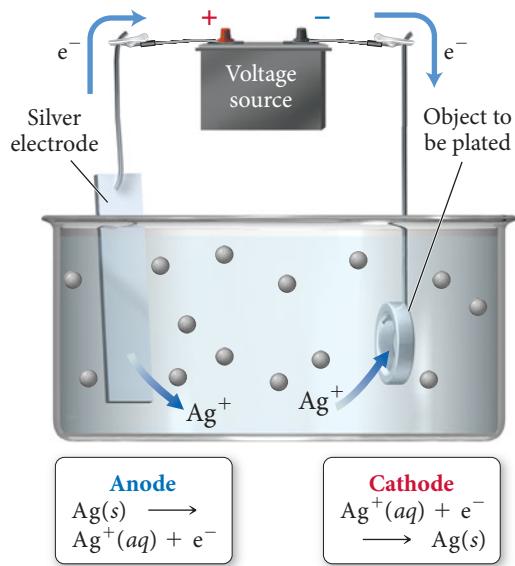
Recall from the previous section that one of the problems associated with the widespread adoption of hydrogen fuel cells is the scarcity of hydrogen. Where will the hydrogen to power these fuel cells come from? One possible answer is to obtain hydrogen from water through solar-powered electrolysis. A solar-powered electrolytic cell can produce hydrogen from water when the sun is shining. The hydrogen made in this way could be converted back to water to generate electricity and could also be used to power fuel-cell vehicles.

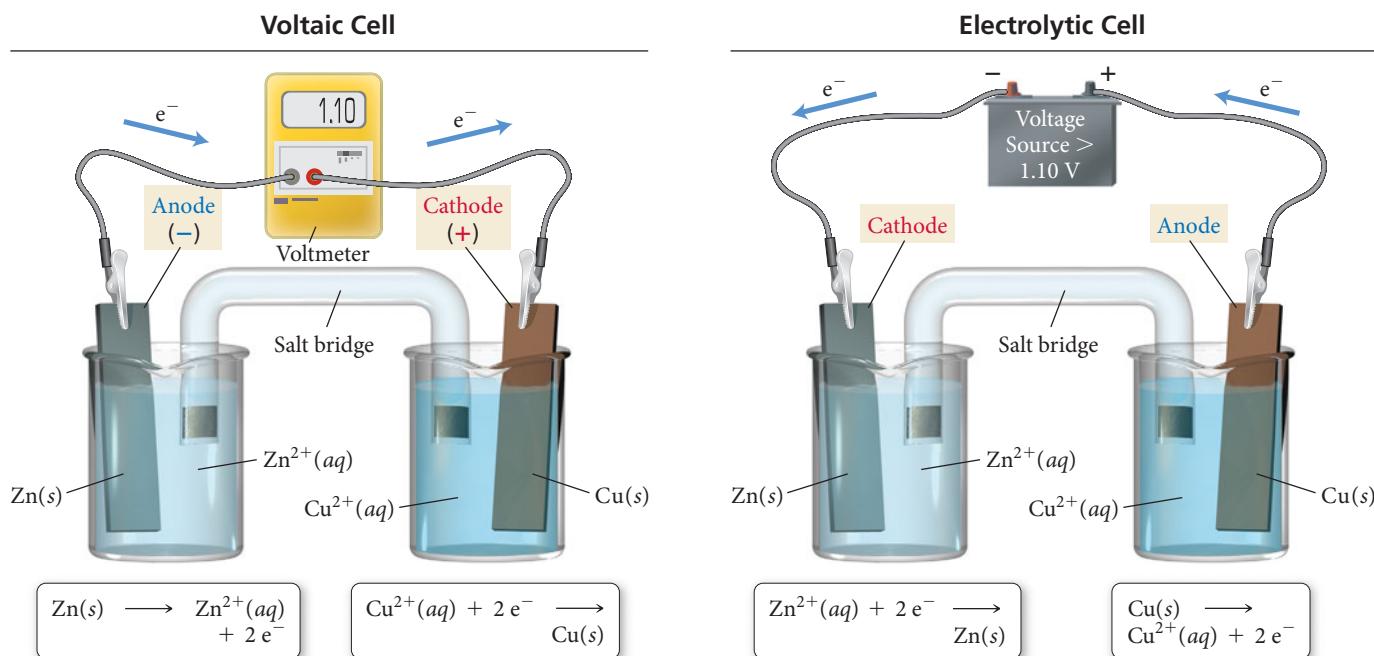
Electrolysis also has numerous other applications. For example, most metals are found in Earth's crust as metal oxides. Converting an oxide to a pure metal requires that the metal be reduced, a nonspontaneous process. Electrolysis can be used to produce these metals. Thus, sodium is produced by the electrolysis of molten sodium chloride (discussed in the following subsection). Electrolysis is also used to plate metals onto other metals. For example, silver can be plated onto a less expensive metal using the electrolytic cell shown in Figure 18.21 ▶. In this cell, a silver electrode is placed in a solution containing silver ions. An electrical current causes the oxidation of silver at the anode (replenishing the silver ions in solution) and the reduction of silver ions at the cathode (coating the less expensive metal with solid silver).



▼ FIGURE 18.21 Silver Plating Silver can be plated from a solution of silver ions onto metallic objects in an electrolytic cell.

Electrolytic Cell for Silver Plating

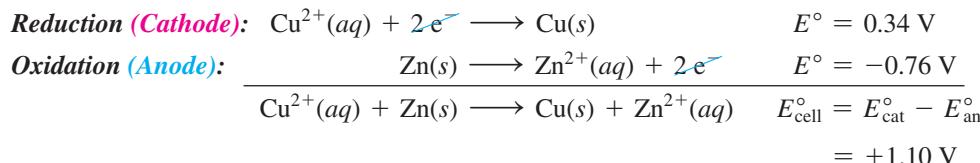




▲ **FIGURE 18.22 Voltaic versus Electrolytic Cells** In a Zn/Cu²⁺ voltaic cell, the reaction proceeds in the spontaneous direction. In a Zn²⁺/Cu electrolytic cell, electrical current drives the reaction in the nonspontaneous direction.

Since the standard cell potential of the reaction is zero, the reaction is not spontaneous under standard conditions. An external power source can be used to drive current flow and cause the reaction to occur.

The voltage required to cause electrolysis depends on the specific half-reactions. For example, we have seen that the oxidation of zinc and the reduction of Cu²⁺ produces a voltage of 1.10 V under standard conditions.



If a power source producing *more than* 1.10 V is inserted into the Zn/Cu²⁺ voltaic cell, electrons can be forced to flow in the opposite direction, causing the reduction of Zn²⁺ and the oxidation of Cu, as shown in Figure 18.22 ▲. Notice that in the electrolytic cell, the anode has become the cathode (oxidation always occurs at the anode) and the cathode has become the anode.

In a *voltaic cell*, the anode is the source of electrons and is therefore labeled with a negative charge. The cathode draws electrons and is therefore labeled with a positive charge. In an *electrolytic cell*, however, the source of the electrons is the external power source. The external power source must *draw electrons away* from the anode; thus, the anode must be connected to the positive terminal of the battery (as shown in Figure 18.22). Similarly, the power source drives electrons toward the cathode (where they will be used in reduction), so the cathode must be connected to the *negative* terminal of the battery. The charge labels (+ and -) on an electrolytic cell are opposite of what they are in a voltaic cell.

Summarizing Characteristics of Electrochemical Cell Types:

In all electrochemical cells:

- ▶ Oxidation occurs at the anode.
- ▶ Reduction occurs at the cathode.

In voltaic cells:

- The anode is the source of electrons and has a negative charge (anode -).
- The cathode draws electrons and has a positive charge (cathode +).

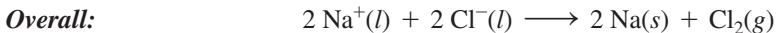
In electrolytic cells:

- Electrons are drawn away from the anode, which must be connected to the positive terminal of the external power source (anode +).
- Electrons are forced to the cathode, which must be connected to the negative terminal of the power source (cathode -).

Predicting the Products of Electrolysis

Predicting the products of an electrolysis reaction is in some cases relatively straightforward and in other cases more complex. We cover the simpler cases first and follow with the more complex ones.

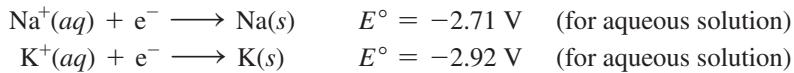
Pure Molten Salts Consider the electrolysis of a molten salt such as sodium chloride, shown in Figure 18.23 ►. Na^+ and Cl^- are the only species present in the cell. The chloride ion cannot be further reduced (-1 is its lowest oxidation state), so it must be oxidized. The sodium ion cannot be further oxidized (+1 is its highest oxidation state), so it must be reduced. Thus, we can write the half-reactions:



Although the reaction as written is not spontaneous, it can be driven to occur in an electrolytic cell by an external power source. We can generalize as follows:

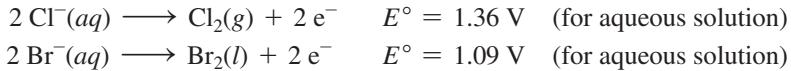
- In the electrolysis of a pure molten salt, the anion is oxidized and the cation is reduced.

Mixtures of Cations or Anions What if a molten salt contains more than one anion or cation? For example, suppose our electrolysis cell contained both NaCl and KCl. Which of the two cations would be reduced at the cathode? In order to answer this question, we must determine which of the two cations is more easily reduced. Although the values of electrode potentials for aqueous solutions given in Table 18.1 do not apply to molten salts, the relative ordering of the electrode potentials does reflect the relative ease with which the metal cations are reduced. We can see from the table that the reduction of Na^+ is listed above the reduction of K^+ ; that is, Na^+ has a more positive electrode potential.



Therefore, Na^+ is easier to reduce than K^+ . Consequently, in a mixture of NaCl and KCl, Na^+ has a greater tendency to be reduced at the cathode.

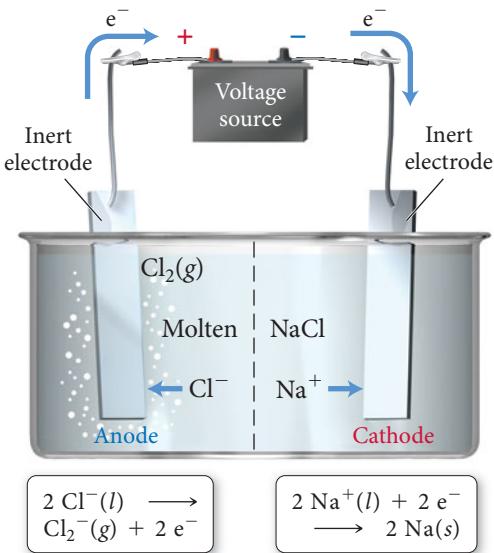
Similarly, what if a mixture of molten salts contained more than one anion? For example, in a mixture of NaBr and NaCl, which of the two anions is oxidized at the cathode? The answer is similar: the anion that is more easily oxidized (the one with the more negative electrode potential).



Since the electrode potential for the bromine half-reaction is more negative, electrons are more easily extracted from it. The bromide ion is therefore oxidized at the anode.

We can generalize as follows:

- The cation that is most easily reduced (the one with the more positive electrode potential) is reduced first.
- The anion that is most easily oxidized (the one with the more negative electrode potential) is oxidized first.

Electrolysis of a Molten Salt**▲ FIGURE 18.23** Electrolysis of Molten NaCl

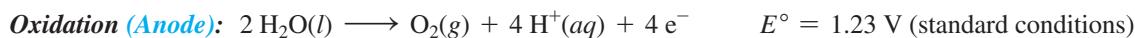
In the electrolysis of a pure molten salt, the anion (in this case Cl^-) is oxidized and the cation (in this case Na^+) is reduced.

Throughout this discussion “more positive” means the same thing as “less negative.”

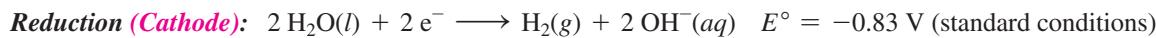
Throughout this discussion “more negative” means the same thing as “less positive.”

Remember NIO and PIR:
N.I.O.—More Negative Is Oxidation
P.I.R.—More Positive Is Reduction

Aqueous Solutions Electrolysis in an aqueous solution is complicated by the possibility of the electrolysis of water itself. Recall that water can be either oxidized or reduced according to the following half-reactions:



$$E = 0.82 \text{ V} ([\text{H}^+] = 10^{-7} \text{ M})$$



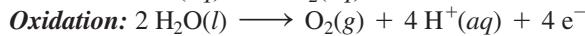
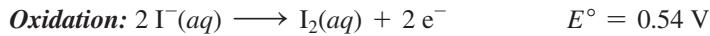
$$E = -0.41 \text{ V} ([\text{OH}^-] = 10^{-7} \text{ M})$$

The electrode potentials under standard conditions are shown to the right of each half-reaction. However, in pure water at room temperature, the concentrations of H^+ and OH^- are not standard. The electrode potentials for $[\text{H}^+] = 10^{-7} \text{ M}$ and $[\text{OH}^-] = 10^{-7} \text{ M}$ are shown in blue. Using those electrode potentials, we can calculate E_{cell} for the electrolysis of water as follows:

$$E_{\text{cell}} = E_{\text{cat}} - E_{\text{an}} = -0.41 \text{ V} - 0.82 \text{ V} = -1.23 \text{ V}$$

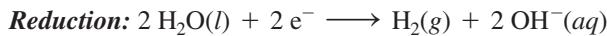
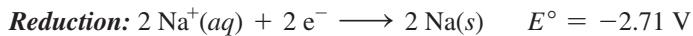
When a battery with a potential of several volts is connected to an electrolysis cell containing pure water, no reaction occurs, because the concentration of ions in pure water is too low to conduct any significant electrical current. When an electrolyte such as Na_2SO_4 is added to the water, however, electrolysis occurs readily.

In any aqueous solution in which electrolysis is to take place, the electrolysis of water is also possible. For example, consider the electrolysis of a sodium iodide solution, as shown in Figure 18.24 ▶. For the electrolysis of molten NaI , we can readily predict that I^- is oxidized at the anode and that Na^+ is reduced at the cathode. In an aqueous solution, however, two different oxidation half-reactions are possible at the anode, the oxidation of I^- and the oxidation of water:



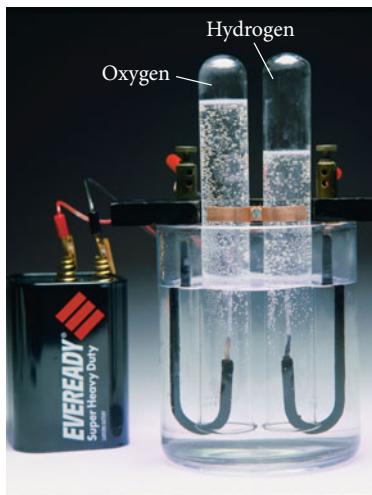
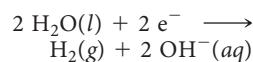
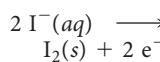
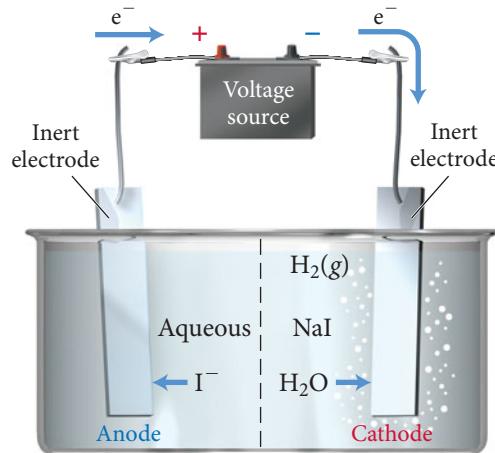
$$E = 0.82 \text{ V} ([\text{H}^+] = 10^{-7} \text{ M})$$

Similarly, two different reduction half-reactions are possible at the cathode, the reduction of Na^+ and the reduction of water:



$$E = -0.41 \text{ V} ([\text{OH}^-] = 10^{-7} \text{ M})$$

Electrolysis of an Aqueous Salt Solution



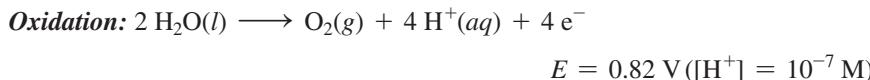
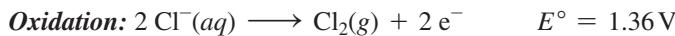
▲ Pure water is a poor conductor of electrical current, but the addition of an electrolyte allows electrolysis to take place, producing hydrogen and oxygen gas in a stoichiometric ratio.

► **FIGURE 18.24** **Electrolysis of Aqueous NaI** In this cell, I^- is oxidized to I_2 at the anode and H_2O is reduced to H_2 at the cathode. Sodium ions are not reduced, because their electrode potential is more negative than the electrode potential of water.

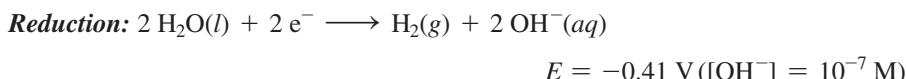
How do we know which reactions actually occur? In both cases, the answer is the same: *the half-reaction that occurs the easiest*. For oxidation, the half-reaction with the more negative electrode potential is the easier one from which to extract electrons. In this case, therefore, the iodide ion is oxidized at the anode. For reduction, the half-reaction with the more positive electrode potential is the easiest one to get to accept electrons. In this case, therefore, water is reduced at the cathode. Notice that Na^+ cannot be reduced in an aqueous solution—water is reduced before Na^+ . We can make the following generalization:

- The cations of active metals—those that are not easily reduced, such as Li^+ , K^+ , Na^+ , Mg^{2+} , Ca^{2+} , and Al^{3+} —cannot be reduced from aqueous solutions by electrolysis because water is reduced at a lower voltage.

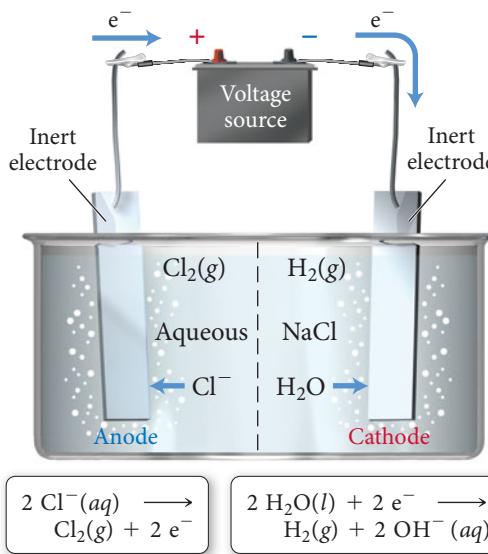
The Electrolysis of Aqueous Sodium Chloride and Overvoltage An additional complication that we must consider when predicting the products of electrolysis is *overvoltage*—an additional voltage that must be applied in order to get some nonspontaneous reactions to occur. We can demonstrate this concept by considering the electrolysis of a sodium chloride solution, shown in Figure 18.25 ▼. In order to predict the product of the electrolysis, we consider the two possible oxidation half-reactions:



and the two possible reduction half-reactions:



Since the oxidation of water has a more negative electrode potential than the oxidation of Cl^- , we would initially predict that it would be easier to remove electrons from water, and thus water should be oxidized at the anode. Similarly, since the reduction of water has a more positive electrode potential than the reduction of Na^+ , we would expect that it would be easier to get water to accept electrons, so water should be reduced at the cathode. In other words, we initially predict that a sodium chloride solution would simply result in the electrolysis of water, producing oxygen gas at the anode and hydrogen gas at the cathode. If we construct such a cell, however, we find that, although hydrogen gas is indeed formed at the cathode (as predicted), oxygen gas is *not* formed at the anode—chlorine gas is formed instead. Why? The answer is that even though the electrode potential for the oxidation of water is 0.82 V, the reaction actually requires a voltage greater



◀ FIGURE 18.25 Electrolysis of Aqueous NaCl : The Effect of Overvoltage Because of overvoltage, the anode reaction of this cell is the oxidation of Cl^- to Cl_2 gas rather than the oxidation of water to H^+ and O_2 gas.

than 0.82 V in order to occur. (The reasons for this behavior are related to kinetic factors that are beyond the scope of our current discussion.) This additional voltage, the *overvoltage*, increases the voltage required for the oxidation of water to about 1.4 V. The result is that the chloride ion oxidizes more easily than water and $\text{Cl}_2(g)$ is observed at the anode.

EXAMPLE 18.9 Predicting the Products of Electrolysis Reactions

Predict the half-reaction occurring at the anode and the cathode for electrolysis for each reaction.

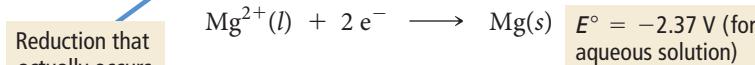
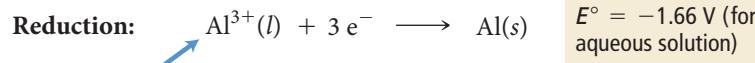
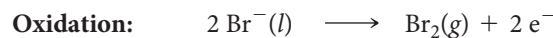
- (a) a mixture of molten AlBr_3 and MgBr_2
- (b) an aqueous solution of LiI

SOLUTION

(a) In the electrolysis of a molten salt, the anion is oxidized and the cation is reduced. However, this mixture contains two cations. Start by writing the possible oxidation and reduction half-reactions that might occur. Since Br^- is the only anion, write the equation for its oxidation, which occurs at the anode. At the cathode, both the reduction of Al^{3+} and the reduction of Mg^{2+} are possible. The one that actually occurs is the one that occurs most easily. Since the reduction of Al^{3+} has a more positive electrode potential in aqueous solution, this ion is more easily reduced. Therefore, the reduction of Al^{3+} occurs at the cathode.

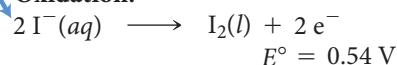
(b) Since LiI is in an aqueous solution, two different oxidation half-reactions are possible at the anode, the oxidation of I^- and the oxidation of water. Write half-reactions for each including the electrode potential. Remember to use the electrode potential of water under conditions in which $[\text{H}^+] = 10^{-7} \text{ M}$. Since the oxidation of I^- has the more negative electrode potential, it will be the half-reaction to occur at the anode.

Similarly, write half-reactions for the two possible reduction half-reactions that might occur at the cathode, the reduction of Li^+ and the reduction of water. Since the reduction of water has the more positive electrode potential (even when considering overvoltage, which would raise the necessary voltage by about 0.4–0.6 V), it will be the half reaction to occur at the cathode.

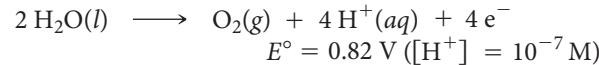


Oxidation that actually occurs (more negative potential)

Oxidation:



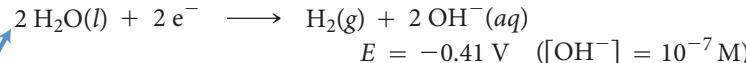
Oxidation:



Reduction:



Reduction:



Reduction that actually occurs (more positive potential)

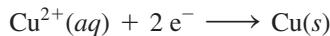
FOR PRACTICE 18.9

Predict the half-reactions occurring at the anode and the cathode for the electrolysis of aqueous Na_2SO_4 .

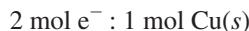
Stoichiometry of Electrolysis

In an electrolytic cell, electrical current is used to drive a particular chemical reaction. In a sense, the electrons act as a reactant and therefore have a stoichiometric relationship with the other reactants and products. Unlike ordinary reactants, for which we usually measure quantity as mass, for electrons we measure quantity as charge. For example, consider an electrolytic cell used to coat copper onto metals, as shown in Figure 18.26 ▶.

The half-reaction by which copper is deposited onto the metal is:



For every 2 mol of electrons that flow through the cell, 1 mol of solid copper is plated. We can write the stoichiometric relationship:



We can determine the number of moles of electrons that have flowed in a given electrolysis cell by measuring the total charge that has flowed through the cell, which in turn depends on the *magnitude* of the current and on the *time* that the current runs. Recall from Section 18.3 that the unit of current is the ampere.

$$1 \text{ A} = 1 \frac{\text{C}}{\text{s}}$$

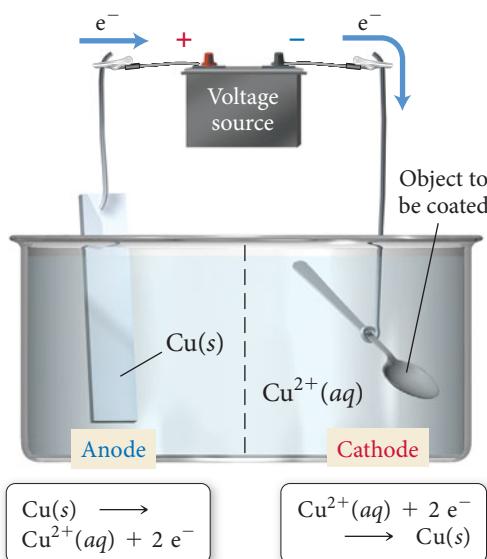
If we multiply the amount of current (in A) flowing through the cell by the time (in s) that the current flowed, we find the total charge that passed through the cell in that time:

$$\text{Current} \left(\frac{\text{C}}{\text{s}} \right) \times \text{time (s)} = \text{charge (C)}$$

The relationship between charge and the number of moles of electrons is given by Faraday's constant, which, as we saw previously, corresponds to the charge in coulombs of 1 mol of electrons.

$$F = \frac{96,485 \text{ C}}{\text{mol } e^-}$$

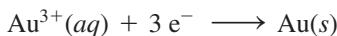
These relationships can be used to solve problems involving the stoichiometry of electrolytic cells, as shown in Example 18.10.



▲ FIGURE 18.26 Electrolytic Cell for Copper Plating In this cell, copper ions are plated onto other metals. It takes two moles of electrons to plate one mole of copper atoms.

EXAMPLE 18.10 Stoichiometry of Electrolysis

Gold can be plated out of a solution containing Au^{3+} according to the half-reaction:



What mass of gold (in grams) is plated by a 25-minute flow of 5.5 A current?

SORT You are given the half-reaction for the plating of gold, which shows the stoichiometric relationship between moles of electrons and moles of gold. You are also given the current and duration. You must find the mass of gold that will be deposited in that time.

STRATEGIZE You need to find the amount of gold, which is related stoichiometrically to the number of electrons that have flowed through the cell. Begin with time in minutes and convert to seconds. Then, since current is a measure of charge per unit time, use the given current and the time to find the number of coulombs. You can use Faraday's constant to calculate the number of moles of electrons and the stoichiometry of the reaction to find the number of moles of gold. Finally, use the molar mass of gold to convert to mass of gold.

SOLVE Follow the conceptual plan to solve the problem, canceling units to arrive at the mass of gold.

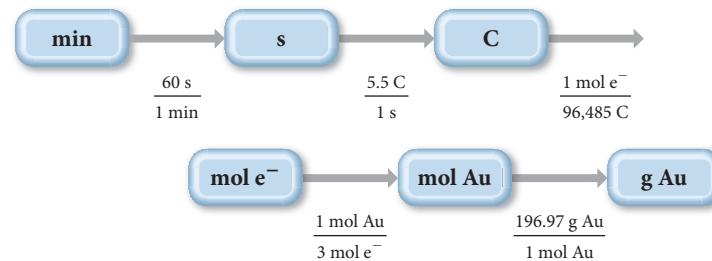
GIVEN: 3 mol e^- : 1 mol Au

5.5 amps

25 min

FIND: g Au

CONCEPTUAL PLAN



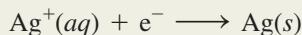
SOLUTION

$$25 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{5.5 \text{ C}}{1 \text{ s}} \times \frac{1 \text{ mol } e^-}{96,485 \text{ C}} \times \frac{1 \text{ mol Au}}{3 \text{ mol } e^-} \times \frac{196.97 \text{ g Au}}{1 \text{ mol Au}} = 5.6 \text{ g Au}$$

CHECK The answer has the correct units (g Au). The magnitude of the answer is reasonable if we consider that 10 amps of current for 1 hour is the equivalent of about 1/3 mol of electrons (check for yourself), which would produce 1/9 mol (or about 20 g) of gold.

FOR PRACTICE 18.10

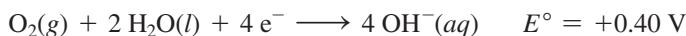
Silver can be plated out of a solution containing Ag^+ according to the half-reaction:



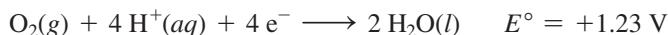
How much time (in minutes) would it take to plate 12 g of silver using a current of 3.0 A?

18.9 Corrosion: Undesirable Redox Reactions

Corrosion is the (usually) gradual, nearly always undesired, oxidation of metals that are exposed to oxidizing agents in the environment. From Table 18.1, we can see that the reduction of oxygen in the presence of water has an electrode potential of +0.40 V.



In the presence of acid, the reduction of oxygen has an even more positive electrode potential of +1.23 V.



The reduction of oxygen, therefore, has a strong tendency to occur and can bring about the oxidation of other substances, especially metals. Notice that the half-reactions for the reduction of most metal ions are listed *below* the half-reactions for the reduction of

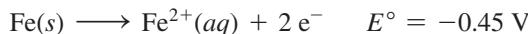


▲ A metal must usually be reduced to extract it from its ore. In corrosion, the metal is oxidized back to its more natural state.

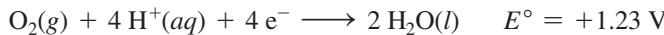
oxygen in Table 18.1. Consequently, the oxidation (or corrosion) of those metals is spontaneous when paired with the reduction of oxygen. Corrosion is the opposite of the process by which metals are extracted from their ores. In extraction, the free metal is reduced out from its ore. In corrosion, the metal is oxidized.

Given the ease with which metals oxidize in the presence of oxygen, acid, and water, why are metals used so frequently as building materials in the first place? Many metals form oxides that coat the surface of the metal and prevent further corrosion. For example, bare aluminum metal, with an electrode potential of -1.66 V , is quickly oxidized in the presence of oxygen. However, the oxide that forms at the surface of aluminum is Al_2O_3 . In its crystalline form, Al_2O_3 is sapphire, a highly inert and structurally solid substance. The Al_2O_3 coating acts to protect the underlying aluminum metal, preventing further corrosion.

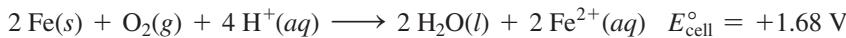
The oxides of iron, however, are not structurally stable, and they tend to flake away from the underlying metal, exposing it to further corrosion. A significant part of the iron produced each year is used to replace rusted iron. Rusting is a redox reaction in which iron is oxidized according to the following half-reaction:



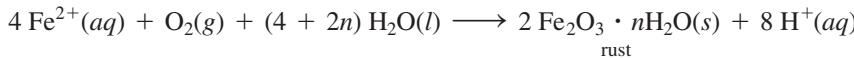
This oxidation reaction tends to occur at defects on the surface of the iron—known as *anodic regions* because oxidation is occurring at these locations—as shown in Figure 18.27 ▼. The electrons produced at the anodic region travel through the metal to areas called *cathodic regions* where they react with oxygen and H^+ ions dissolved in moisture. (The H^+ ions come from carbonic acid, which naturally forms in water from carbon dioxide in air.)



The overall reaction has a cell potential of $+1.68\text{ V}$ and is highly spontaneous.



The Fe^{2+} ions formed in the anodic regions can migrate through moisture on the surface of the iron to cathodic regions, where they are further oxidized by reaction with more oxygen.



Rust is a hydrated form of iron(III) oxide whose exact composition depends on the conditions under which it forms.

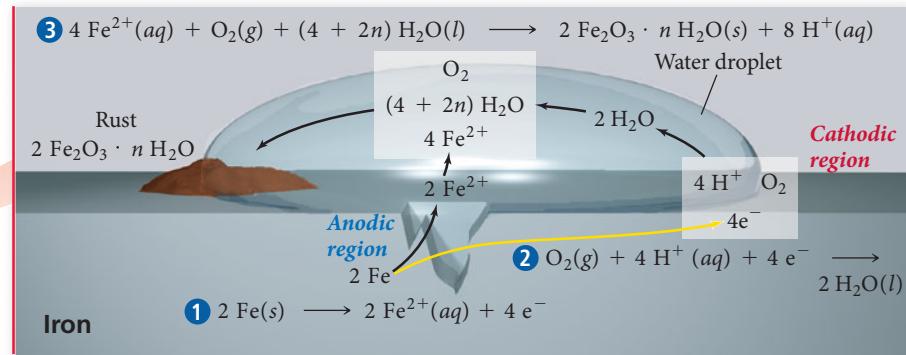
Consider each of the following important components in the formation of rust:

- *Moisture must be present for rusting to occur.* The presence of water is necessary because water is a reactant in the last reaction and because charge (either electrons or ions) must be free to flow between the anodic and cathodic regions.
- *Additional electrolytes promote rusting.* The presence of an electrolyte (such as sodium chloride) on the surface of iron promotes rusting because it enhances current flow. This is why cars rust so quickly in cold climates where roads are salted, or in coastal areas where salt water mist is present.
- *The presence of acids promotes rusting.* Since H^+ ions are involved in the reduction of oxygen, lower pH enhances the cathodic reaction and leads to faster rusting.



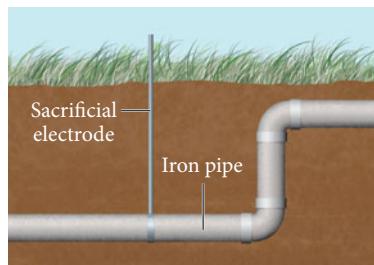
▲ Aluminum is stable because its oxide forms a protective film over the underlying metal, preventing further oxidation.

The Rusting of Iron





▲ A scratch in paint often allows the underlying iron to rust.



▲ If a metal more active than iron, such as magnesium or aluminum, is in electrical contact with iron, the metal rather than the iron will be oxidized. This principle underlies the use of sacrificial electrodes to prevent the corrosion of iron.

Preventing Corrosion

Preventing the rusting of iron is a major industry. The most obvious way to prevent rust is to keep iron dry. Without water, the redox reaction cannot occur. Another way to prevent rust is to coat iron with a substance that is impervious to water. Cars, for example, are painted and sealed to prevent rust. A scratch in the paint can lead to rusting of the underlying iron.

Rust can also be prevented by placing a *sacrificial electrode* in electrical contact with the iron. The sacrificial electrode must be composed of a metal that oxidizes more easily than iron (that is, it must be below iron in Table 18.1). The sacrificial electrode oxidizes in place of the iron (just as the more easily oxidizable species in a mixture is the one to oxidize), protecting the iron from oxidation. A related way to protect iron from rusting is to coat it with a metal that oxidizes more easily than iron. Galvanized nails, for example, are coated with a thin layer of zinc. Since zinc has a more negative electrode potential than iron, it will oxidize in place of the underlying iron (just as a sacrificial electrode does). The oxide of zinc is not crumbly and remains on the nail as a protective coating.



▲ In galvanized nails, a layer of zinc prevents the underlying iron from rusting. The zinc oxidizes in place of the iron, forming a protective layer of zinc oxide.

Conceptual Connection 18.8 Sacrificial Electrodes

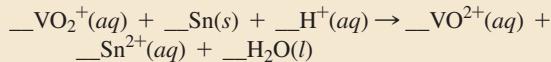
Which of these metals does not act as a sacrificial electrode for iron?

Zn, Mg, Mn, Cu

CHAPTER IN REVIEW

Self Assessment Quiz

- Q1.** Balance the redox reaction equation (occurring in acidic solution) and choose the correct coefficients for each reactant and product.



- a) 2,1,4 → 2,1,2 b) 1,1,2 → 1,1,1
c) 2,1,2 → 2,1,1 d) 2,1,2 → 2,1,2

- Q2.** Which statement is true for voltaic cells?

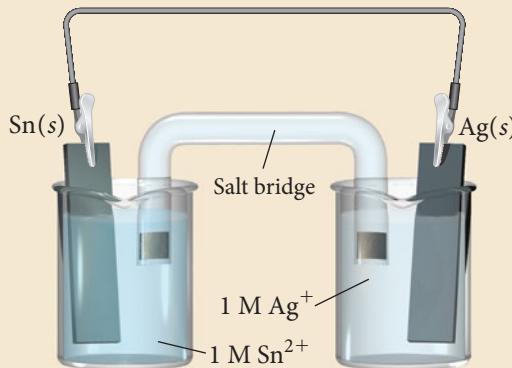
- a) Electrons flow from the anode to the cathode.
b) Electrons flow from the more negatively charged electrode to the more positively charged electrode.
c) Electrons flow from higher potential energy to lower potential energy.
d) All of the above

- Q3.** Use data from Table 18.1 to calculate E_{cell}° for the reaction.



- a) 1.77 V
b) 2.03 V
c) 0.82 V
d) 1.08 V

- Q4.** Use data from Table 18.1 to determine which statement is true of the voltaic cell picture here.



- a) Sn is the anode; Ag is the cathode; electrons flow from left to right
- b) Sn is the cathode; Ag is the anode; electrons flow from left to right
- c) Sn is the anode; Ag is the cathode; electrons flow from right to left
- d) Sn is the cathode; Ag is the anode; electrons flow from right to left

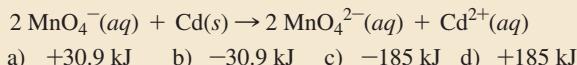
- Q5.** Use data from Table 18.1 to determine which metal *does not* dissolve in hydrochloric acid (HCl).

- a) Zn
- b) Cd
- c) Cu
- d) Fe

- Q6.** The Zn/Zn²⁺ electrode has a standard electrode potential of $E^\circ = -0.76$ V. How does the relative potential energy of an electron at the Zn/Zn²⁺ electrode compare to the potential energy of an electron at the standard hydrogen electrode?

- a) An electron at the Zn/Zn²⁺ electrode has a higher potential energy than an electron at the standard hydrogen electrode.
- b) An electron at the Zn/Zn²⁺ electrode has a lower potential energy than an electron at the standard hydrogen electrode.
- c) An electron at the Zn/Zn²⁺ electrode has the same potential energy as an electron at the standard hydrogen electrode.
- d) Nothing can be concluded about the relative potential energy of an electron at the standard electrode potential.

- Q7.** Use data from Table 18.1 to calculate ΔG° for the reaction.

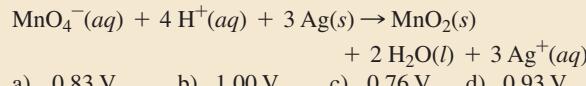


Answers: 1. (a) 2. (d) 3. (d) 4. (a) 5. (c) 6. (a) 7. (c) 8. (a) 9. (b) 10. (d) 11. (c) 12. (a) 13. (c) 14. (c) 15. (d)

- Q8.** A redox reaction has an $E_{\text{cell}}^\circ = -0.56$ V. What can you conclude about the equilibrium constant (K) for the reaction?

- a) $K < 1$
- b) $K > 1$
- c) $K = 0$
- d) Nothing can be concluded about K from E_{cell}° .

- Q9.** Find E_{cell} for an electrochemical cell based on the following reaction with $[\text{MnO}_4^-] = 2.0$ M, $[\text{H}^+] = 1.0$ M, and $[\text{Ag}^+] = 0.010$ M. E_{cell}° for the reaction is +0.88 V.



- Q10.** In an electrochemical cell, $Q = 0.010$ and $K = 855$. What can you conclude about E_{cell} and E_{cell}° ?

- a) E_{cell} is positive and E_{cell}° is negative.
- b) E_{cell} is negative and E_{cell}° is positive.
- c) E_{cell} and E_{cell}° are both negative.
- d) E_{cell} and E_{cell}° are both positive.

- Q11.** Which reaction occurs at the *anode* of a lead storage battery?

- a) $\text{Zn}(s) + 2 \text{OH}^-(aq) \rightarrow \text{Zn}(\text{OH})_2(s) + 2 \text{e}^-$
- b) $\text{PbO}_2(s) + \text{HSO}_4^-(aq) + 3 \text{H}^+(aq) + 2 \text{e}^- \rightarrow \text{PbSO}_4(s) + 2 \text{H}_2\text{O}(l)$
- c) $\text{Pb}(s) + \text{HSO}_4^-(aq) \rightarrow \text{PbSO}_4(s) + \text{H}^+(aq) + 2 \text{e}^-$
- d) $\text{O}_2(g) + 2 \text{H}_2\text{O}(l) + 4 \text{e}^- \rightarrow 4 \text{OH}^-(aq)$

- Q12.** Which reaction could be used to generate electricity in a voltaic electrochemical cell?

- a) $\text{Pb}^{2+}(aq) + \text{Mg}(s) \rightarrow \text{Mg}^{2+}(aq) + \text{Pb}(s)$
- b) $\text{Zn}^{2+}(aq) + \text{Sn}(s) \rightarrow \text{Sn}^{2+}(aq) + \text{Zn}(s)$
- c) $\text{NaCl}(aq) + \text{AgNO}_3(aq) \rightarrow \text{AgCl}(s) + \text{NaNO}_3(aq)$
- d) None of the above

- Q13.** Which reaction occurs at the cathode of an electrolytic cell containing a mixture of molten KCl and ZnCl₂?

- a) $\text{K}(s) \rightarrow \text{K}^+(l) + \text{e}^-$
- b) $\text{K}^+(l) + \text{e}^- \rightarrow \text{K}(s)$
- c) $\text{Zn}^{2+}(l) + 2 \text{e}^- \rightarrow \text{Zn}(s)$
- d) $2 \text{Cl}^-(l) \rightarrow \text{Cl}_2(g) + 2 \text{e}^-$

- Q14.** Copper is plated onto the cathode of an electrolytic cell containing CuCl₂(aq). How long does it take to plate 111 mg of copper with a current of 3.8 A?

- a) 1.3×10^3 s
- b) 44 s
- c) 89 s
- d) 22 s

- Q15.** Which metal can be used as a sacrificial electrode to prevent the rusting of an iron pipe?

- a) Au
- b) Ag
- c) Cu
- d) Mn

Answers: 1. (a) 2. (d) 3. (d) 4. (a) 5. (c) 6. (a) 7. (c) 8. (a) 9. (b) 10. (d) 11. (c) 12. (a) 13. (c) 14. (c) 15. (d)

Key Terms

Section 18.3

- electrical current (865)
- electrochemical cell (866)
- voltaic (galvanic) cell (866)
- electrolytic cell (866)
- half-cell (866)
- electrode (866)
- ampere (A) (867)
- potential difference (867)
- volt (V) (867)
- electromotive force (emf) (867)
- cell potential (cell emf) (E_{cell}) (868)
- standard cell potential (standard emf) (E_{cell}°) (868)

Section 18.4

- anode (868)
- cathode (868)
- salt bridge (868)
- standard electrode potential (870)
- standard hydrogen electrode (SHE) (870)

Section 18.5

- Faraday's constant (F) (878)

Section 18.6

- Nernst equation (882)

Section 18.7

- dry-cell battery (886)
- alkaline battery (887)
- lead-acid storage battery (887)
- nickel-cadmium (NiCad) battery (888)
- nickel–metal hydride (NiMH) battery (888)
- lithium ion battery (888)
- fuel cell (889)

Section 18.8

- electrolysis (890)

Section 18.9

- corrosion (898)

Key Concepts

Pulling the Plug on the Power Grid (18.1)

- Oxidation–reduction reactions are reactions in which electrons are transferred from one reactant to another
- In the most common form of fuel cell, an electrical current is created as hydrogen is oxidized and oxygen is reduced; water is the only product.

Balancing Oxidation–Reduction Equations (18.2)

- Oxidation is the loss of electrons and corresponds to an increase in oxidation state; reduction is the gain of electrons and corresponds to a decrease in oxidation state.
- We can balance redox reactions using the half-reaction method, in which the oxidation and reduction reactions are balanced separately and then added. This method differs slightly for redox reactions in acidic and in basic solutions.

Voltaic (or Galvanic) Cells: Generating Electricity from Spontaneous Chemical Reactions (18.3)

- A voltaic electrochemical cell separates the reactants of a spontaneous redox reaction into two half-cells that are connected by a wire and a means to exchange ions so that electricity is generated.
- In an electrochemical cell, the electrode where oxidation occurs is the anode and the electrode where reduction occurs is the cathode; electrons flow from the anode to the cathode.
- The rate of electrons flowing through a wire is measured in amperes (A), and the cell potential is measured in volts (V).
- A salt bridge is commonly used to allow ions to flow between the half-cell solutions and prevent the build up of charge.
- Cell diagram or line notation is a technique for symbolizing electrochemical cells concisely by separating the components of the reaction using lines or commas.

Standard Electrode Potentials (18.4)

- The electrode potentials of half-cells are measured in relation to that of a standard hydrogen electrode, which is assigned an electrode potential of zero under standard conditions (solution concentrations of 1 M, gas pressures of 1 atm, and a temperature of 25 °C).
- A species with a highly positive E° has a strong tendency to attract electrons and undergo reduction (and is therefore an excellent oxidizing agent).
- A species with a highly negative E° has a strong tendency to repel electrons and undergo oxidation (and is therefore an excellent reducing agent).

Cell Potential, Free Energy, and the Equilibrium Constant (18.5)

- In a spontaneous reaction, E_{cell}° is positive, the change in free energy (ΔG°) is negative, and the equilibrium constant (K) is greater than 1.

- In a nonspontaneous reaction, E_{cell}° is negative, ΔG° is positive, and K is less than 1.
- Because E_{cell}° , ΔG° , and K all relate to spontaneity, we can derive equations relating all three quantities.

Cell Potential and Concentration (18.6)

- The standard cell potential (E_{cell}°) is related to the cell potential (E_{cell}) by the Nernst equation, $E_{\text{cell}} = E_{\text{cell}}^\circ - (0.0592 \text{ V}/n) \log Q$.
- As shown by the Nernst equation, E_{cell} is related to the reaction quotient (Q); E_{cell} equals zero when Q equals K .
- In a concentration cell, the reactions at both electrodes are identical and electrons flow because of a difference in concentration. Nerve cells are a biological example of concentration cells.

Batteries: Using Chemistry to Generate Electricity (18.7)

- Batteries are packaged voltaic cells.
- Dry-cell batteries, including alkaline batteries, do not contain large amounts of water.
- The reactions in rechargeable batteries, such as lead–acid storage, nickel–cadmium, nickel–metal hydride, and lithium ion batteries, can be reversed.
- Fuel cells are similar to batteries except that fuel-cell reactants must be continually replenished from an external source.

Electrolysis: Driving Nonspontaneous Chemical Reactions with Electricity (18.8)

- An electrolytic electrochemical cell differs from a voltaic cell in that (1) an electrical charge is used to drive the reaction, and (2) although the anode is still the site of oxidation and the cathode the site of reduction, they are represented with signs opposite those of a voltaic cell (anode +, cathode –).
- In electrolysis reactions, the anion is oxidized; if there is more than one anion, the anion with the more negative E° is oxidized.
- We can use stoichiometry to calculate the quantity of reactants consumed or products produced in an electrolytic cell.

Corrosion: Undesirable Redox Reactions (18.9)

- Corrosion is the undesired oxidation of metal by environmental oxidizing agents.
- When some metals, such as aluminum, oxidize they form a stable compound that prevents further oxidation. Iron, however, does not form a structurally stable compound when oxidized and therefore rust flakes off and exposes more iron to corrosion.
- Iron corrosion can be prevented by preventing water contact, minimizing the presence of electrolytes and acids, or using a sacrificial electrode.

Key Equations and Relationships

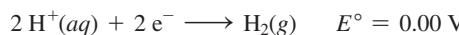
Definition of an Ampere (18.3)

$$1 \text{ A} = 1 \text{ C/s}$$

Definition of a Volt (18.3)

$$1 \text{ V} = 1 \text{ J/C}$$

Standard Hydrogen Electrode (18.4)



Equation for Cell Potential (18.4)

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$$

Relating ΔG° and E_{cell}° (18.5)

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ \quad F = \frac{96,485 \text{ C}}{\text{mol e}^-}$$

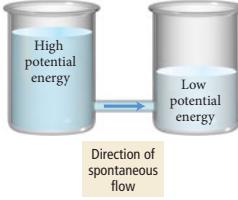
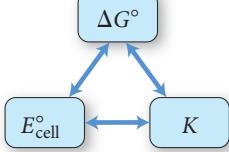
Relating E_{cell}° and K (18.5)

$$E_{\text{cell}}^\circ = \frac{0.0592 \text{ V}}{n} \log K \quad (\text{at } 25^\circ\text{C})$$

The Nernst Equation (18.6)

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592 \text{ V}}{n} \log Q \quad (\text{at } 25^\circ\text{C})$$

Key Learning Outcomes

Chapter Objectives	Assessment
Half-Reaction Method of Balancing Aqueous Redox Equations in Acidic Solution (18.2)	Examples 18.1, 18.2 For Practice 18.1, 18.2 Exercises 37–40
Balancing Redox Reactions Occurring in Basic Solution (18.2)	Example 18.3 For Practice 18.3 Exercises 41, 42
Calculating Standard Potentials for Electrochemical Cells from Standard Electrode Potentials of the Half-Reactions (18.4)	Example 18.4 For Practice 18.4 Exercises 45, 46, 61, 62
	
Predicting Spontaneous Redox Reactions and Sketching Electrochemical Cells (18.4)	Example 18.5 For Practice 18.5 Exercises 43, 44, 47, 48, 51–54
Relating ΔG° and E_{cell}° (18.5)	Example 18.6 For Practice 18.6 Exercises 65, 66
Relating E_{cell}° and K (18.5)	Example 18.7 For Practice 18.7 Exercises 67–72
	
Calculating E_{cell} under Nonstandard Conditions (18.6)	Example 18.8 For Practice 18.8 Exercises 73–78
Predicting the Products of Electrolysis Reactions (18.8)	Example 18.9 For Practice 18.9 Exercises 91–96
Stoichiometry of Electrolysis (18.8)	Example 18.10 For Practice 18.10 Exercises 99–102

EXERCISES**Review Questions**

- In electrochemistry, spontaneous redox reactions are used for what purpose?
- In electrochemistry, what kind of reaction can be driven by electricity?
- Give the basic definitions of oxidation and reduction and explain the basic procedure for balancing redox reactions.
- Explain the difference between a voltaic (or galvanic) electrochemical cell and an electrolytic one.
- What reaction (oxidation or reduction) occurs at the anode of a voltaic cell? What is the sign of the anode? Do electrons flow toward or away from the anode?

6. What reaction (oxidation or reduction) occurs at the cathode of a voltaic cell? What is the sign of the cathode? Do electrons flow toward or away from the cathode?
7. Explain the purpose of a salt bridge in an electrochemical cell.
8. What unit is used to measure the magnitude of electrical current? What unit is used to measure the magnitude of a potential difference? Explain how electrical current and potential difference differ.
9. What is the definition of the standard cell potential (E_{cell}°)? What does a large positive standard cell potential imply about the spontaneity of the redox reaction occurring in the cell? What does a negative standard cell potential imply about the reaction?
10. Describe the basic features of a cell diagram (or line notation) for an electrochemical cell.
11. Why do some electrochemical cells employ inert electrodes such as platinum?
12. Describe the standard hydrogen electrode (SHE) and explain its use in determining standard electrode potentials.
13. How is the cell potential of an electrochemical cell (E_{cell}) related to the potentials of the half-cells?
14. Does a large positive electrode potential indicate a strong oxidizing agent or a strong reducing agent? What about a large negative electrode potential?
15. Is a spontaneous redox reaction obtained by pairing any reduction half-reaction with one listed above it or with one listed below it in Table 18.1?
16. How can Table 18.1 be used to predict whether or not a metal will dissolve in HCl? In HNO_3 ?
17. Explain why E_{cell}° , $\Delta G_{\text{rxn}}^{\circ}$, and K are all interrelated.
18. Does a redox reaction with a small equilibrium constant ($K < 1$) have a positive or a negative E_{cell}° ? Does it have a positive or a negative $\Delta G_{\text{rxn}}^{\circ}$?
19. How does E_{cell} depend on the concentrations of the reactants and products in the redox reaction occurring in the cell? What effect does increasing the concentration of a reactant have on E_{cell} ? Increasing the concentration of a product?
20. Use the Nernst equation to show that $E_{\text{cell}} = E_{\text{cell}}^{\circ}$ under standard conditions.
21. What is a concentration electrochemical cell?
22. What are the anode and cathode reactions in a common dry-cell battery? In an alkaline battery?
23. What are the anode and cathode reactions in a lead–acid storage battery? What happens when the battery is recharged?
24. What are the three common types of portable rechargeable batteries and how does each one work?
25. What is a fuel cell? What is the most common type of fuel cell and what reactions occur at its anode and cathode?
26. Explain how a fuel-cell breathalyzer works.
27. List some applications of electrolysis.
28. The anode of an electrolytic cell must be connected to which terminal—positive or negative—of the power source?
29. What species is oxidized and what species is reduced in the electrolysis of a pure molten salt?
30. If an electrolytic cell contains a mixture of species that can be oxidized, how do you determine which species will actually be oxidized? If it contains a mixture of species that can be reduced, how do you determine which one will actually be reduced?
31. Why does the electrolysis of an aqueous sodium chloride solution produce hydrogen gas at the cathode?
32. What is overvoltage in an electrochemical cell? Why is it important?
33. How is the amount of current flowing through an electrolytic cell related to the amount of product produced in the redox reaction?
34. What is corrosion? Why is corrosion only a problem for some metals (such as iron)?
35. Explain the role of each of the following in promoting corrosion: moisture, electrolytes, and acids.
36. How can the corrosion of iron be prevented?

Problems by Topic

Balancing Redox Reactions

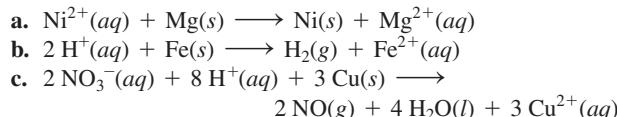
37. Balance each redox reaction occurring in acidic aqueous solution.
 - a. $\text{K}(s) + \text{Cr}^{3+}(aq) \longrightarrow \text{Cr}(s) + \text{K}^{+}(aq)$
 - b. $\text{Al}(s) + \text{Fe}^{2+}(aq) \longrightarrow \text{Al}^{3+}(aq) + \text{Fe}(s)$
 - c. $\text{BrO}_3^-(aq) + \text{N}_2\text{H}_4(g) \longrightarrow \text{Br}^-(aq) + \text{N}_2(g)$
38. Balance each redox reaction occurring in acidic aqueous solution.
 - a. $\text{Zn}(s) + \text{Sn}^{2+}(aq) \longrightarrow \text{Zn}^{2+}(aq) + \text{Sn}(s)$
 - b. $\text{Mg}(s) + \text{Cr}^{3+}(aq) \longrightarrow \text{Mg}^{2+}(aq) + \text{Cr}(s)$
 - c. $\text{MnO}_4^-(aq) + \text{Al}(s) \longrightarrow \text{Mn}^{2+}(aq) + \text{Al}^{3+}(aq)$
39. Balance each redox reaction occurring in acidic aqueous solution.
 - a. $\text{PbO}_2(s) + \text{I}^-(aq) \longrightarrow \text{Pb}^{2+}(aq) + \text{I}_2(s)$
 - b. $\text{SO}_3^{2-}(aq) + \text{MnO}_4^-(aq) \longrightarrow \text{SO}_4^{2-}(aq) + \text{Mn}^{2+}(aq)$
 - c. $\text{S}_2\text{O}_3^{2-}(aq) + \text{Cl}_2(g) \longrightarrow \text{SO}_4^{2-}(aq) + \text{Cl}^-(aq)$
40. Balance each redox reaction occurring in acidic aqueous solution.
 - a. $\text{I}^-(aq) + \text{NO}_2^-(aq) \longrightarrow \text{I}_2(s) + \text{NO}(g)$
 - b. $\text{ClO}_4^-(aq) + \text{Cl}^-(aq) \longrightarrow \text{ClO}_3^-(aq) + \text{Cl}_2(g)$
 - c. $\text{NO}_3^-(aq) + \text{Sn}^{2+}(aq) \longrightarrow \text{Sn}^{4+}(aq) + \text{NO}(g)$

41. Balance each redox reaction occurring in basic aqueous solution.
 - a. $\text{H}_2\text{O}_2(aq) + \text{ClO}_2(aq) \longrightarrow \text{ClO}_2^-(aq) + \text{O}_2(g)$
 - b. $\text{Al}(s) + \text{MnO}_4^-(aq) \longrightarrow \text{MnO}_2(s) + \text{Al}(\text{OH})_4^-(aq)$
 - c. $\text{Cl}_2(g) \longrightarrow \text{Cl}^-(aq) + \text{ClO}^-(aq)$
42. Balance each redox reaction occurring in basic aqueous solution.
 - a. $\text{MnO}_4^-(aq) + \text{Br}^-(aq) \longrightarrow \text{MnO}_2(s) + \text{BrO}_3^-(aq)$
 - b. $\text{Ag}(s) + \text{CN}^-(aq) + \text{O}_2(g) \longrightarrow \text{Ag}(\text{CN})_2^-(aq)$
 - c. $\text{NO}_2^-(aq) + \text{Al}(s) \longrightarrow \text{NH}_3(g) + \text{AlO}_2^-(aq)$

Voltaic Cells, Standard Cell Potentials, and Direction of Spontaneity

43. Sketch a voltaic cell for each redox reaction. Label the anode and cathode and indicate the half-reaction that occurs at each electrode and the species present in each solution. Also indicate the direction of electron flow.
 - a. $2 \text{Ag}^+(aq) + \text{Pb}(s) \longrightarrow 2 \text{Ag}(s) + \text{Pb}^{2+}(aq)$
 - b. $2 \text{ClO}_2(g) + 2 \text{I}^-(aq) \longrightarrow 2 \text{ClO}_2^-(aq) + \text{I}_2(s)$
 - c. $\text{O}_2(g) + 4 \text{H}^+(aq) + 2 \text{Zn}(s) \longrightarrow 2 \text{H}_2\text{O}(l) + 2 \text{Zn}^{2+}(aq)$

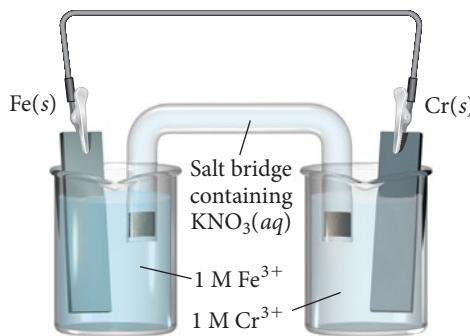
44. Sketch a voltaic cell for each redox reaction. Label the anode and cathode and indicate the half-reaction that occurs at each electrode and the species present in each solution. Also indicate the direction of electron flow.



45. Calculate the standard cell potential for each of the electrochemical cells in Problem 43.

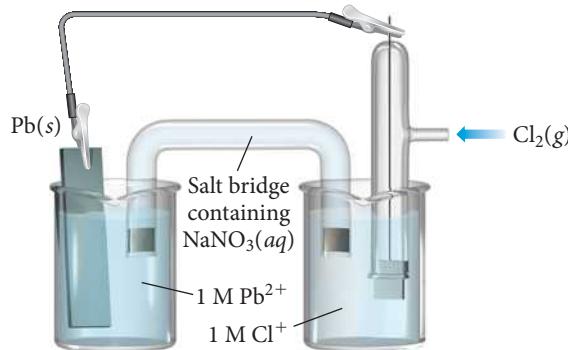
46. Calculate the standard cell potential for each of the electrochemical cells in Problem 44.

47. Consider the voltaic cell:



- Determine the direction of electron flow and label the anode and the cathode.
- Write a balanced equation for the overall reaction and calculate E_{cell}° .
- Label each electrode as negative or positive.
- Indicate the direction of anion and cation flow in the salt bridge.

48. Consider the voltaic cell:

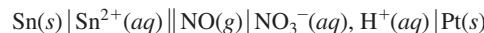


- Determine the direction of electron flow and label the anode and the cathode.
- Write a balanced equation for the overall reaction and calculate E_{cell}° .
- Label each electrode as negative or positive.
- Indicate the direction of anion and cation flow in the salt bridge.

49. Use line notation to represent each electrochemical cell in Problem 43.

50. Use line notation to represent each electrochemical cell in Problem 44.

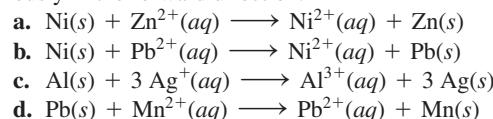
51. Make a sketch of the voltaic cell represented by the line notation. Write the overall balanced equation for the reaction and calculate E_{cell}° .



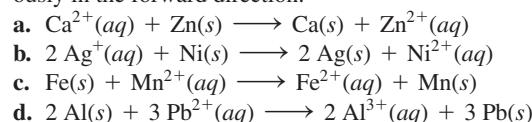
52. Make a sketch of the voltaic cell represented by the line notation. Write the overall balanced equation for the reaction and calculate E_{cell}° .



53. Determine whether or not each redox reaction occurs spontaneously in the forward direction.



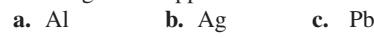
54. Determine whether or not each redox reaction occurs spontaneously in the forward direction.



55. Which metal could you use to reduce Mn^{2+} ions but not Mg^{2+} ions?

56. Which metal can be oxidized with an Sn^{2+} solution but not with an Fe^{2+} solution?

57. Determine whether or not each metal dissolves in 1 M HCl. For those metals that do dissolve, write a balanced redox reaction showing what happens when the metal dissolves.



58. Determine whether or not each metal dissolves in 1 M HCl. For those metals that do dissolve, write a balanced redox reaction showing what happens when the metal dissolves.



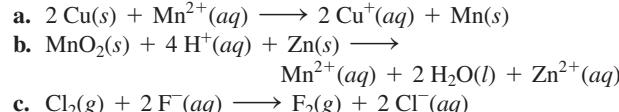
59. Determine whether or not each metal dissolves in 1 M HNO_3 . For those metals that do dissolve, write a balanced redox reaction showing what happens when the metal dissolves.



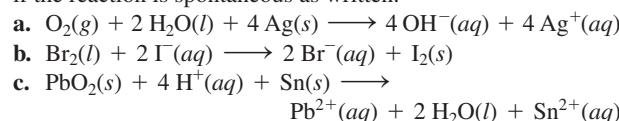
60. Determine whether or not each metal dissolves in 1 M HIO_3 . For those metals that do dissolve, write a balanced redox equation for the reaction that occurs.



61. Calculate E_{cell}° for each balanced redox reaction and determine if the reaction is spontaneous as written.



62. Calculate E_{cell}° for each balanced redox reaction and determine if the reaction is spontaneous as written.



63. Which metal cation is the best oxidizing agent?

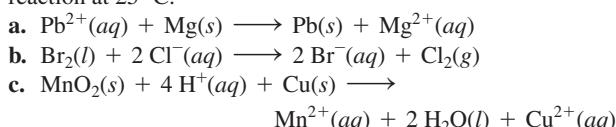


64. Which metal is the best reducing agent?

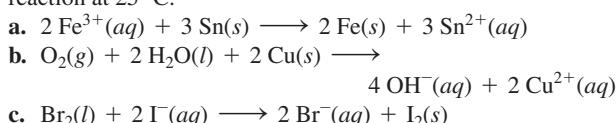


Cell Potential, Free Energy, and the Equilibrium Constant

65. Use tabulated electrode potentials to calculate $\Delta G_{\text{rxn}}^{\circ}$ for each reaction at 25 °C.



66. Use tabulated electrode potentials to calculate $\Delta G_{\text{rxn}}^{\circ}$ for each reaction at 25 °C.



67. Calculate the equilibrium constant for each of the reactions in Problem 65.

68. Calculate the equilibrium constant for each of the reactions in Problem 66.

69. Calculate the equilibrium constant for the reaction between $\text{Ni}^{2+}(aq)$ and $\text{Cd}(s)$ (at 25 °C).

70. Calculate the equilibrium constant for the reaction between $\text{Fe}^{2+}(aq)$ and $\text{Zn}(s)$ (at 25 °C).

71. Calculate $\Delta G_{\text{rxn}}^{\circ}$ and E_{cell}° for a redox reaction with $n = 2$ that has an equilibrium constant of $K = 25$ (at 25 °C).

72. Calculate $\Delta G_{\text{rxn}}^{\circ}$ and E_{cell}° for a redox reaction with $n = 3$ that has an equilibrium constant of $K = 0.050$ (at 25 °C).

Nonstandard Conditions and the Nernst Equation

73. A voltaic cell employs the following redox reaction:



Calculate the cell potential at 25 °C under each set of conditions.

- standard conditions
- $[\text{Sn}^{2+}] = 0.0100 \text{ M}$; $[\text{Mn}^{2+}] = 2.00 \text{ M}$
- $[\text{Sn}^{2+}] = 2.00 \text{ M}$; $[\text{Mn}^{2+}] = 0.0100 \text{ M}$

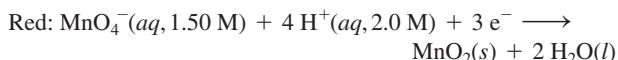
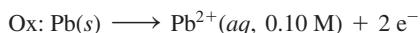
74. A voltaic cell employs the redox reaction:



Calculate the cell potential at 25 °C under each set of conditions.

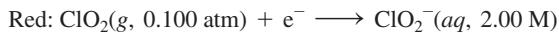
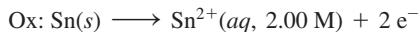
- standard conditions
- $[\text{Fe}^{3+}] = 1.0 \times 10^{-3} \text{ M}$; $[\text{Mg}^{2+}] = 2.50 \text{ M}$
- $[\text{Fe}^{3+}] = 2.00 \text{ M}$; $[\text{Mg}^{2+}] = 1.5 \times 10^{-3} \text{ M}$

75. An electrochemical cell is based on these two half-reactions:



Calculate the cell potential at 25 °C.

76. An electrochemical cell is based on these two half-reactions:



Calculate the cell potential at 25 °C.

77. A voltaic cell consists of a Zn/Zn^{2+} half-cell and a Ni/Ni^{2+} half-cell at 25 °C. The initial concentrations of Ni^{2+} and Zn^{2+} are 1.50 M and 0.100 M, respectively.

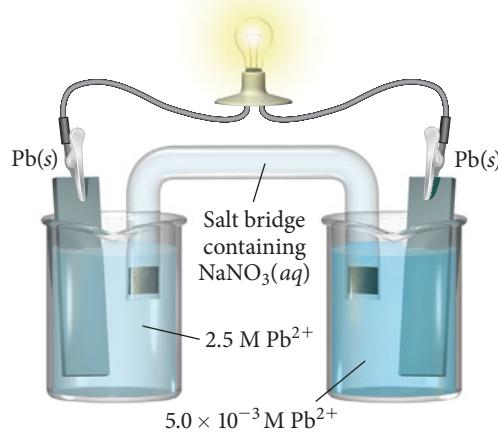
- What is the initial cell potential?
- What is the cell potential when the concentration of Ni^{2+} has fallen to 0.500 M?
- What are the concentrations of Ni^{2+} and Zn^{2+} when the cell potential falls to 0.45 V?

78. A voltaic cell consists of a Pb/Pb^{2+} half-cell and a Cu/Cu^{2+} half-cell at 25 °C. The initial concentrations of Pb^{2+} and Cu^{2+} are 0.0500 M and 1.50 M, respectively.

- What is the initial cell potential?
- What is the cell potential when the concentration of Cu^{2+} has fallen to 0.200 M?
- What are the concentrations of Pb^{2+} and Cu^{2+} when the cell potential falls to 0.35 V?

79. Make a sketch of a concentration cell employing two Zn/Zn^{2+} half-cells. The concentration of Zn^{2+} in one of the half-cells is 2.0 M and the concentration in the other half-cell is 1.0×10^{-3} M. Label the anode and the cathode and indicate the half-reaction occurring at each electrode. Also indicate the direction of electron flow.

80. Consider the concentration cell:



- Label the anode and cathode.
- Indicate the direction of electron flow.
- Indicate what happens to the concentration of Pb^{2+} in each half-cell.

81. A concentration cell consists of two Sn/Sn^{2+} half-cells. The cell has a potential of 0.10 V at 25 °C. What is the ratio of the Sn^{2+} concentrations in the two half-cells?

82. A Cu/Cu^{2+} concentration cell has a voltage of 0.22 V at 25 °C. The concentration of Cu^{2+} in one of the half-cells is 1.5×10^{-3} M. What is the concentration of Cu^{2+} in the other half-cell? (Assume the concentration in the unknown cell to be the lower of the two concentrations.)

Batteries, Fuel Cells, and Corrosion

83. Determine the optimum mass ratio of Zn to MnO_2 in an alkaline battery.

84. What mass of lead sulfate is formed in a lead-acid storage battery when 1.00 g of Pb undergoes oxidation?

85. Refer to the tabulated values of ΔG_f° in Appendix IIB to calculate E_{cell}° for a fuel cell that employs the reaction between methane gas (CH_4) and oxygen to form carbon dioxide and gaseous water.

86. Refer to the tabulated values of ΔG_f° in Appendix IIB to calculate E_{cell}° for the fuel cell breathalyzer, which employs the following reaction. (ΔG_f° for $\text{HC}_2\text{H}_3\text{O}_2(g) = -374.2 \text{ kJ/mol}$)



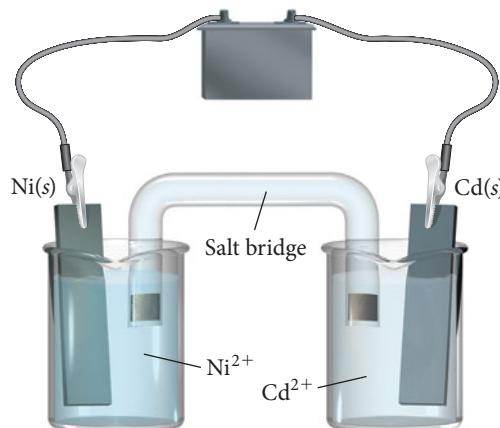
87. Determine whether or not each metal, if coated onto iron, would prevent the corrosion of iron.

- Zn
- Sn
- Mn

88. Determine whether or not each metal, if coated onto iron, would prevent the corrosion of iron.
 a. Mg b. Cr c. Cu

Electrolytic Cells and Electrolysis

89. Consider the electrolytic cell:



- a. Label the anode and the cathode and indicate the half-reactions occurring at each.
 b. Indicate the direction of electron flow.
 c. Label the terminals on the battery as positive or negative and calculate the minimum voltage necessary to drive the reaction.
90. Draw an electrolytic cell in which Mn^{2+} is reduced to Mn and Sn is oxidized to Sn^{2+} . Label the anode and cathode, indicate the direction of electron flow, and write an equation for the half-reaction occurring at each electrode. What minimum voltage is necessary to drive the reaction?
91. Write equations for the half-reactions that occur in the electrolysis of molten potassium bromide.
92. What products are obtained in the electrolysis of molten NaI?

93. Write equations for the half-reactions that occur in the electrolysis of a mixture of molten potassium bromide and molten lithium bromide.

94. What products are obtained in the electrolysis of a molten mixture of KI and KBr?

95. Write equations for the half-reactions that occur at the anode and cathode for the electrolysis of each aqueous solution:
 a. $NaBr(aq)$ b. $PbI_2(aq)$ c. $Na_2SO_4(aq)$

96. Write equations for the half-reactions that occur at the anode and cathode for the electrolysis of each aqueous solution:
 a. $Ni(NO_3)_2(aq)$ b. $KCl(aq)$ c. $CuBr_2(aq)$

97. Make a sketch of an electrolysis cell that electroplates copper onto other metal surfaces. Label the anode and the cathode and indicate the reactions that occur at each.

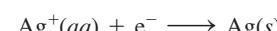
98. Make a sketch of an electrolysis cell that electroplates nickel onto other metal surfaces. Label the anode and the cathode and indicate the reactions that occur at each.

99. Copper can be electroplated at the cathode of an electrolysis cell by the half-reaction:



How much time would it take for 325 mg of copper to be plated at a current of 5.6 A?

100. Silver can be electroplated at the cathode of an electrolysis cell by the half-reaction:



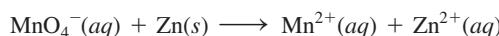
What mass of silver would plate onto the cathode if a current of 6.8 A flowed through the cell for 72 min?

101. A major source of sodium metal is the electrolysis of molten sodium chloride. What magnitude of current produces 1.0 kg of sodium metal in 1 hour?

102. What mass of aluminum metal can be produced per hour in the electrolysis of a molten aluminum salt by a current of 25 A?

Cumulative Problems

103. Consider the unbalanced redox reaction:



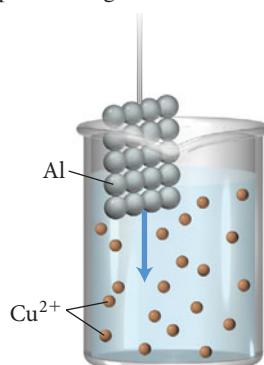
Balance the equation and determine the volume of a 0.500 M $KMnO_4$ solution required to completely react with 2.85 g of Zn.

104. Consider the unbalanced redox reaction:

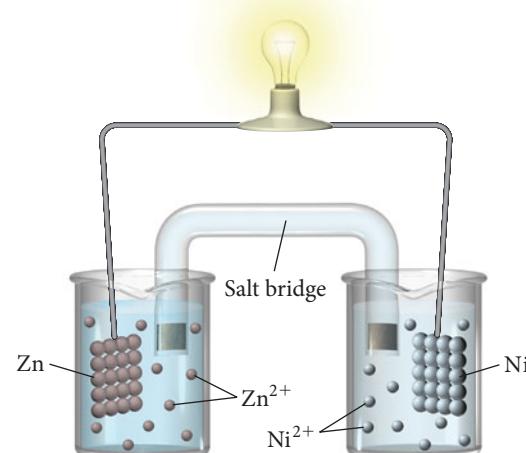


Balance the equation and determine the volume of a 0.850 M $K_2Cr_2O_7$ solution required to completely react with 5.25 g of Cu.

105. Consider the molecular views of an Al strip and Cu^{2+} solution. Draw a similar sketch showing what happens to the atoms and ions after the Al strip is submerged in the solution for a few minutes.



106. Consider the molecular view of an electrochemical cell involving the overall reaction:



Draw a similar sketch of the cell after it has generated a substantial amount of electrical current.

- 107.** Determine whether HI can dissolve each metal sample. If it can, write a balanced chemical reaction showing how the metal dissolves in HI and determine the minimum volume of 3.5 M HI required to completely dissolve the sample.
- 2.15 g Al
 - 4.85 g Cu
 - 2.42 g Ag
- 108.** Determine if HNO₃ can dissolve each metal sample. If it can, write a balanced chemical reaction showing how the metal dissolves in HNO₃ and determine the minimum volume of 6.0 M HNO₃ required to completely dissolve the sample.
- 5.90 g Au
 - 2.55 g Cu
 - 4.83 g Sn
- 109.** The cell potential of this electrochemical cell depends on the pH of the solution in the anode half-cell.
- $$\text{Pt}(s) \mid \text{H}_2(g, 1 \text{ atm}) \mid \text{H}^+(aq, ? \text{ M}) \parallel \text{Cu}^{2+}(aq, 1.0 \text{ M}) \mid \text{Cu}(s)$$
- What is the pH of the solution if E_{cell} is 355 mV?
- 110.** The cell potential of this electrochemical cell depends on the gold concentration in the cathode half-cell.
- $$\text{Pt}(s) \mid \text{H}_2(g, 1.0 \text{ atm}) \mid \text{H}^+(aq, 1.0 \text{ M}) \parallel \text{Au}^{3+}(aq, ? \text{ M}) \mid \text{Au}(s)$$
- What is the concentration of Au³⁺ in the solution if E_{cell} is 1.22 V?
- 111.** A friend wants you to invest in a new battery she has designed that produces 24 V in a single voltaic cell. Why should you be wary of investing in such a battery?
- 112.** What voltage can theoretically be achieved in a battery in which lithium metal is oxidized and fluorine gas is reduced? Why might such a battery be difficult to produce?
- 113.** A battery relies on the oxidation of magnesium and the reduction of Cu²⁺. The initial concentrations of Mg²⁺ and Cu²⁺ are 1.0×10^{-4} M and 1.5 M, respectively, in 1.0-liter half-cells.
- What is the initial voltage of the battery?
 - What is the voltage of the battery after delivering 5.0 A for 8.0 h?
 - How long can the battery deliver 5.0 A before going dead?
- 114.** A rechargeable battery is constructed based on a concentration cell constructed of two Ag/Ag⁺ half-cells. The volume of each half-cell is 2.0 L and the concentrations of Ag⁺ in the half-cells are 1.25 M and 1.0×10^{-3} M.
- How long can this battery deliver 2.5 A of current before it goes dead?
 - What mass of silver is plated onto the cathode by running at 3.5 A for 5.5 h?
 - Upon recharging, how long would it take to redissolve 1.00×10^2 g of silver at a charging current of 10.0 amps?
- 115.** If a water electrolysis cell operates at a current of 7.8 A, how long will it take to generate 25.0 L of hydrogen gas at a pressure of 25.0 atm and a temperature of 25 °C?
- 116.** When a suspected drunk driver blows 188 mL of his breath through the fuel-cell breathalyzer described in Section 18.7, the breathalyzer produces an average of 324 mA of current for 10 s. Assuming a pressure of 1.0 atm and a temperature of 25 °C, what percent (by volume) of the driver's breath is ethanol?
- 117.** The K_{sp} of CuI is 1.1×10^{-12} . Find E_{cell} for the cell:
- $$\text{Cu}(s) \mid \text{CuI}(s) \mid \text{I}^-(aq)(1.0 \text{ M}) \parallel \text{Cu}^{2+}(aq)(1.0 \text{ M}) \mid \text{Cu}(s)$$
- 118.** The K_{sp} of Zn(OH)₂ is 1.8×10^{-14} . Find E_{cell} for the half-reaction:
- $$\text{Zn(OH)}_2(s) + 2 \text{e}^- \rightleftharpoons \text{Zn}(s) + 2 \text{OH}^-(aq)$$
- 119.** Calculate $\Delta G_{\text{rxn}}^\circ$ and K for each reaction.
- The disproportionation of Mn²⁺(aq) to Mn(s) and MnO₂(s) in acid solution at 25 °C.
 - The disproportionation of MnO₂(s) to Mn²⁺(aq) and MnO₄⁻(aq) in acid solution at 25 °C.
- 120.** Calculate $\Delta G_{\text{rxn}}^\circ$ and K for each reaction.
- The reaction of Cr²⁺(aq) with Cr₂O₇²⁻(aq) in acid solution to form Cr³⁺(aq).
 - The reaction of Cr³⁺(aq) and Cr(s) to form Cr²⁺(aq). [The electrode potential of Cr²⁺(aq) to Cr(s) is -0.91 V.]
- 121.** The molar mass of a metal (M) is 50.9 g/mol; it forms a chloride of unknown composition. Electrolysis of a sample of the molten chloride with a current of 6.42 A for 23.6 minutes produces 1.20 g of M at the cathode. Determine the empirical formula of the chloride.
- 122.** A metal forms the fluoride MF₃. Electrolysis of the molten fluoride by a current of 3.86 A for 16.2 minutes deposits 1.25 g of the metal. Calculate the molar mass of the metal.
- 123.** A sample of impure tin of mass 0.535 g is dissolved in strong acid to give a solution of Sn²⁺. The solution is then titrated with a 0.0448 M solution of NO₃⁻, which is reduced to NO(g). The equivalence point is reached upon the addition of 0.0344 L of the NO₃⁻ solution. Find the percent by mass of tin in the original sample, assuming that it contains no other reducing agents.
- 124.** A 0.0251 L sample of a solution of Cu⁺ requires 0.0322 L of 0.129 M KMnO₄ solution to reach the equivalence point. The products of the reaction are Cu²⁺ and Mn²⁺. What is the concentration of the Cu²⁺ solution?
- 125.** A current of 11.3 A is applied to 1.25 L of a solution of 0.552 M HBr converting some of the H⁺ to H₂(g), which bubbles out of solution. What is the pH of the solution after 73 minutes?
- 126.** A 215 mL sample of a 0.500 M NaCl solution with an initial pH of 7.00 is subjected to electrolysis. After 15.0 minutes, a 10.0 mL portion (or aliquot) of the solution was removed from the cell and titrated with 0.100 M HCl solution. The endpoint in the titration was reached upon addition of 22.8 mL of HCl. Assuming constant current, what was the current (in A) running through the cell?
- 127.** An MnO₂(s)/Mn²⁺(aq) electrode in which the pH is 10.24 is prepared. Find the [Mn²⁺] necessary to lower the potential of the half-cell to 0.00 V (at 25 °C).
- 128.** To what pH should you adjust a standard hydrogen electrode to get an electrode potential of -0.122 V? (Assume that the partial pressure of hydrogen gas remains at 1 atm.)

Challenge Problems

- 129.** Suppose a hydrogen–oxygen fuel-cell generator produces electricity for a house. Use the balanced redox reactions and the standard cell potential to predict the volume of hydrogen gas (at STP) required each month to generate the electricity. Assume the home uses 1.2×10^3 kWh of electricity per month.
- 130.** A voltaic cell designed to measure [Cu²⁺] is constructed of a standard hydrogen electrode and a copper metal electrode in the Cu²⁺ solution of interest. If you want to construct a calibration curve for how the cell potential varies with the concentration of copper(II), what do you plot in order to obtain a straight line? What is the slope of the line?

- 131.** The surface area of an object to be gold plated is 49.8 cm^2 and the density of gold is 19.3 g/cm^3 . A current of 3.25 A is applied to a solution that contains gold in the +3 oxidation state. Calculate the time required to deposit an even layer of gold $1.00 \times 10^{-3} \text{ cm}$ thick on the object.
- 132.** To electrodeposit all the Cu and Cd from a solution of CuSO_4 and CdSO_4 required 1.20 F of electricity ($1 \text{ F} = 1 \text{ mol e}^-$). The mixture of Cu and Cd that was deposited had a mass of 50.36 g . What mass of CuSO_4 was present in the original mixture?
- 133.** Sodium oxalate, $\text{Na}_2\text{C}_2\text{O}_4$, in solution is oxidized to $\text{CO}_2(g)$ by MnO_4^- , which is reduced to Mn^{2+} . A 50.1 mL volume of a solution of MnO_4^- is required to titrate a 0.339 g sample of sodium oxalate. This solution of MnO_4^- is used to analyze uranium-containing samples. A 4.62 g sample of a uranium-

containing material requires 32.5 mL of the solution for titration. The oxidation of the uranium can be represented by the change $\text{UO}_2^{2+} \longrightarrow \text{UO}_2^{2+}$. Calculate the percentage of uranium in the sample.

- 134.** Three electrolytic cells are connected in a series. The electrolytes in the cells are aqueous copper(II) sulfate, gold(III) sulfate, and silver nitrate. A current of 2.33 A is applied, and after some time 1.74 g Cu is deposited. How long was the current applied? What mass of gold and silver were deposited?
- 135.** The cell $\text{Pt}(s) \mid \text{Cu}^+(1 \text{ M}), \text{Cu}^{2+}(1 \text{ M}) \parallel \text{Cu}^+(1 \text{ M}) \mid \text{Cu}(s)$ has $E^\circ = 0.364 \text{ V}$. The cell $\text{Cu}(s) \mid \text{Cu}^{2+}(1 \text{ M}) \parallel \text{Cu}^+(1 \text{ M}) \mid \text{Cu}(s)$ has $E^\circ = 0.182 \text{ V}$. Write the cell reaction for each cell and explain the differences in E° . Calculate ΔG° for each cell reaction to help explain these differences.

Conceptual Problems

- 136.** An electrochemical cell has a positive standard cell potential but a negative cell potential. Which statement is true for the cell?
- $K > 1; Q > K$
 - $K < 1; Q > K$
 - $K > 1; Q < K$
 - $K < 1; Q < K$
- 137.** Which oxidizing agent will oxidize Br^- but not Cl^- ?
- $\text{K}_2\text{Cr}_2\text{O}_7$ (in acid)
 - KMnO_4 (in acid)
 - HNO_3

- 138.** A redox reaction employed in an electrochemical cell has a negative $\Delta G_{\text{rxn}}^\circ$. Which statement is true?
- E_{cell}° is positive; $K < 1$
 - E_{cell}° is positive; $K > 1$
 - E_{cell}° is negative; $K > 1$
 - E_{cell}° is negative; $K < 1$
- 139.** A redox reaction has an equilibrium constant of $K = 0.055$. What is true of $\Delta G_{\text{rxn}}^\circ$ and E_{cell}° for this reaction?

Answers to Conceptual Problems

Voltaic Cells

- 18.1** (a) Electrons are negatively charged and therefore flow away from the more negatively charged electrode and toward the more positively charged electrode.

Standard Electrode Potentials

- 18.2** (b) A negative electrode potential indicates that an electron at that electrode has greater potential energy than it has at a standard hydrogen electrode.

Selective Oxidation

- 18.3** (d) The reduction of HNO_3 is listed below the reduction of Br_2 and above the reduction of I_2 in Table 18.1. Since any reduction half-reaction is spontaneous when paired with the reverse of a half-reaction below it in the table, the reduction of HNO_3 is spontaneous when paired with the oxidation of I^- but is not spontaneous when paired with the oxidation of Br^- .

Metals Dissolving in Acids

- 18.4** (c) Ag falls *above* the half-reaction for the reduction of H^+ but *below* the half-reaction for the reduction of NO_3^- in Table 18.1.

Periodic Trends and the Direction of Spontaneity for Redox Reactions

- 18.5** (a) Br is more electronegative than I. If the two atoms were in competition for the electron, the electron would go to the more electronegative atom (Br). Therefore, I_2 does not spontaneously gain electrons from Br^- .

Relating K , $\Delta G_{\text{rxn}}^\circ$, and E_{cell}°

- 18.6** (c) Since $K > 1$, the reaction is spontaneous under standard conditions (when $Q = 1$, the reaction proceeds toward the products). Therefore, E_{cell}° is positive and $\Delta G_{\text{rxn}}^\circ$ is negative.

Relating Q , K , E_{cell} , and E_{cell}°

- 18.7** (a) Since $K < 1$, E_{cell}° is negative (under standard conditions, the reaction is not spontaneous). Since $Q < K$, E_{cell} is positive (the reaction is spontaneous under the nonstandard conditions of the cell).

Sacrificial Electrodes

- 18.8** Cu. The electrode potential for Fe is more negative than that of Cu. Therefore, Fe will oxidize more easily than Cu.

19

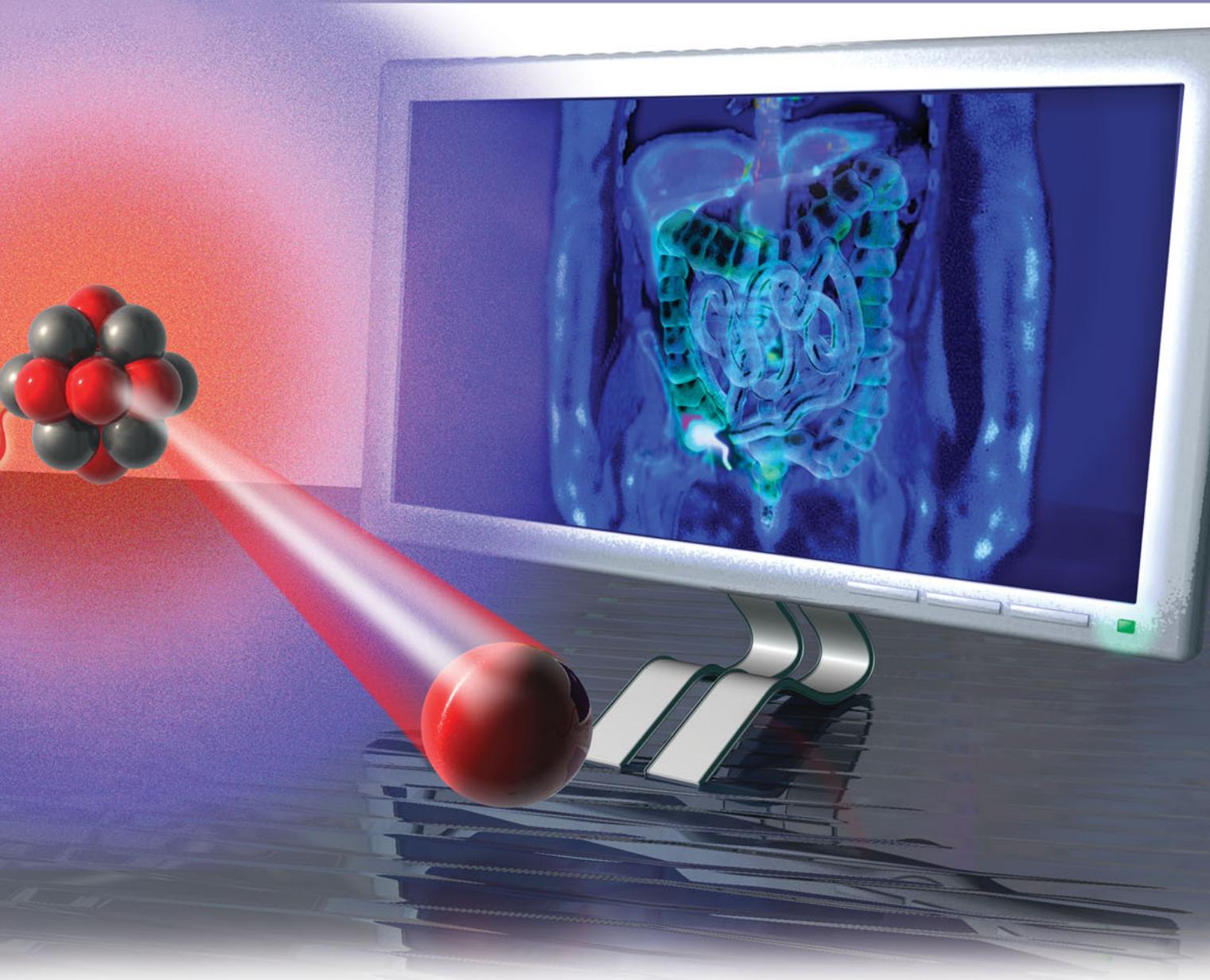
Radioactivity and Nuclear Chemistry

I am among those who think that science has great beauty. A scientist in his laboratory is not only a technician; he is also a child placed before natural phenomena which impress him like a fairy tale.

—Marie Curie (1867–1934)

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IN THIS CHAPTER, WE EXAMINE RADIOACTIVITY and nuclear chemistry, both of which involve changes within the *nuclei* of atoms. Unlike ordinary chemical processes, in which elements retain their identity, nuclear processes often result in one element changing into another, frequently emitting tremendous amounts of energy. Radioactivity has numerous applications, including the diagnosis and treatment of medical conditions such as cancer, thyroid disease, abnormal kidney and bladder function, and heart disease. Naturally occurring radioactivity allows us to estimate the age of fossils, rocks, and ancient artifacts. And radioactivity, perhaps most famously, led to the discovery of nuclear fission, used for electricity generation and nuclear weapons. In this chapter, we discuss radioactivity—how it was discovered, what it is, and how we use it.



19.1 Diagnosing Appendicitis

One morning a few years ago I awoke with a dull pain on the lower right side of my abdomen that was worse by early afternoon. Since pain in this area can indicate appendicitis (inflammation of the appendix), and since I know that appendicitis can be dangerous if left untreated, I went to the hospital emergency room. The doctor who examined me recommended a simple blood test to determine my white blood cell count. Patients with appendicitis usually have a high white blood cell count because the body is trying to fight the infection. In my case, the test was negative—I had a normal white blood cell count.

Although my symptoms were consistent with appendicitis, the negative blood test clouded the diagnosis. The doctor said that I could elect to have my appendix removed anyway (even though it might be healthy) or I could submit to another test that might confirm the appendicitis. I chose the additional test, which involved *nuclear medicine*, an area of medical practice that employs *radioactivity* to diagnose and treat disease. **Radioactivity** is

Antibodies labeled with radioactive atoms can be used to diagnose an infected appendix.

the emission of subatomic particles or high-energy electromagnetic radiation by the nuclei of certain atoms. Such atoms are said to be **radioactive**. Most radioactive emissions can pass through many types of matter (such as skin and muscle, in this case).

During the test, antibodies—naturally occurring molecules that fight infection—were labeled with radioactive atoms and then injected into my bloodstream. Since antibodies attack infection, they migrate to areas of the body where infection is present. If my appendix was indeed infected, the antibodies would accumulate there. I waited about an hour, and then the technician took me to a room and laid me on a table. She inserted a photographic film in a panel above me and removed the covering that prevents exposure of the film. Radioactivity is invisible to the eye, but it exposes photographic film. If my appendix had been infected, it would have (by then) contained a high concentration of the radioactively labeled antibodies. The antibodies would emit radiation and expose the film. The test, however, was negative. No radioactivity was emanating from my appendix. After several hours, the pain in my abdomen subsided and I went home. I never did find out what caused the pain.

19.2 The Discovery of Radioactivity

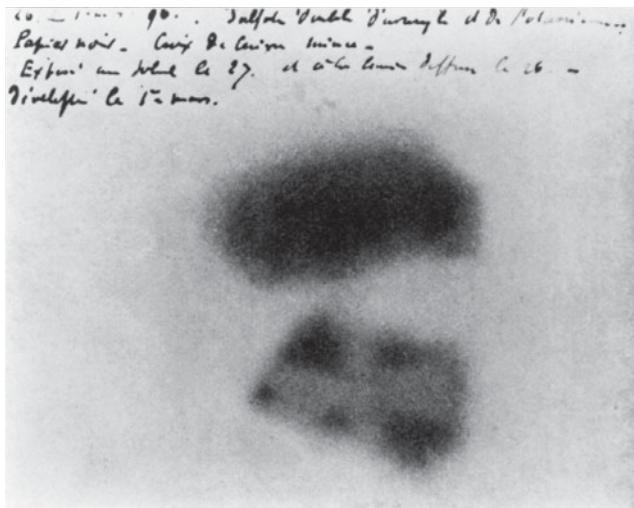


▲ The greenish light emitted from glow-in-the-dark toys is phosphorescence.

Radioactivity was discovered in 1896 by a French scientist named Antoine-Henri Becquerel (1852–1908). Becquerel was interested in the newly discovered X-rays (see Chapter 7), which were a hot topic of physics research in his time. He hypothesized that X-rays were emitted in conjunction with **phosphorescence**, the long-lived *emission* of light that sometimes follows the absorption of light by certain atoms and molecules. Phosphorescence is probably most familiar to you as the *glow* in glow-in-the-dark products (such as toys or stickers). After such a product is exposed to light, it reemits some of that light, usually at slightly longer wavelengths. If you turn off the room lights or put the glow-in-the-dark product in the dark, you see the greenish glow of the emitted light. Becquerel hypothesized that this visible greenish glow was associated with the emission of X-rays (which are invisible).

To test his hypothesis, Becquerel placed crystals—composed of potassium uranyl sulfate, a compound known to phosphoresce—on top of a photographic plate wrapped in black cloth. He then exposed the crystals to sunlight. He knew the crystals had phosphoresced because he could see the emitted light when he brought them back into the dark. If the crystals had also emitted X-rays, the X-rays would have passed through the black cloth and exposed the underlying photographic plate. Becquerel performed the experiment several times and always got the same result—the photographic plate showed a dark exposure spot where the crystals had been (Figure 19.1 ▼). Becquerel believed his hypothesis was correct and presented the results—that phosphorescence and X-rays were linked—to the French Academy of Sciences.

Becquerel later retracted his results, however, when he discovered that a photographic plate with the same crystals showed a dark exposure spot even when the plate and the crystals were stored in a drawer and not exposed to sunlight. Becquerel realized



► FIGURE 19.1 The Discovery of

Radioactivity This photographic plate (with Becquerel's original comments at top) played a key role in the discovery of radioactivity. Becquerel placed a uranium-containing compound on the plate (which was wrapped in black cloth to shield it from visible light). He found that the plate was darkened by some unknown form of penetrating radiation that was produced continuously, independently of phosphorescence.

that the crystals themselves were constantly emitting something that exposed the photographic plate, regardless of whether or not they phosphoresced. Becquerel concluded that it was the uranium within the crystals that was the source of the emissions, and he named the emissions *uranic rays*.

Soon after Becquerel's discovery, a young graduate student named Marie Skłodowska Curie (1867–1934) (one of the first women in France to pursue doctoral work) decided to study uranic rays for her doctoral thesis. Her first task was to determine whether any other substances besides uranium (the heaviest known element at the time) emitted these rays. In her search, Curie discovered two new elements, both of which also emitted uranic rays. Curie named one of her newly discovered elements polonium, after her home country of Poland. The other element she named radium, because of its high level of radioactivity. Radium is so radioactive that it gently glows in the dark and emits significant amounts of heat. Since it was clear that these rays were not unique to uranium, Curie changed the name of uranic rays to radioactivity. In 1903, Curie and her husband, Pierre Curie, as well as Becquerel were all awarded the Nobel Prize in physics for the discovery of radioactivity. In 1911, Curie received a second Nobel Prize, this time in chemistry, for her discovery of the two new elements.

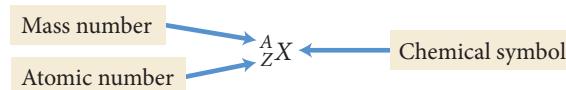


▲ Marie Curie, one of the first women in France to pursue a doctoral degree, was twice awarded the Nobel Prize, in 1903 and 1911. She is seen here with her daughters, in about 1905. Irène (left) became a distinguished nuclear physicist in her own right, winning a Nobel Prize in 1935. Eve (right) wrote a highly acclaimed biography of her mother.

19.3 Types of Radioactivity

While Curie focused her work on discovering the different kinds of radioactive elements, Ernest Rutherford and others focused on characterizing the radioactivity itself. These scientists found that the emissions are produced by the nuclei of radioactive atoms. Such nuclei are unstable and spontaneously decompose, emitting small pieces of themselves to gain stability. These fragments are the radioactivity that Becquerel and Curie detected. Natural radioactivity can be categorized into several different types, including *alpha (α) decay*, *beta (β) decay*, *gamma (γ) ray emission*, and *positron emission*. In addition, some unstable atomic nuclei can attain greater stability by absorbing an electron from one of the atom's own orbitals, a process called *electron capture*.

In order to understand these different types of radioactivity, we must briefly review the notation for symbolizing isotopes from Section 2.6. Recall that we can represent any isotope with the following notation:



Mass number (A) = the sum of the number of protons and number of neutrons in the nucleus

Atomic number (Z) = the number of protons in the nucleus

Since A represents the sum of the number of protons and neutrons, and since Z represents the number of protons, the number of neutrons (N) is $A - Z$.

$$N = A - Z$$

↑
Number of neutrons

For example, the symbol ${}^{21}_{10}\text{Ne}$ represents the neon isotope containing 10 protons and 11 neutrons. The symbol ${}^{20}_{10}\text{Ne}$ represents the neon isotope containing 10 protons and 10 neutrons. Remember that most elements have several different isotopes. When we are discussing nuclear properties, we often refer to a particular isotope (or species) of an element as a **nuclide**.

We represent the main subatomic particles—protons, neutrons, and electrons—with similar notation.

Proton symbol ${}^1_1\text{p}$ Neutron symbol ${}^1_0\text{n}$ Electron symbol ${}^0_{-1}\text{e}$



▲ Radium, discovered by Marie Curie, is so radioactive that it glows visibly and emits heat.

Alpha Decay



▲ FIGURE 19.2 Alpha Decay In alpha decay, a nucleus emits a particle composed of two protons and two neutrons (a helium-4 nucleus).

As we will discuss in Section 19.4, nuclei are unstable when they are too large or when they contain an unbalanced ratio of neutrons to protons.

In nuclear chemistry, we are primarily interested in changes within the nucleus; therefore, the $2+$ charge that we would normally write for a helium nucleus is omitted for an alpha particle.

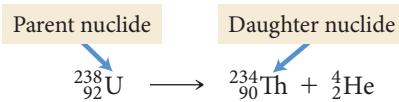
The 1 in the lower left of the proton symbol represents 1 proton, and the 0 in the lower left corner of the neutron symbol represents 0 protons. The -1 in the lower left corner of the electron symbol is a bit different from the other atomic numbers, but it will make sense when we see it in the context of nuclear decay a bit later in this section.

Alpha (α) Decay

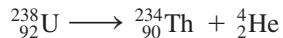
Alpha (α) decay occurs when an unstable nucleus emits a particle composed of two protons and two neutrons (Figure 19.2 ◀). Since two protons and two neutrons combined are identical to a helium-4 nucleus, the symbol for alpha radiation is the symbol for helium-4:



When an element emits an alpha particle, the number of protons in its nucleus changes, transforming the element into a different element. We symbolize this phenomenon with a **nuclear equation**, an equation that represents nuclear processes such as radioactivity. For example, the nuclear equation for the alpha decay of uranium-238 is:



The original atom is called the *parent nuclide*, and the product of the decay is called the *daughter nuclide*. In this case, uranium-238 (the parent nuclide) becomes thorium-234 (the daughter nuclide). Unlike a chemical reaction, in which elements retain their identities, in a nuclear reaction elements often change their identities. Like a chemical equation, however, a nuclear equation must be balanced. *The sum of the atomic numbers on both sides of a nuclear equation must be equal, and the sum of the mass numbers on both sides must also be equal.*



Reactants	Products
Sum of mass numbers = 238	Sum of mass numbers = $234 + 4 = 238$
Sum of atomic numbers = 92	Sum of atomic numbers = $90 + 2 = 92$

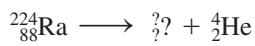
We can deduce the identity and symbol of the daughter nuclide in any alpha decay from the mass and atomic number of the parent nuclide. During alpha decay, the mass number decreases by 4 and the atomic number decreases by 2, as shown in Example 19.1.

EXAMPLE 19.1 Writing Nuclear Equations for Alpha Decay

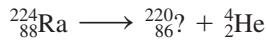
Write the nuclear equation for the alpha decay of Ra-224.

SOLUTION

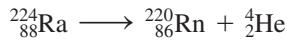
Begin with the symbol for Ra-224 on the left side of the equation and the symbol for an alpha particle on the right side.



Equalize the sum of the mass numbers and the sum of the atomic numbers on both sides of the equation by writing the appropriate mass number and atomic number for the unknown daughter nuclide.



Refer to the periodic table to deduce the identity of the unknown daughter nuclide from its atomic number and write its symbol. Since the atomic number is 86, the daughter nuclide is radon (Rn).



FOR PRACTICE 19.1

Write the nuclear equation for the alpha decay of Po-216.

Alpha radiation is the 18-wheeler truck of radioactivity. The alpha particle is by far the most massive of all particles emitted by radioactive nuclei. Consequently, alpha radiation has the most potential to interact with and damage other molecules, including biological ones. Highly energetic radiation interacts with other molecules and atoms by ionizing them. When radiation ionizes molecules within the cells of living organisms, those molecules may undergo damaging chemical reactions, and the cells can die or begin to reproduce abnormally. The ability of radiation to ionize other molecules and atoms is called its **ionizing power**. Of all types of radioactivity, alpha radiation has the highest ionizing power.

However, alpha particles, because of their large size, have the lowest **penetrating power**—the ability to penetrate matter. (Imagine a semitruck trying to get through a traffic jam.) In order for radiation to damage important molecules within living cells, it must penetrate into the cell. Alpha radiation does not easily penetrate into cells because it can be stopped by a sheet of paper, by clothing, or even by air. Consequently, a low-level alpha emitter that remains outside the body is relatively safe. If an alpha emitter is ingested, however, it becomes very dangerous because the alpha particles then have direct access to the molecules that compose organs and tissues.

Beta (β) Decay

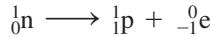
Beta (β) decay occurs when an unstable nucleus emits an electron (Figure 19.3 ▶). How does a nucleus, which contains only protons and neutrons, emit an electron? In some unstable nuclei, a neutron changes into a proton and emits an electron.



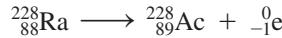
The symbol for a beta (β) particle in a nuclear equation is:



We can represent beta decay with this nuclear equation:



The -1 reflects the charge of the electron, which is equivalent to an atomic number of -1 in a nuclear equation. When an atom emits a beta particle, its atomic number increases by 1 because it now has an additional proton. For example, the nuclear equation for the beta decay of radium-228 is:

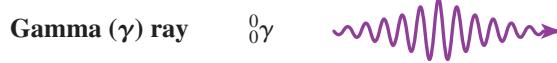


Notice that the nuclear equation is balanced—the sum of the mass numbers on both sides is equal and the sum of the atomic numbers on both sides is equal.

Beta radiation is the four-door sedan of radioactivity. Beta particles are much less massive than alpha particles and consequently have a lower ionizing power. However, because of their smaller size, beta particles have a higher penetrating power and only something as substantive as a sheet of metal or a thick piece of wood will stop them. Consequently, a beta emitter outside of the body poses a higher risk than an alpha emitter. If ingested, however, the beta emitter does less damage than an alpha emitter.

Gamma (γ) Ray Emission

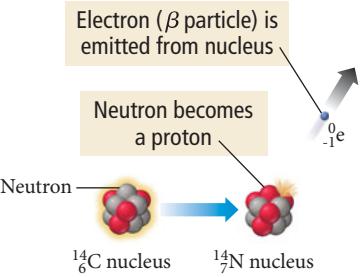
Gamma (γ) ray emission is significantly different from alpha or beta radiation. Gamma radiation is a form of *electromagnetic* radiation (see Section 7.2). Gamma rays are high-energy (short-wavelength) photons. The symbol for a gamma ray is:



A gamma ray has no charge and no mass. When a gamma-ray photon is emitted from a radioactive atom, it does not change the mass number or the atomic number of the element. Gamma rays, however, are usually emitted in conjunction with other types of radiation. For example, the alpha emission of U-238 (discussed previously) is also accompanied by the emission of a gamma ray.



Beta Decay



▲ **FIGURE 19.3 Beta Decay** In beta decay, a neutron emits an electron and becomes a proton.

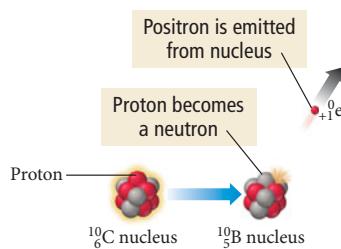
This kind of beta radiation is also called beta minus (β^-) radiation due to its negative charge.

See Section 7.2 for a review of electromagnetic radiation.

Gamma rays are the motorbikes of radioactivity. They have the lowest ionizing power, but the highest penetrating power. (Imagine a motorbike zipping through a traffic jam.) Stopping gamma rays requires several inches of lead shielding or thick slabs of concrete.

Positron Emission

Positron Emission



▲ FIGURE 19.4 Positron Emission

In positron emission, a proton emits a positron and becomes a neutron.

Positron emission can be thought of as a type of beta emission and is sometimes referred to as beta plus emission (β^+).

Positron emission occurs when an unstable nucleus emits a positron (Figure 19.4 ◀). A **positron** is the *antiparticle* of the electron; it has the same mass as an electron, but the opposite charge. If a positron collides with an electron, the two particles annihilate each other, releasing energy in the form of gamma rays. In positron emission, a proton is converted into a neutron and emits a positron.

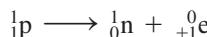
Positron emission



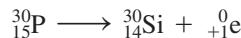
The symbol for a positron in a nuclear equation is:



We can represent positron emission with this nuclear equation:



When an atom emits a positron, its atomic number *decreases* by 1 because it has one less proton after emission. Consider the nuclear equation for the positron emission of phosphorus-30 as an example:



We can determine the identity and symbol of the daughter nuclide in any positron emission in a manner similar to that used for alpha and beta decay, as shown in Example 19.2. Positrons are similar to beta particles in their ionizing and penetrating power.

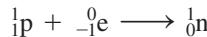
Electron Capture

Unlike the forms of radioactive decay that we have discussed so far, electron capture involves a particle being *absorbed* by instead of *emitted from* an unstable nucleus. **Electron capture** occurs when a nucleus assimilates an electron from an inner orbital of its electron cloud. Like positron emission, the net effect of electron capture is the conversion of a proton into a neutron.

Electron capture



We can represent electron capture with this nuclear equation:



When an atom undergoes electron capture, its atomic number decreases by 1 because it has one less proton. For example, when Ru-92 undergoes electron capture, its atomic number changes from 44 to 43:

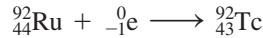


Table 19.1 summarizes the different kinds of radiation.

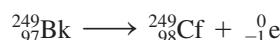
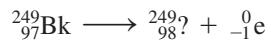
EXAMPLE 19.2 Writing Nuclear Equations for Beta Decay, Positron Emission, and Electron Capture

Write the nuclear equation for each type of decay.

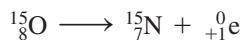
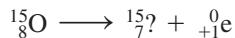
- (a) beta decay in Bk-249
- (b) positron emission in O-15
- (c) electron capture in I-111

SOLUTION

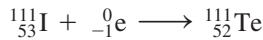
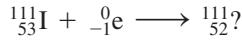
- (a) In beta decay, the atomic number *increases* by 1 and the mass number remains unchanged.
The daughter nuclide is element number 98, californium.



- (b) In positron emission, the atomic number *decreases* by 1 and the mass number remains unchanged.
The daughter nuclide is element number 7, nitrogen.



- (c) In electron capture, the atomic number also *decreases* by 1 and the mass number remains unchanged.
The daughter nuclide is element number 52, tellurium.



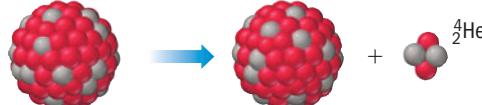
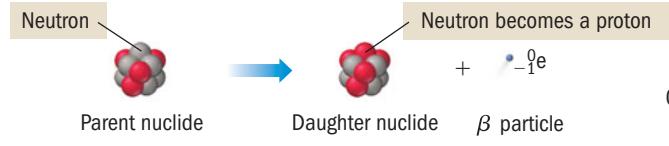
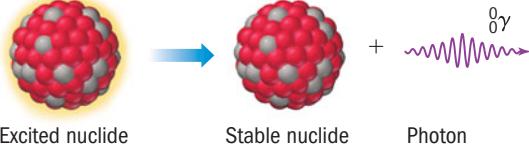
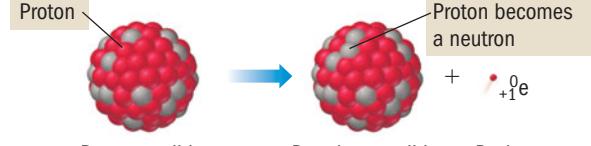
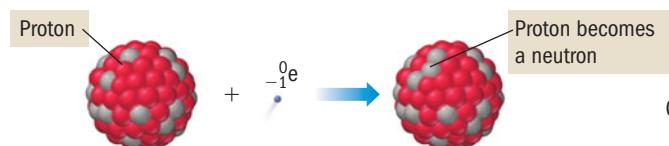
FOR PRACTICE 19.2

- (a) Write three nuclear equations to represent the nuclear decay sequence that begins with the alpha decay of U-235 followed by a beta decay of the daughter nuclide and then another alpha decay.
(b) Write the nuclear equation for the positron emission of Na-22.
(c) Write the nuclear equation for electron capture in Kr-76.

FOR MORE PRACTICE 19.2

Potassium-40 decays to produce Ar-40. What is the method of decay? Write the nuclear equation for this decay.

TABLE 19.1 Modes of Radioactive Decay

Decay Mode	Process	A	Change in: Z N/Z*	Example
α		-4	-2 Increase	${}_{\text{92}}^{\text{238}}\text{U} \longrightarrow {}_{\text{90}}^{\text{234}}\text{Th} + {}_{\text{2}}^{\text{4}}\text{He}$
β		0	+1 Decrease	${}_{\text{88}}^{\text{228}}\text{Ra} \longrightarrow {}_{\text{89}}^{\text{228}}\text{Ac} + {}_{\text{-1}}^{\text{0}}\text{e}$
γ		0	0 None	${}_{\text{90}}^{\text{234}}\text{Th} \longrightarrow {}_{\text{90}}^{\text{234}}\text{Th} + {}_{\text{0}}^{\text{0}}\gamma$
Positron emission		0	-1 Increase	${}_{\text{15}}^{\text{30}}\text{P} \longrightarrow {}_{\text{14}}^{\text{30}}\text{Si} + {}_{\text{+1}}^{\text{0}}\text{e}$
Electron capture		0	-1 Increase	${}_{\text{44}}^{\text{92}}\text{Ru} + {}_{\text{-1}}^{\text{0}}\text{e} \longrightarrow {}_{\text{43}}^{\text{92}}\text{Tc}$

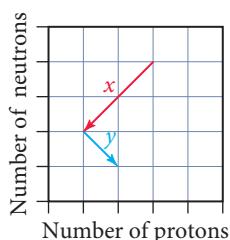
* Neutron-to-proton ratio

Conceptual Connection 19.1 Alpha and Beta Decay

Consider the graphical representation of a series of decays shown here.

The arrow labeled *x* and the arrow labeled *y* each correspond to what kind of decay?

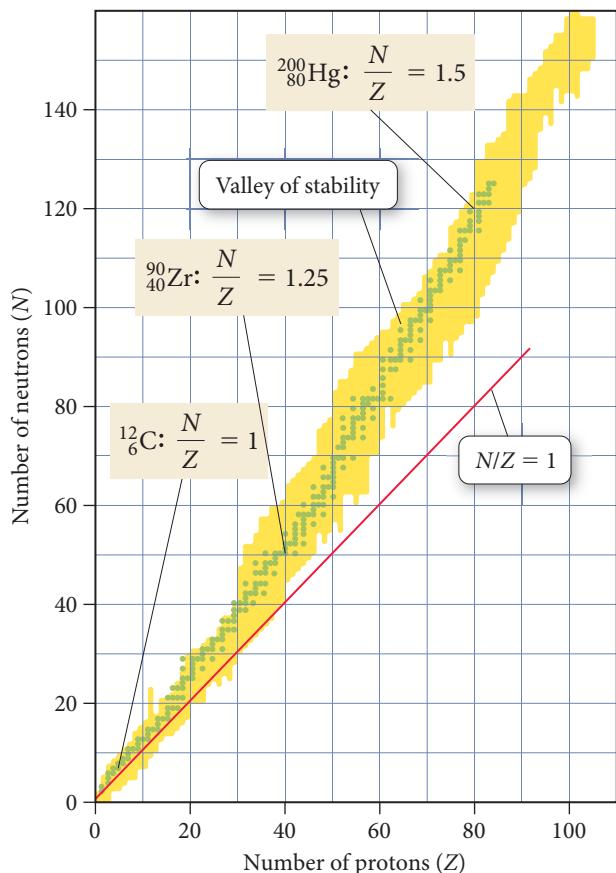
- x* corresponds to alpha decay and *y* corresponds to positron emission.
- x* corresponds to positron emission and *y* corresponds to alpha decay.
- x* corresponds to alpha decay and *y* corresponds to beta decay.
- x* corresponds to beta decay and *y* corresponds to alpha decay.



▼ FIGURE 19.5 Stable and Unstable Nuclei

A plot of N (the number of neutrons) versus Z (the number of protons) for all known stable nuclei—represented by green dots on this graph—shows that these nuclei cluster together in a region known as the valley (or island) of stability. Nuclei with an N/Z ratio that is too high tend to undergo beta decay. Nuclei with an N/Z ratio that is too low tend to undergo positron emission or electron capture.

The Valley of Stability



19.4 The Valley of Stability: Predicting the Type of Radioactivity

So far, we have described various different types of radioactivity. But what causes a particular nuclide to be radioactive in the first place? And why do some nuclides decay via alpha decay, while others decay via beta decay or positron emission? The answers to these questions are not simple, but we can get a basic idea of the factors that influence the stability of the nucleus and the nature of its decay.

A nucleus is a collection of protons (positively charged) and neutrons (uncharged). We know that positively charged particles such as protons repel one another. So what binds the nucleus together? The binding is provided by a fundamental force of physics known as the **strong force**. All **nucleons**—protons and neutrons—are attracted to one another by the strong force. However, the strong force acts only at very short distances. We can think of the stability of a nucleus as a balance between the *repulsive* coloumbic force among protons and the *attractive* strong force among all nucleons. The neutrons in a nucleus, therefore, play an important role in stabilizing the nucleus because they attract other nucleons (through the strong force) but lack the repulsive force associated with positive charge. (It might seem that adding more neutrons would *always* lead to greater stability, so that the more neutrons the better. This is not the case, however, because protons and neutrons occupy energy levels in a nucleus that are similar to those occupied by electrons in an atom. As you add more neutrons, they must occupy increasingly higher energy levels within the nucleus. At some point, the energy payback from the strong force is not enough to compensate for the high energy state that the neutrons must occupy.)

An important number in determining nuclear stability is the *ratio* of neutrons to protons (N/Z). Figure 19.5 ▲ shows a plot of the number of neutrons versus the number of protons for all known stable nuclei. The green dots along the diagonal of the graph represent stable nuclei; this region is known as the *valley (or island) of stability*. Notice that for the lighter elements, the N/Z ratio of stable isotopes is about one (equal numbers of neutrons and protons). For example, the most abundant isotope of carbon ($Z = 6$) is carbon-12, which contains six protons and six neutrons. However, beyond about $Z = 20$, the N/Z ratio of stable nuclei begins to get larger. For example, at $Z = 40$, stable nuclei have an N/Z ratio of about 1.25 and at $Z = 80$, the N/Z ratio reaches about 1.5. Above $Z = 83$, stable nuclei do not exist—bismuth ($Z = 83$) is the heaviest element with stable (nonradioactive) isotopes.

The type of radioactivity emitted by a nuclide depends in part on the N/Z ratio.

N/Z too high: Nuclides that lie above the valley of stability have too many neutrons and tend to convert neutrons to protons via beta decay. The process of undergoing beta decay moves the nuclide down in the plot in Figure 19.5 and closer to (or into) the valley of stability.

N/Z too low: Nuclides that lie below the valley of stability have too many protons and tend to convert protons to neutrons via positron emission or electron capture. This moves the nuclide up in the plot in Figure 19.5 and closer to (or into) the valley of stability. (Alpha decay also raises the N/Z ratio for nuclides in which $N/Z > 1$, but the effect is smaller than for positron emission or electron capture.)

One way to decide whether a particular nuclide has an N/Z that is too high, too low, or about right is to consult Figure 19.5. Those nuclides that lie within the valley of stability are stable. Alternatively, we can also compare the mass number of the nuclide to the atomic mass listed in the periodic table for the corresponding element. The atomic mass is an average of the masses of the stable nuclides for an element and thus represents an N/Z that is about right. For example, suppose we want to evaluate N/Z for Ru-112. Ruthenium has an atomic mass of 101.07 so we know that the nuclide with a mass number of 112 must contain too many neutrons and therefore have an N/Z that is too high. The following example shows how to apply these considerations in predicting the mode of decay for a nucleus.

EXAMPLE 19.3 Predicting the Type of Radioactive Decay

Predict whether each nuclide is more likely to decay via beta decay or positron emission.

- (a) Mg-28 (b) Mg-22 (c) Mo-102

SOLUTION

- (a) Magnesium-28 has 16 neutrons and 12 protons, so $N/Z = 1.33$. However, for $Z = 12$, you can see from Figure 19.5 that stable nuclei should have an N/Z of about 1. Alternatively, you can see from the periodic table that the atomic mass of magnesium is 24.31. Therefore, a nuclide with a mass number of 28 is too heavy to be stable because the N/Z ratio is too high and Mg-28 undergoes *beta decay*, resulting in the conversion of a neutron to a proton.
- (b) Magnesium-22 has 10 neutrons and 12 protons, so $N/Z = 0.83$ (too low). Alternatively you can see from the periodic table that the atomic mass of magnesium is 24.31. A nuclide with a mass number of 22 is too light; the N/Z ratio is too low. Therefore, Mg-22 undergoes *positron emission*, resulting in the conversion of a proton to a neutron. (Electron capture would accomplish the same thing as positron emission, but in Mg-22, positron emission is the only decay mode observed.)
- (c) Molybdenum-102 has 60 neutrons and 42 protons, so $N/Z = 1.43$. However, for $Z = 42$, you can see from Figure 19.5 that stable nuclei should have an N/Z ratio of about 1.3. Alternatively you can see from the periodic table that the atomic mass of molybdenum is 95.94. A nuclide with a mass number of 102 is too heavy to be stable; the N/Z ratio is too high. Therefore, Mo-102 undergoes *beta decay*, resulting in the conversion of a neutron to a proton.

FOR PRACTICE 19.3

Predict whether each nuclide is more likely to decay via beta decay or positron emission.

- (a) Pb-192 (b) Pb-212 (c) Xe-114

Magic Numbers

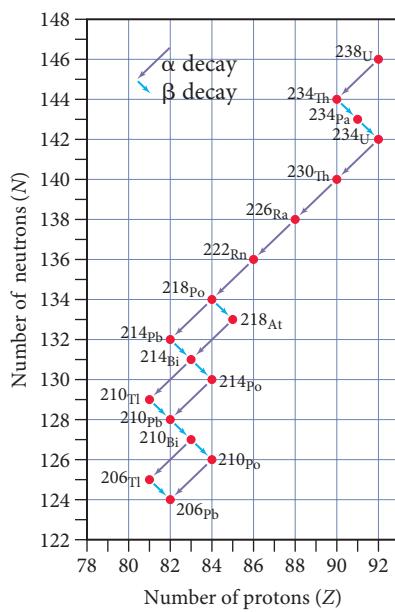
In addition to the N/Z ratio, the *actual number* of protons and neutrons also affects the stability of the nucleus. Table 19.2 shows the number of nuclei with different possible combinations of even or odd nucleons. Notice that a large number of stable nuclides have both an even number of protons and an even number of neutrons. Only five stable nuclides have an odd and odd combination.

The reason for this is that nucleons occupy energy levels within the nucleus much as electrons occupy energy levels within an atom. Just as atoms with certain numbers of electrons are uniquely stable (in particular, the number of electrons associated with the

TABLE 19.2 Number of Stable Nuclides with Even and Odd Numbers of Nucleons

Z	N	Number of Nuclides
Even	Even	157
Even	Odd	53
Odd	Even	50
Odd	Odd	5

A Decay Series



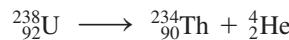
▲ FIGURE 19.6 The Uranium-238

Radioactive Decay Series Uranium-238 decays via a series of steps ending in Pb-206, a stable element. Each diagonal line to the left represents an alpha decay and each diagonal line to the right represents a beta decay.

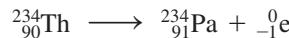
noble gases: 2, 10, 18, 36, 54, etc.), so atoms with certain numbers of nucleons (N or $Z = 2, 8, 20, 28, 50, 82$, and $N = 126$) are uniquely stable. These numbers are often referred to as **magic numbers**. Nuclei containing a magic number of protons or neutrons are particularly stable. Since the magic numbers are even, this accounts in part for the abundance of stable nuclides with even numbers of nucleons. Moreover, nucleons also have a tendency to pair together (much as electrons pair together). This tendency and the resulting stability of paired nucleons also contribute to the abundance of stable nuclides with even numbers of nucleons.

Radioactive Decay Series

Atoms with $Z > 83$ are radioactive and decay in one or more steps involving primarily alpha and beta decay (with some gamma decay to carry away excess energy). For example, uranium (atomic number 92) is the heaviest naturally occurring element. Its most common isotope is U-238, an alpha emitter that decays to Th-234.



The daughter nuclide, Th-234, is itself radioactive—it is a beta emitter that decays to Pa-234.



Protactinium-234 is also radioactive, decaying to U-234 via beta emission. Radioactive decay continues until a stable nuclide, Pb-206, is reached. Figure 19.6 ▲ illustrates the entire uranium-238 decay series.

19.5 Detecting Radioactivity

The particles emitted by radioactive nuclei have a lot of energy and can therefore be readily detected. In a radiation detector, the particles are detected through their interactions with atoms or molecules. The simplest radiation detectors are pieces of photographic film that become exposed when radiation passes through them. **Film-badge dosimeters**—which consist of photographic film held in a small case that is pinned to clothing—are issued to most people working with or near radioactive substances (Figure 19.7 ◀). These badges are collected and processed (or developed) regularly as a way to monitor a person's exposure. The more exposed the film has become in a given period of time, the more radioactivity the person has been exposed to during that period.

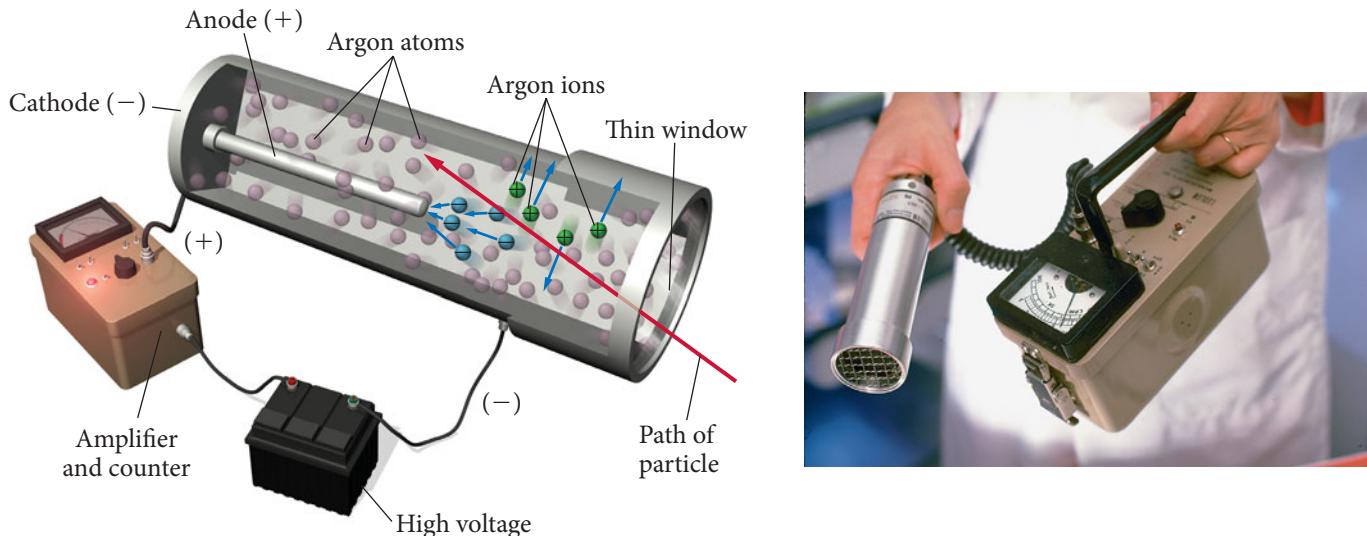
Radioactivity can be instantly detected with devices such as a **Geiger-Müller counter** (Figure 19.8 ▶). In this instrument (commonly referred to as a Geiger counter), particles emitted by radioactive nuclei pass through an argon-filled chamber. The energetic particles create a trail of ionized argon atoms. High voltage applied between a wire within the chamber and the chamber itself causes these newly formed ions to produce an electrical signal that can be displayed on a meter or turned into an audible click. Each click corresponds to a radioactive particle passing through the argon gas chamber. This clicking is the stereotypical sound most people associate with a radiation detector.

A second type of device commonly used to detect radiation instantly is a **scintillation counter**. In a scintillation counter, radioactive emissions pass through a material (such as NaI or CsI) that emits ultraviolet or visible light in response to excitation by energetic particles. The radioactivity excites the atoms to a higher energy state. The atoms release this energy as light, which is detected and turned into an electrical signal that can be read on a meter.



▲ FIGURE 19.7 Film-Badge Dosimeter

A film-badge dosimeter consists of a piece of photographic film in a light-resistant container. The film's exposure in a given time is proportional to the amount of radiation it receives.



▲ FIGURE 19.8 Geiger-Müller Counter When ionizing radiation passes through the argon-filled chamber, it ionizes the argon atoms, giving rise to a brief, tiny pulse of electrical current that is transduced onto a meter or into an audible click.

19.6 The Kinetics of Radioactive Decay and Radiometric Dating

Radioactivity is a natural component of our environment. The ground beneath you most likely contains radioactive atoms that emit radiation. The food you eat contains a residual quantity of radioactive atoms that are absorbed into your body fluids and incorporated into tissues. Small amounts of radiation from space make it through our atmosphere to constantly bombard Earth. Humans and other living organisms have evolved in this environment and have adapted to survive in it.

One reason for the radioactivity in our environment is the instability of all atomic nuclei beyond atomic number 83 (bismuth). Every element with more than 83 protons in its nucleus is unstable and therefore radioactive. In addition, some isotopes of elements with fewer than 83 protons are also unstable and radioactive. Radioactive nuclides *persist* in our environment because new ones are constantly being formed, and because many of the existing ones decay away only very slowly.

All radioactive nuclei decay via first-order kinetics, so the rate of decay in a particular sample is directly proportional to the number of nuclei present as indicated in the equation:

$$\text{Rate} = kN$$

where N is the number of radioactive nuclei and k is the rate constant. Different radioactive nuclides decay into their daughter nuclides with different rate constants. Some nuclides decay quickly (large rate constant) while others decay slowly (small rate constant).

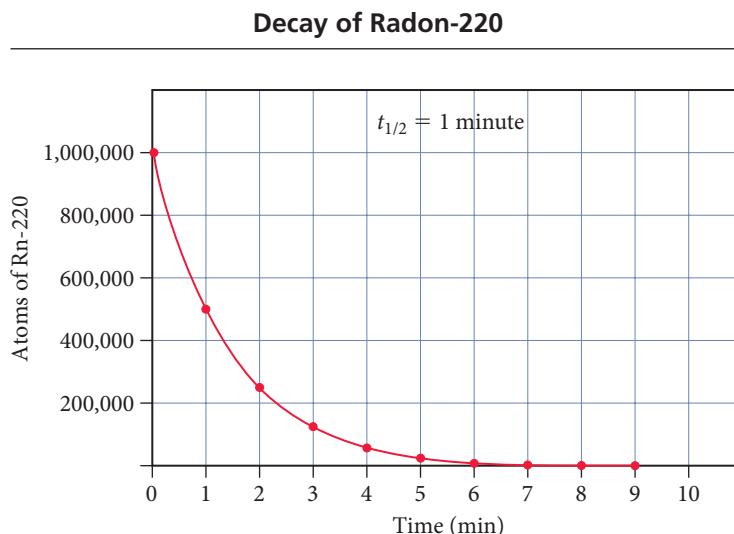
The time it takes for one-half of the parent nuclides in a radioactive sample to decay to the daughter nuclides is the *half-life*, and is identical to the concept of half-life for chemical reactions that we discussed in Chapter 13. Thus, the relationship between the half-life of a nuclide and its rate constant is given by the same expression (Equation 13.19) that we derived for a first-order reaction in Section 13.4:

$$t_{1/2} = \frac{0.693}{k} \quad [19.1]$$

Nuclides that decay quickly have short half-lives and large rate constants—they are considered very active (many decay events per unit time). Nuclides that decay slowly have long half-lives and are less active (fewer decay events per unit time). For example, thorium-232 is an alpha emitter with a half-life of 1.4×10^{10} years, or 14 billion years.

You may find it useful to review the discussion of first-order kinetics in Section 13.3.

► FIGURE 19.9 The Decay of Radon-220 Radon-220 decays with a half-life of approximately 1 minute.



A sample of Th-232 containing 1 million atoms decays to $\frac{1}{2}$ million atoms in 14 billion years and then to $\frac{1}{4}$ million in another 14 billion years and so on. Notice that a radioactive sample does *not* decay to zero atoms in two half-lives—you can't add two half-lives together to get a “whole” life. The amount that remains after one half-life is always one-half of what was present at the start. The amount that remains after two half-lives is one-quarter of what was present at the start, and so on.

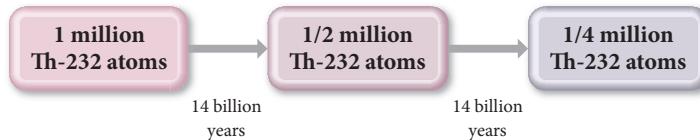
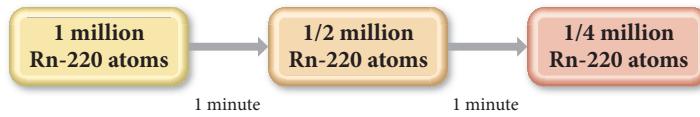


TABLE 19.3 Selected Nuclides and Their Half-Lives

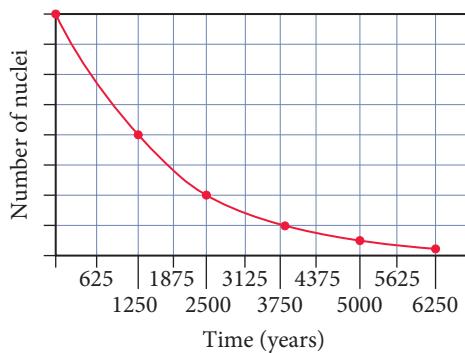
Nuclide	Half-Life	Type of Decay
$^{232}_{90}\text{Th}$	1.4×10^{10} yr	Alpha
$^{238}_{92}\text{U}$	4.5×10^9 yr	Alpha
$^{14}_{6}\text{C}$	5730 yr	Beta
$^{220}_{86}\text{Rn}$	55.6 s	Alpha
$^{219}_{90}\text{Th}$	1.05×10^{-6} s	Alpha

Some nuclides have very short half-lives. For example, radon-220 has a half-life of approximately 1 minute (Figure 19.9 ▲). A 1-million-atom sample of radon-220, decays to $\frac{1}{4}$ million radon-220 atoms in just 2 minutes and to approximately 1000 atoms in 10 minutes. Table 19.3 lists several nuclides and their half-lives.



Conceptual Connection 19.2 Half-Life

Consider this graph representing the decay of a radioactive nuclide.



What is the half-life of the nuclide?

- (a) 625 years (b) 1250 years (c) 2500 years (d) 3125 years

The Integrated Rate Law

Recall from Chapter 13 that for first-order chemical reactions, the concentration of a reactant as a function of time is given by the integrated rate law:

$$\ln \frac{[A]_t}{[A]_0} = -kt \quad [19.2]$$

Since nuclear decay follows first-order kinetics, we can substitute the number of nuclei for concentration to arrive at the equation:

$$\ln \frac{N_t}{N_0} = -kt \quad [19.3]$$

where N_t is the number of radioactive nuclei at time t and N_0 is the initial number of radioactive nuclei. Example 19.4 demonstrates the use of this equation.

EXAMPLE 19.4 Radioactive Decay Kinetics

Plutonium-236 is an alpha emitter with a half-life of 2.86 years. If a sample initially contains 1.35 mg of Pu-236, what mass of Pu-236 is present after 5.00 years?



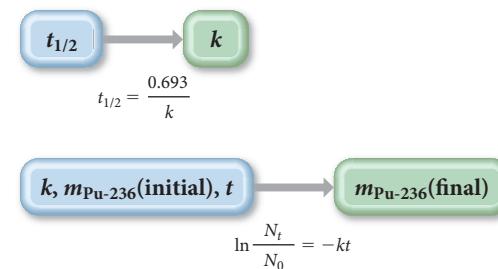
SORT You are given the initial mass of Pu-236 in a sample and asked to find the mass after 5.00 years.

GIVEN: $m_{\text{Pu-236}}(\text{initial}) = 1.35 \text{ mg}$;
 $t = 5.00 \text{ yr}$; $t_{1/2} = 2.86 \text{ yr}$

FIND: $m_{\text{Pu-236}}(\text{final})$

STRATEGIZE Use the integrated rate law (Equation 19.3) to solve this problem. You must determine the value of the rate constant (k) from the half-life expression (Equation 19.1).

CONCEPTUAL PLAN



Use the value of the rate constant, the initial mass of Pu-236, and the time along with integrated rate law to find the final mass of Pu-236. Since the mass of the Pu-236 ($m_{\text{Pu-236}}$) is directly proportional to the number of atoms (N), and since the integrated rate law contains the ratio (N_t/N_0), the initial and final masses can be substituted for the initial and final number of atoms.

SOLVE Follow your plan. Begin by determining the rate constant from the half-life.

SOLUTION

$$t_{1/2} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.86 \text{ yr}}$$

$$= 0.2423/\text{yr}$$

Solve the integrated rate law for N_t and substitute the values of the rate constant, the initial mass of Pu-236, and the time into the solved equation. Calculate the final mass of Pu-236.

$$\ln \frac{N_t}{N_0} = -kt$$

$$\frac{N_t}{N_0} = e^{-kt}$$

$$N_t = N_0 e^{-kt}$$

$$N_t = 1.35 \text{ mg} [e^{-(0.2423/\text{yr})(5.00 \text{ yr})}]$$

$$N_t = 0.402 \text{ mg}$$

CHECK The units of the answer (mg) are correct. The magnitude of the answer (0.402 mg) is about one-third of the original mass (1.35 mg), which seems reasonable given that the amount of time is between one and two half-lives. (One half-life would result in one-half of the original mass and two half-lives would result in one-fourth of the original mass.)

FOR PRACTICE 19.4

How long will it take for the 1.35 mg sample of Pu-236 in Example 19.4 to decay to 0.100 mg?

Since radioactivity is a first-order process, the rate of decay is linearly proportional to the number of nuclei in the sample. Therefore, the initial rate of decay (rate_0) and the rate of decay at time t (rate_t) can also be used in the integrated rate law.

$$\text{Rate}_t = kN_t \quad \text{Rate}_0 = kN_0$$

$$\frac{N_t}{N_0} = \frac{\text{rate}_t/k}{\text{rate}_0/k} = \frac{\text{rate}_t}{\text{rate}_0}$$

Substituting into Equation 19.3, we get the following result:

$$\ln \frac{\text{rate}_t}{\text{rate}_0} = -kt \quad [19.4]$$

We can use Equation 19.4 to predict how the rate of decay of a radioactive sample will change with time or how much time has passed based on how the rate has changed (see examples later in this section).

The radioactive isotopes in our environment and their predictable decay with time can therefore be used to estimate the age of rocks or artifacts containing those isotopes. The technique is known as **radiometric dating**, and we examine two different types individually.



Conceptual Connection 19.3 Half-Life and the Amount of Radioactive Sample

A sample initially contains 1.6 moles of a radioactive isotope. How much of the sample remains after four half-lives?

- (a) 0.0 mol (b) 0.10 mol (c) 0.20 mol (d) 0.40 mol



▲ The Dead Sea Scrolls are 2000-year-old biblical manuscripts. Their age was determined by radiocarbon dating.

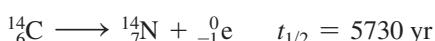
Radiocarbon Dating: Using Radioactivity to Measure the Age of Fossils and Artifacts

Archeologists, geologists, anthropologists, and other scientists use **radiocarbon dating**, a technique devised in 1949 by Willard Libby at the University of Chicago, to estimate the ages of fossils and artifacts. For example, in 1947, young shepherds searching for a stray goat near the Dead Sea (east of Jerusalem) entered a cave and discovered ancient scrolls that had been stuffed into jars. These scrolls—now named the Dead Sea Scrolls—are 2000-year-old texts of the Hebrew Bible, predating other previously discovered manuscripts by almost a thousand years.

The Dead Sea Scrolls, like other ancient artifacts, contain a radioactive signature that reveals their age. This signature results from the presence of carbon-14 (which is radioactive) in the environment. Carbon-14 is constantly formed in the upper atmosphere by the neutron bombardment of nitrogen.



After it forms, carbon-14 decays back to nitrogen by beta emission with a half-life of 5730 years.



Libby received the Nobel Prize in 1960 for the development of radiocarbon dating.

The continuous formation of carbon-14 in the atmosphere and its continuous decay to nitrogen-14 produce a nearly constant equilibrium amount of atmospheric carbon-14. The atmospheric carbon-14 is oxidized to carbon dioxide and incorporated into plants by photosynthesis. The C-14 then makes its way up the food chain and ultimately into all living organisms. As a result, the tissues in all living plants, animals, and humans contain the same ratio of carbon-14 to carbon-12 ($^{14}\text{C} : ^{12}\text{C}$) as that found in the atmosphere. When a living organism dies, however, it stops incorporating new carbon-14 into its tissues. The $^{14}\text{C} : ^{12}\text{C}$ ratio then begins to decrease with a half-life of 5730 years. Since many artifacts, including the Dead Sea Scrolls, are made from materials that were once living—such as papyrus, wood, or other plant and animal derivatives—the $^{14}\text{C} : ^{12}\text{C}$ ratio in these artifacts indicates their age. For example, suppose an ancient artifact has a $^{14}\text{C} : ^{12}\text{C}$ ratio that is 25% of that found in living organisms. How old is the artifact? Since it contains one-quarter as much carbon-14 as a living organism, it must be two half-lives or 11,460 years old. The maximum age that can be estimated from carbon-14 dating is about 50,000 years—beyond that, the amount of carbon-14 becomes too low to measure accurately.

The accuracy of carbon-14 dating can be checked against objects whose ages are known from historical sources. These kinds of comparisons reveal that ages obtained from C-14 dating may deviate from the actual ages by up to about 5%. For a 6000-year-old object, that would result in an error of about 300 years. The reason for the deviations is the variance of atmospheric C-14 levels over time.

In order to make C-14 dating more accurate, scientists have studied the carbon-14 content of western bristlecone pine trees, which can live up to 5000 years. Each tree trunk contains growth rings corresponding to each year of the tree's life, and the wood laid down in each ring incorporates carbon derived from the carbon dioxide in the atmosphere at that time. The rings thus provide a record of the historical atmospheric carbon-14 content. In addition, the rings of living trees can be correlated with the rings of dead trees (if part of the lifetimes of the trees overlapped), allowing the record to be extended back about 11,000 years. Using the data from the bristlecone pine, the 5% deviations from historical dates can be corrected. In this way, the known ages of bristlecone pine trees are used to calibrate C-14 dating, resulting in more accurate results.



▲ Western bristlecone pine trees can live up to 5000 years; scientists can precisely determine the age of a tree by counting the annual rings in its trunk. The trees can therefore be used to calibrate the timescale for radiocarbon dating.

EXAMPLE 19.5 Radiocarbon Dating

A skull believed to belong to an ancient human being has a carbon-14 decay rate of 4.50 disintegrations per minute per gram of carbon (4.50 dis/min · g C). If living organisms have a decay rate of 15.3 dis/min · g C, how old is the skull? (The decay rate is directly proportional to the amount of carbon-14 present.)



SORT You are given the current rate of decay for the skull and the assumed initial rate. You are asked to find the age of the skull, which is the time that passed in order for the rate to have reached its current value.

STRATEGIZE Use the expression for half-life (Equation 19.1) to find the rate constant (k) from the half-life for C-14, which is 5730 yr (Table 19.3).

Use the value of the rate constant and the initial and current rates to find t from the integrated rate law (Equation 19.4).

GIVEN: $\text{rate}_t = 4.50 \text{ dis/min} \cdot \text{g C}$;
 $\text{rate}_0 = 15.3 \text{ dis/min} \cdot \text{g C}$;

FIND: t

CONCEPTUAL PLAN

$$t_{1/2} \rightarrow k$$

$$t_{1/2} = \frac{0.693}{k}$$

$$k, \text{rate}_t, \text{rate}_0 \rightarrow t$$

$$\ln \frac{\text{rate}_t}{\text{rate}_0} = -kt$$

SOLVE Follow your plan. Begin by finding the rate constant from the half-life.

SOLUTION

$$t_{1/2} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730 \text{ yr}}$$

$$= 1.209 \times 10^{-4}/\text{yr}$$

$$\ln \frac{\text{rate}_t}{\text{rate}_0} = -kt$$

$$t = -\frac{\ln \frac{\text{rate}_t}{\text{rate}_0}}{k} = -\frac{\ln \frac{4.50 \text{ dis/min} \cdot \text{g C}}{15.3 \text{ dis/min} \cdot \text{g C}}}{1.209 \times 10^{-4}/\text{yr}}$$

$$= 1.0 \times 10^4 \text{ yr}$$

Substitute the rate constant and the initial and current rates into the integrated rate law and solve for t .

CHECK The units of the answer (yr) are correct. The magnitude of the answer is about 10,000 years, which is a little less than two half-lives. This value is reasonable given that two half-lives would result in a decay rate of about 3.8 dis/min · g C.

FOR PRACTICE 19.5

A researcher claims that an ancient scroll originated from Greek scholars in about 500 B.C. A measure of its carbon-14 decay rate gives a value that is 89% of that found in living organisms. How old is the scroll and could it be authentic?



Chemistry in Your Day

Radiocarbon Dating and the Shroud of Turin

The Shroud of Turin—kept in the cathedral of Turin in Italy—is an old linen cloth that bears a mysterious image. Many people have interpreted the image as that of a man who appears to have been crucified. The image becomes clearer if the shroud is photographed and viewed as a negative. Some claim that the shroud is the original burial cloth of Jesus, miraculously imprinted with his image. In 1988, the Roman Catholic Church chose three independent laboratories to perform radiocarbon dating on the shroud. The laboratories took samples of the cloth and measured the carbon-14 content. The three independent laboratories all arrived at similar results—the shroud was made from linen originating in about A.D. 1325. Although some have disputed the results (and continue to do so), and although no scientific test is 100% reliable, newspapers around the world announced that the Shroud did not date back to biblical times.



► The linen cloth known as the Shroud of Turin bears the image of a man believed by some to be Jesus.

Uranium/Lead Dating

Radiocarbon dating can only measure the ages of objects that were once living and that are relatively young (<50,000 years). Other radiometric dating techniques can measure the ages of prehistoric objects that were never alive. The most dependable technique relies on the ratio of uranium-238 to lead-206 within igneous rocks (rocks of volcanic origin). This technique measures the time that has passed since the rock solidified (at which point the “radiometric clock” was reset).

Since U-238 decays into Pb-206 with a half-life of 4.5×10^9 years, the relative amounts of U-238 and Pb-206 in a uranium-containing rock reveal its age. For example, if a rock originally contained U-238 and currently contains equal amounts of U-238 and Pb-206, it would be 4.5 billion years old, assuming that the rock did not contain any Pb-206 when it was formed. The latter assumption can be tested because the lead that results from the decay of uranium has a different isotopic composition than the lead that was deposited in rocks at the time of their formation. Example 19.6 shows how the relative amounts of Pb-206 and U-238 in a rock can be used to estimate its age.

EXAMPLE 19.6 Using Uranium/Lead Dating to Estimate the Age of a Rock

A meteor contains 0.556 g of Pb-206 to every 1.00 g of U-238. Assuming that the meteor did not contain any Pb-206 at the time of its formation, determine the age of the meteor. Uranium-238 decays to lead-206 with a half-life of 4.5 billion years.

SORT You are given the current masses of Pb-206 and U-238 in a rock and asked to find its age. You are also given the half-life of U-238.

STRATEGIZE Use the integrated rate law (Equation 19.3) to solve this problem. To do so, you must first determine the value of the rate constant (k) from the half-life expression (Equation 19.1).

Before substituting into the integrated rate law, you also need the ratio of the current amount of U-238 to the original amount (N_t/N_0). The current mass of uranium is simply 1.00 g. The initial mass includes the current mass (1.00 g) plus the mass that has decayed into lead-206, which can be determined from the current mass of Pb-206.

Use the value of the rate constant and the initial and current amounts of U-238 along with the integrated rate law to find t .

SOLVE Follow your plan. Begin by finding the rate constant from the half-life.

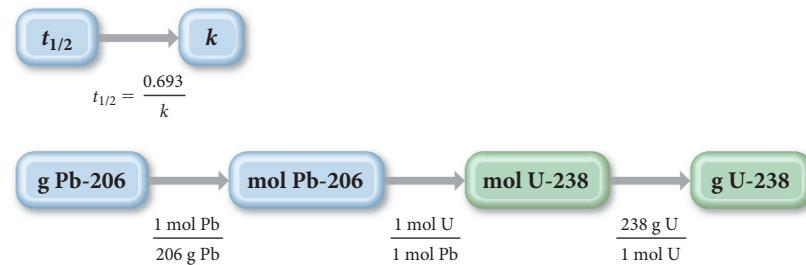
Determine the mass in grams of U-238 that is required to form the given mass of Pb-206.

Substitute the rate constant and the initial and current masses of U-238 into the integrated rate law and solve for t . (The initial mass of U-238 is the sum of the current mass and the mass that is required to form the given mass of Pb-206.)

GIVEN: $m_{\text{U-238}} = 1.00 \text{ g}$; $m_{\text{Pb-206}} = 0.556 \text{ g}$;
 $t_{1/2} = 4.5 \times 10^9 \text{ yr}$

FIND: t

CONCEPTUAL PLAN



$$k, N_t, N_0 \rightarrow t$$

$$\ln \frac{N_t}{N_0} = -kt$$

SOLUTION

$$t_{1/2} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{4.5 \times 10^9 \text{ yr}}$$

$$= 1.54 \times 10^{-10}/\text{yr}$$

$$0.556 \text{ g Pb-206} \times \frac{1 \text{ mol Pb-206}}{206 \text{ g Pb-206}} \times \frac{1 \text{ mol U-238}}{1 \text{ mol Pb-206}} \times \frac{238 \text{ g U-238}}{1 \text{ mol U-238}} = 0.6424 \text{ g U-238}$$

$$\ln \frac{N_t}{N_0} = -kt$$

$$t = -\frac{\ln \frac{N_t}{N_0}}{k} = -\frac{\ln \frac{1.00 \text{ g}}{1.00 \text{ g} + 0.6424 \text{ g}}}{1.54 \times 10^{-10}/\text{yr}}$$

$$= 3.2 \times 10^9 \text{ yr}$$

CHECK The units of the answer (yr) are correct. The magnitude of the answer is about 3.2 billion years, which is less than one half-life. This value is reasonable given that less than half of the uranium in the meteor has decayed into lead.

FOR PRACTICE 19.6

A rock contains a Pb-206 to U-238 mass ratio of 0.145 : 1.00. Assuming that the rock did not contain any Pb-206 at the time of its formation, determine its age.

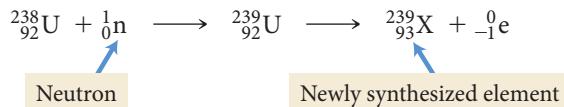
The age of the universe is estimated from its expansion rate, which can be measured by examining changes in the wavelength of light from distant galaxies.

The Age of Earth The uranium/lead radiometric dating technique as well as other radiometric dating techniques (such as the decay of potassium-40 to argon-40) have been widely used to measure the ages of rocks on Earth and have produced highly consistent results. Rocks with ages greater than 3.5 billion years have been found on every continent. The oldest rocks have an age of approximately 4.0 billion years, establishing a lower limit for Earth's age (Earth must be at least as old as its oldest rocks). The ages of about 70 meteorites that have struck Earth have also been extensively studied and have been found to be about 4.5 billion years old. Since the meteorites were formed at the same time as our solar system (which includes Earth), the best estimate for Earth's age is therefore about 4.5 billion years. That age is consistent with the estimated age of our universe—about 13.7 billion years.

19.7 The Discovery of Fission: The Atomic Bomb and Nuclear Power

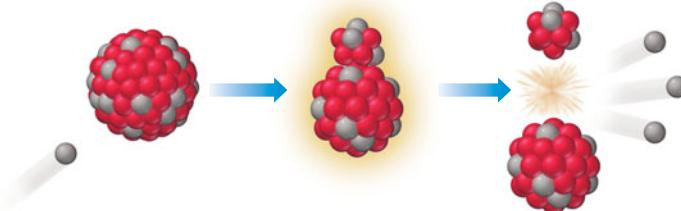
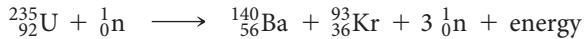
The element with atomic number 100 is named fermium in honor of Enrico Fermi.

In the mid-1930s Enrico Fermi (1901–1954), an Italian physicist, attempted to synthesize a new element by bombarding uranium—the heaviest known element at that time—with neutrons. Fermi speculated that if a neutron could be incorporated into the nucleus of a uranium atom, the nucleus might undergo beta decay, converting a neutron into a proton. If that happened, a new element, with atomic number 93, would be synthesized for the first time. The nuclear equation for the process is shown here.



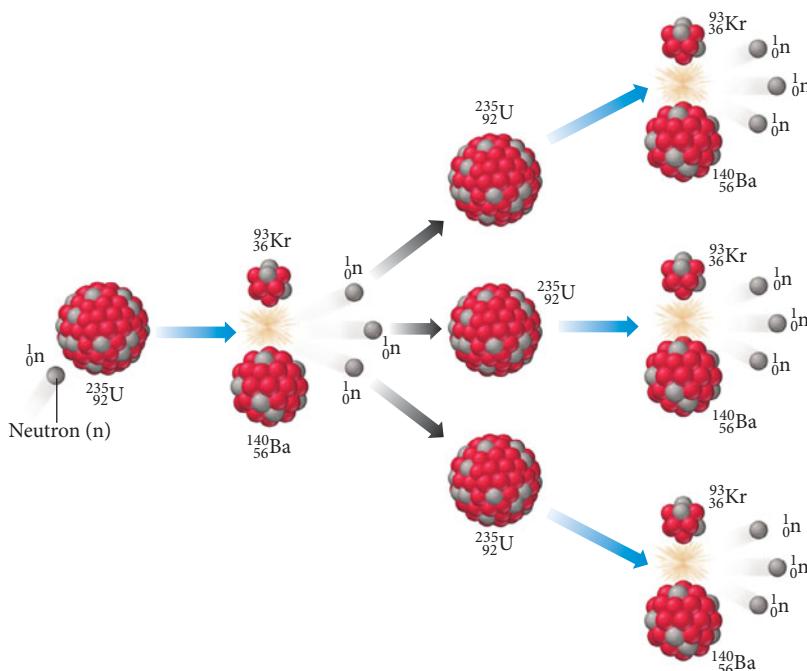
Fermi performed the experiment and detected the emission of beta particles. However, his results were inconclusive. Had he synthesized a new element? Fermi never chemically examined the products to determine their composition and therefore could not say with certainty that he had.

Three researchers in Germany—Lise Meitner (1878–1968), Fritz Strassmann (1902–1980), and Otto Hahn (1879–1968)—repeated Fermi's experiments, and then performed careful chemical analysis of the products. What they found in the products—several elements *lighter* than uranium—would change the world forever. On January 6, 1939, Meitner, Strassmann, and Hahn reported that the neutron bombardment of uranium resulted in **nuclear fission**—the splitting of the uranium atom. The nucleus of the neutron-bombarded uranium atom had been split into barium, krypton, and other smaller products. They also determined that the process emits enormous amounts of energy. A nuclear equation for a fission reaction, showing how uranium breaks apart into the daughter nuclides, is shown here.



The element with atomic number 109 is named meitnerium in honor of Lise Meitner.

Fission Chain Reaction



▲ FIGURE 19.10 A Self-Amplifying Chain Reaction The fission of one U-235 nucleus emits neutrons that can then initiate fission in other U-235 nuclei, resulting in a chain reaction that releases enormous amounts of energy.

Notice that the initial uranium atom is the U-235 isotope, which constitutes less than 1% of all naturally occurring uranium. U-238, the most abundant uranium isotope, does not undergo fission. Notice also that the process produces three neutrons, which have the potential to initiate fission in three other U-235 atoms.

Scientists quickly realized that a sample rich in U-235 could undergo a **chain reaction** in which neutrons produced by the fission of one uranium nucleus would induce fission in other uranium nuclei (Figure 19.10 ▲). This self-amplifying reaction is capable of producing an enormous amount of energy. This is the energy that is harnessed in an atomic bomb. However, to make a bomb, a **critical mass** of U-235—enough U-235 to produce a self-sustaining reaction—is necessary. Fearing that Nazi Germany would develop such a bomb, several U.S. scientists persuaded Albert Einstein, the most famous scientist of the time, to write a letter to President Franklin Roosevelt warning of this possibility. Einstein wrote, “. . . and it is conceivable—though much less certain—that extremely powerful bombs of a new type may thus be constructed. A single bomb of this type, carried by boat and exploded in a port, might very well destroy the whole port together with some of the surrounding territory.”

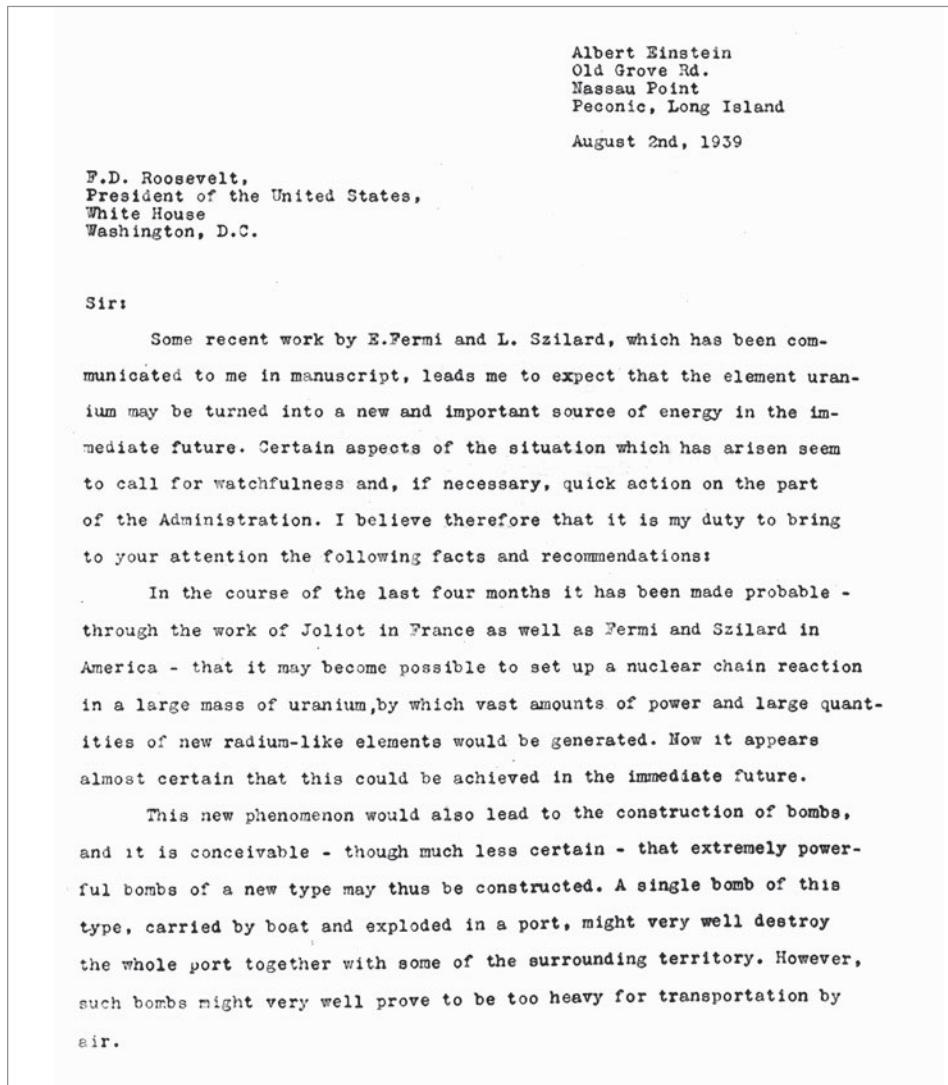
Einstein’s letter convinced Roosevelt, and in 1941 he assembled the resources to begin the costliest scientific project ever attempted. The top-secret endeavor was called the *Manhattan Project* and its main goal was to build an atomic bomb before the Germans did. The project was led by physicist J. R. Oppenheimer (1904–1967) at a high-security research facility in Los Alamos, New Mexico. Four years later, on July 16, 1945, the world’s first nuclear weapon was successfully detonated at a test site in New Mexico. The first atomic bomb exploded with a force equivalent to 18,000 tons of dynamite. Ironically, the Germans—who had *not* made a successful nuclear bomb—had already been defeated by this time. Instead, the United States used the atomic bomb on Japan. One bomb was dropped on Hiroshima and a second bomb was dropped on Nagasaki. Together, the bombs killed approximately 200,000 people and led to Japan’s surrender.



▲ Lise Meitner in Otto Hahn’s Berlin laboratory. Together with Hahn and Fritz Strassmann, Meitner determined that U-235 could undergo nuclear fission.



▲ On July 16, 1945, in the New Mexico desert, the world’s first atomic bomb was detonated. It had the power of 18,000 tons of dynamite.

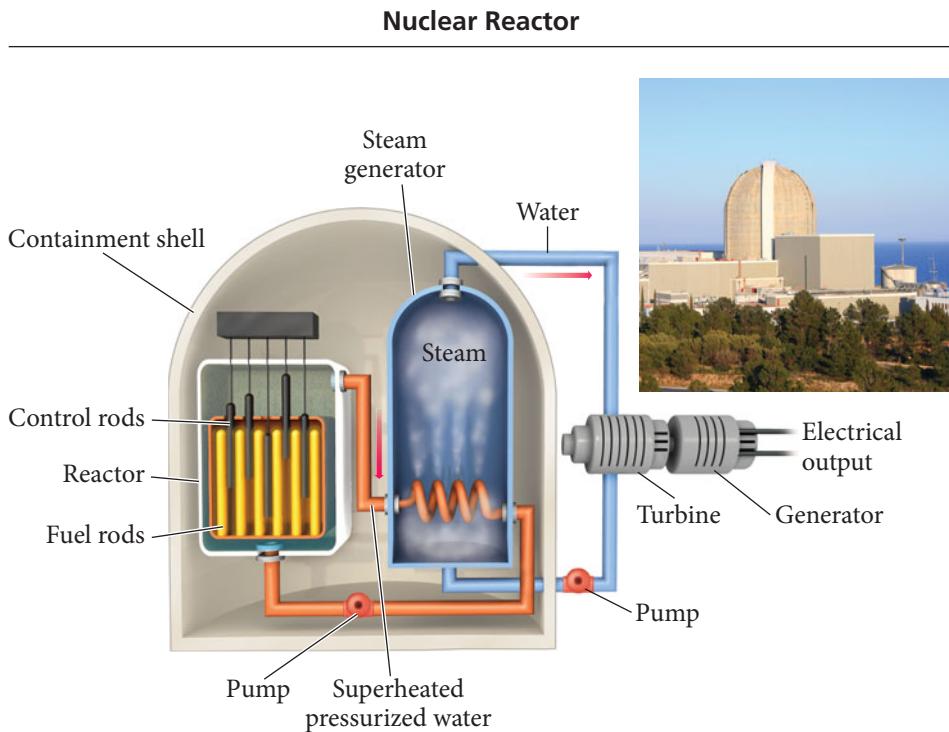


▲ Einstein's letter (part of which is shown here) helped persuade Franklin Roosevelt to begin research into the building of a fission bomb.

Nuclear Power: Using Fission to Generate Electricity

Nuclear reactions, such as fission, generate enormous amounts of energy. In a nuclear bomb, the energy is released all at once. The energy can also be released more slowly and used for peaceful purposes such as electricity generation. In the United States, nuclear fission generates about 20% of electricity. In some other countries, nuclear fission generates as much as 70% of electricity. To get an idea of the amount of energy released during fission, imagine a hypothetical nuclear-powered car. Suppose the fuel for such a car was a uranium cylinder about the size of a pencil. How often would you have to refuel the car? The energy content of the uranium cylinder is equivalent to about 1000 twenty-gallon tanks of gasoline. If you refuel your gasoline-powered car once a week, your nuclear-powered car could go 1000 weeks—almost 20 years—before refueling.

Similarly, a nuclear-powered electricity generation plant can produce a lot of electricity from a small amount of fuel. Such plants exploit the heat created by fission, using it to boil water and make steam, which then turns the turbine on a generator to produce electricity (Figure 19.11 ▶). The fission reaction occurs in the nuclear core of the power plant. The core consists of uranium fuel rods—enriched to about 3.5% U-235—interspersed between retractable neutron-absorbing control rods. When the control rods



◀ FIGURE 19.11 A Nuclear Reactor

The fission of U-235 in the core of a nuclear power plant generates heat that creates steam and turns a turbine on an electrical generator. Control rods are raised or lowered to control the fission reaction. (Note that the water carrying heat away from the reactor core is contained within its own pipes and does not come into direct contact with the steam that drives the turbines.)



▲ In 1986, the reactor core at Chernobyl (in what is now Ukraine) overheated, exploded, and destroyed part of the containment structure. The release of radioactive nuclides into the environment forced the government to relocate over 335,000 people. It is estimated that there may eventually be several thousand additional cancer deaths among the exposed populations.

are fully retracted from the fuel rod assembly, the chain reaction can occur. When the control rods are fully inserted into the fuel assembly, however, they absorb the neutrons that would otherwise induce fission, shutting down the chain reaction. By retracting or inserting the control rods, the operator can increase or decrease the rate of fission. In this way, the fission reaction is controlled to produce the right amount of heat needed for electricity generation. In case of a power failure, the control rods automatically drop into the fuel rod assembly, shutting down the fission reaction.

A typical nuclear power plant generates enough electricity for a city of about 1 million people and uses about 50 kg of fuel per day. In contrast, a coal-burning power plant uses about 2,000,000 kg of fuel to generate the same amount of electricity. Furthermore, a nuclear power plant generates no air pollution and no greenhouse gases. A coal-burning power plant emits pollutants such as carbon monoxide, nitrogen oxides, and sulfur oxides. Coal-burning power plants also emit carbon dioxide, a greenhouse gas.

Nuclear power generation, however, is not without problems. Foremost among them is the danger of nuclear accidents. In spite of safety precautions, the fission reaction occurring in a nuclear power plant can overheat. The most famous examples of this occurred in Chernobyl, in the former Soviet Union, on April 26, 1986, and at the Fukushima Daiichi Nuclear Power Plant in Japan in March of 2011.

In the Chernobyl incident, operators of the plant were performing an experiment designed to reduce maintenance costs. In order to perform the experiment they had to disable many of the safety features of the reactor core. The experiment failed with disastrous results. The nuclear core, composed partly of graphite, overheated and began to burn. The accident caused 31 immediate deaths and produced a fire that scattered radioactive debris into the atmosphere, making much of the surrounding land (within about a 32-kilometer radius) uninhabitable. As bad as the accident was, however, it was not a nuclear detonation. A nuclear power plant *cannot* become a nuclear bomb. The uranium fuel used in electricity generation is not sufficiently enriched in U-235 to produce a nuclear detonation. U.S. nuclear power plants have additional safety features designed to prevent similar accidents. For example, U.S. nuclear power plants have large containment structures to contain radioactive debris in the event of an accident.

Reactor cores in the United States are not made of graphite and cannot burn in the way that the Chernobyl core did.

In the 2011 Japanese accident, a 9.0 magnitude earthquake triggered a tsunami that flooded the coastal plant and caused the cooling system pumps to fail. Several of the nuclear cores within the plant dramatically overheated and at least one of the cores experienced a partial meltdown (in which the fuel gets so hot that it melts). The accident was intensified by the loss of water in the fuel storage ponds (pools of water used to keep spent fuel as well as future fuel cool), which caused the fuel stored in the ponds to also overheat. The release of radiation into the environment, however, while significant, was lower in Japan than at Chernobyl. As of press time, no radioactivity-related deaths have been reported at the Fukushima plant or the surrounding area. The cleanup of the site, however, will continue for many years.

A second problem associated with nuclear power is waste disposal. Although the amount of nuclear fuel used in electricity generation is small compared to other fuels, the products of the reaction are radioactive and have long half-lives. What do we do with this waste? Currently, in the United States, nuclear waste is stored on site at the nuclear power plants. A single permanent disposal site was being developed in Yucca Mountain, Nevada to store U.S. waste. However, in the Spring of 2010, the Obama administration halted the development of this project and formed the Blue Ribbon Commission on America's Nuclear Future to explore alternatives.

19.8 Converting Mass to Energy: Mass Defect and Nuclear Binding Energy

Nuclear fission produces large amounts of energy. But where does the energy come from? We can answer this question by carefully examining the masses of the reactants and products in the fission equation from Section 19.7.

$^{235}_{92}\text{U} + {}^1_0\text{n}$	\longrightarrow	${}^{140}_{56}\text{Ba} + {}^{93}_{36}\text{Kr} + 3 {}^1_0\text{n}$
Mass Reactants		Mass Products
$^{235}_{92}\text{U}$	235.04392 amu	${}^{140}_{56}\text{Ba}$
${}^1_0\text{n}$	1.00866 amu	${}^{93}_{36}\text{Kr}$
		$3 {}^1_0\text{n}$
Total	236.05258 amu	235.86769 amu

In a chemical reaction, there are also mass changes associated with the emission or absorption of energy. Because the energy involved in chemical reactions is so much smaller than that of nuclear reactions, however, these mass changes are completely negligible.

Notice that the products of the nuclear reaction have *less mass* than the reactants. The missing mass is converted to energy. In Chapter 1, we learned that matter is conserved in chemical reactions. In nuclear reactions matter can be converted to energy. The relationship between the amount of matter that is lost and the amount of energy formed is given by Einstein's famous equation relating the two quantities:

$$E = mc^2$$

where E is the energy produced, m is the mass lost, and c is the speed of light. For example, in the fission reaction just shown, we calculate the quantity of energy produced as follows:

$$\begin{aligned} \text{Mass lost } (m) &= 236.05258 \text{ amu} - 235.86769 \text{ amu} \\ &= 0.18489 \text{ amu} \times \frac{1.66054 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \\ &= 3.0702 \times 10^{-28} \text{ kg} \end{aligned}$$

$$\begin{aligned} \text{Energy produced } (E) &= mc^2 \\ &= 3.0702 \times 10^{-28} \text{ kg} (2.9979 \times 10^8 \text{ m/s})^2 \\ &= 2.7593 \times 10^{-11} \text{ J} \end{aligned}$$

The result (2.7593×10^{-11} J) is the energy produced when one nucleus of U-235 undergoes fission. This may not seem like much energy, but it is only the energy produced by the fission of a *single* nucleus. Let's calculate the energy produced *per mole* of U-235 to compare it to a chemical reaction.

$$2.7593 \times 10^{-11} \frac{\text{J}}{\text{U-235 atoms}} \times \frac{6.0221 \times 10^{23} \text{ U-235 atoms}}{1 \text{ mol U-235}}$$

$$= 1.6617 \times 10^{13} \text{ J/mol U-235}$$

The energy produced by the fission of 1 mol of U-235 is about 17 billion kJ. In contrast, a highly exothermic chemical reaction produces 1000 kJ per mole of reactant. Fission produces over a million times more energy per mole than chemical processes.

Mass Defect

We can examine the formation of a stable nucleus from its component particles as a nuclear reaction in which mass is converted to energy. For example, consider the formation of helium-4 from its components:

$2 \frac{1}{1}\text{H} + 2 \frac{1}{0}\text{n}$	\longrightarrow	$\frac{4}{2}\text{He}$
Mass Reactants		Mass Products
$2 \frac{1}{1}\text{H}$	$2(1.00783)$ amu	$\frac{4}{2}\text{He}$
$2 \frac{1}{0}\text{n}$	$2(1.00866)$ amu	4.00260 amu
Total	4.03298 amu	4.00260 amu

A helium-4 atom has less mass than the sum of the masses of its separate components. This difference in mass, known as the **mass defect**, exists in all stable nuclei. The energy corresponding to the mass defect—obtained by substituting the mass defect into the equation $E = mc^2$ —is known as the **nuclear binding energy**, the amount of energy required to break apart the nucleus into its component nucleons.

Although chemists typically report energies in joules, nuclear physicists often use the electron volt (eV) or megaelectron volt (MeV): $1 \text{ MeV} = 1.602 \times 10^{-13} \text{ J}$. Unlike energy in joules, which is usually reported per mole, energy in electron volts is usually reported per nucleus. A particularly useful conversion for calculating and reporting nuclear binding energies is the relationship between amu (mass units) and MeV (energy units).

$$1 \text{ amu} = 931.5 \text{ MeV}$$

A mass defect of 1 amu, when substituted into the equation $E = mc^2$, gives an energy of 931.5 MeV. Using this conversion factor, we can readily calculate the binding energy of the helium nucleus.

$$\begin{aligned} \text{Mass defect} &= 4.03298 \text{ amu} - 4.00260 \text{ amu} \\ &= 0.03038 \text{ amu} \end{aligned}$$

$$\begin{aligned} \text{Nuclear binding energy} &= 0.03038 \text{ amu} \times \frac{931.5 \text{ MeV}}{1 \text{ amu}} \\ &= 28.30 \text{ MeV} \end{aligned}$$

So the binding energy of the helium nucleus is 28.30 MeV. In order to compare the binding energy of one nucleus to that of another, we calculate the *binding energy per nucleon*, which is the nuclear binding energy of a nuclide divided by the number of nucleons in the nuclide. For helium-4, we calculate the binding energy per nucleon as follows:

$$\begin{aligned} \text{Binding energy per nucleon} &= \frac{28.30 \text{ MeV}}{4 \text{ nucleons}} \\ &= 7.075 \text{ MeV per nucleon} \end{aligned}$$

We can calculate the binding energy per nucleon for other nuclides in the same way. For example, the nuclear binding energy of carbon-12 is 7.680 MeV per nucleon. Since the binding energy per nucleon of carbon-12 is greater than that of helium-4, we conclude the carbon-12 nuclide is more *stable* (it has lower potential energy).

The electrons are contained on the left side in the two $\frac{1}{1}\text{H}$, and on the right side in $\frac{4}{2}\text{He}$. If you write the equation using only two protons on the left ($\frac{1}{1}\text{p}$), you must also add two electrons to the left.

An electron volt is defined as the kinetic energy of an electron that has been accelerated through a potential difference of 1 V.

EXAMPLE 19.7 Mass Defect and Nuclear Binding Energy

Calculate the mass defect and nuclear binding energy per nucleon (in MeV) for C-16, a radioactive isotope of carbon with a mass of 16.014701 amu.

SOLUTION

Calculate the mass defect as the difference between the mass of one C-16 atom and the sum of the masses of 6 hydrogen atoms and 10 neutrons.

$$\begin{aligned}\text{Mass defect} &= 6(\text{mass } {}_1^1\text{H}) + 10(\text{mass } {}_0^1\text{n}) - \text{mass } {}_{16}^1\text{C} \\ &= 6(1.00783 \text{ amu}) + 10(1.00866 \text{ amu}) - 16.014701 \text{ amu} \\ &= 0.118879 \text{ amu}\end{aligned}$$

Calculate the nuclear binding energy by converting the mass defect (in amu) into MeV. (Use 1 amu = 931.5 MeV.)

$$0.118879 \text{ amu} \times \frac{931.5 \text{ MeV}}{\text{amu}} = 110.74 \text{ MeV}$$

Determine the nuclear binding energy per nucleon by dividing by the number of nucleons in the nucleus.

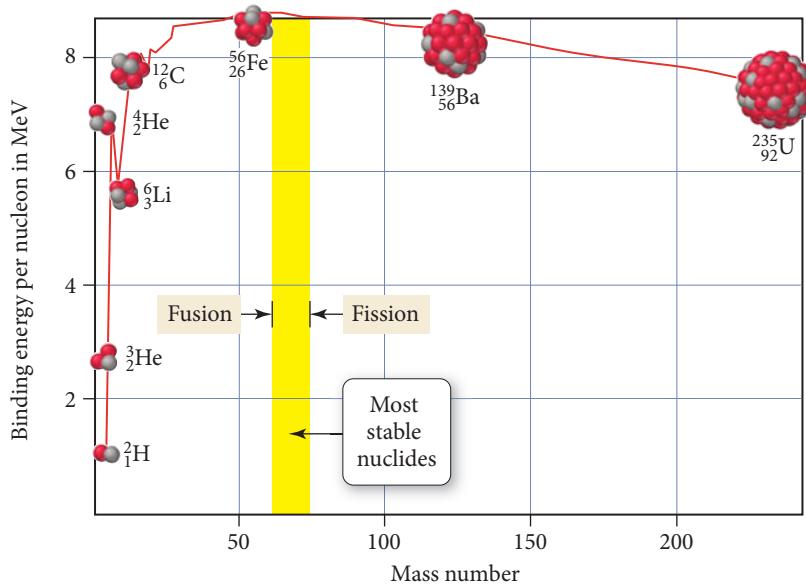
$$\begin{aligned}\text{Nuclear binding energy per nucleon} &= \frac{110.74 \text{ MeV}}{16 \text{ nucleons}} \\ &= 6.921 \text{ MeV/nucleon}\end{aligned}$$

FOR PRACTICE 19.7

Calculate the mass defect and nuclear binding energy per nucleon (in MeV) for U-238, which has a mass of 238.050784 amu.

Figure 19.12 ▼ shows the binding energy per nucleon plotted as a function of mass number (A). The binding energy per nucleon is relatively low for small mass numbers and increases until about $A = 60$, where it reaches a maximum. Nuclides with mass numbers of about 60, therefore, are among the most stable. Beyond $A = 60$, the binding energy per nucleon decreases again. Figure 19.12 illustrates why nuclear fission is a highly exothermic process. When a heavy nucleus, such as U-235, breaks up into smaller nuclei, such as Ba-140 and Kr-93, the binding energy per nucleon increases. This is analogous to a chemical reaction in which weak bonds break and strong bonds form. In both cases, the

The Curve of Binding Energy



▲ FIGURE 19.12 Nuclear Binding Energy per Nucleon The nuclear binding energy per nucleon (a measure of the stability of a nucleus) reaches a maximum at Fe-56. Energy can be obtained either by breaking a heavy nucleus up into lighter ones (fission) or by combining lighter nuclei into heavier ones (fusion).

process is exothermic. Figure 19.12 also reveals that the *combining* of two lighter nuclei (below $A = 60$) to form a heavier nucleus should be exothermic as well. This process is called *nuclear fusion*, which we discuss in the next section of this chapter.

19.9 Nuclear Fusion: The Power of the Sun

Nuclear fission is the *splitting* of a heavy nucleus to form two or more lighter ones. **Nuclear fusion**, by contrast, is the *combination* of two light nuclei to form a heavier one. Both fusion and fission emit large amounts of energy because, as we have just seen, they both form daughter nuclides with greater binding energies per nucleon than the parent nuclides. Nuclear fusion is the energy source of stars, including our sun. In stars, hydrogen atoms fuse together to form helium atoms, emitting energy in the process.

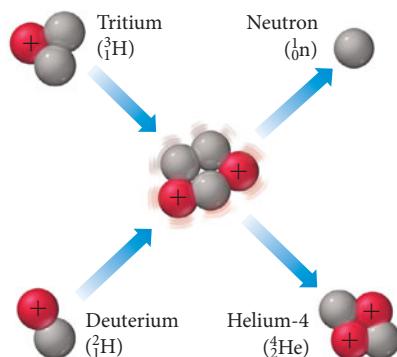
Nuclear fusion is also the basis of modern nuclear weapons called hydrogen bombs. A modern hydrogen bomb has up to 1000 times the explosive force of the first atomic bombs. These bombs employ the fusion reaction shown here:



In this reaction, deuterium (the isotope of hydrogen with one neutron) and tritium (the isotope of hydrogen with two neutrons) combine to form helium-4 and a neutron (Figure 19.13 ▶). Because fusion reactions require two positively charged nuclei (which repel each other) to fuse together, extremely high temperatures are required. In a hydrogen bomb, a small fission bomb is detonated first, creating temperatures high enough for fusion to proceed.

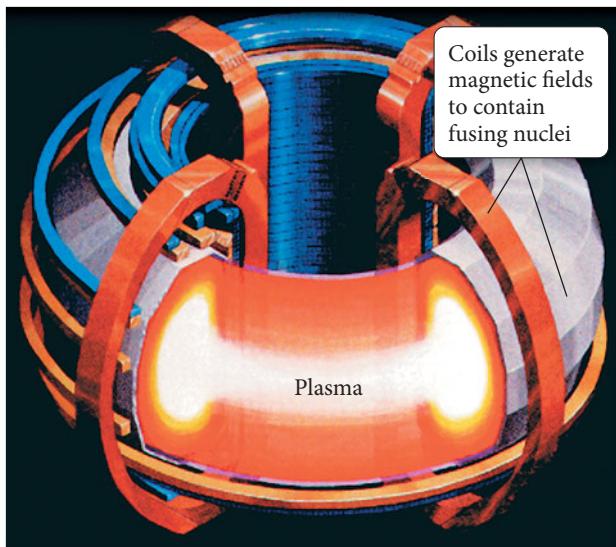
Nuclear fusion has been intensely investigated as a way to produce electricity. Because of the higher energy density—fusion provides about 10 times more energy per gram of fuel than does fission—and because the products of the reaction are less problematic than those of fission, fusion holds promise as a future energy source. However, despite concerted efforts, the generation of electricity by fusion remains elusive. One of the main problems is the high temperature required for fusion to occur—no material can withstand those temperatures. Using powerful magnetic fields or laser beams, scientists have succeeded in compressing and heating nuclei to the point where fusion has been initiated and even sustained for brief periods of time (Figure 19.14 ▼). To date, however, the amount of energy generated by fusion reactions has been less than the amount required to get it to occur. After years of spending billions of dollars on fusion research, the U.S. Congress has reduced funding for these projects. Whether fusion will ever be a viable energy source remains uncertain.

Deuterium-Tritium Fusion Reaction



▲ **FIGURE 19.13** A Nuclear Fusion Reaction In this reaction, two heavy isotopes of hydrogen, deuterium (hydrogen-2) and tritium (hydrogen-3), fuse to form helium-4 and a neutron.

Tokamak Fusion Reactor



◀ **FIGURE 19.14** Tokamak Fusion Reactor A tokamak uses powerful magnetic fields to confine nuclear fuel at the enormous temperatures needed for fusion. The high temperatures produce a plasma, a state of matter in which some fraction of the atoms are ionized.

19.10 Nuclear Transmutation and Transuranium Elements

One of the goals of the early chemists of the Middle Ages, who were known as *alchemists*, was the transformation of ordinary metals into gold. Many alchemists hoped to turn low-cost metals, such as lead or tin, into precious metals, and in this way become wealthy. These alchemists were never successful because their attempts were merely chemical—they mixed different metals together or tried to get them to react with other substances in order to turn them into gold. In a chemical reaction, an element retains its identity, so a less valuable metal—such as lead—always remains lead, even when it forms a compound with another element.

Nuclear reactions, by contrast, result in the transformation of one element into another, a process known as **transmutation**. We have already seen how this occurs in radioactive decay, in fission, and in fusion. In addition, other nuclear reactions that transmute elements are possible. For example, in 1919 Ernest Rutherford bombarded nitrogen-17 with alpha particles to form oxygen:



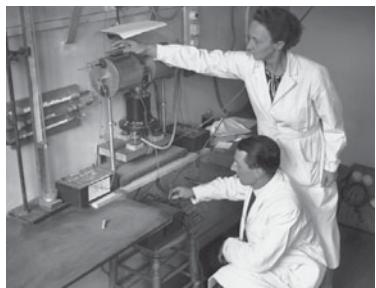
Irène Joliot-Curie (daughter of Marie Curie) and her husband Frédéric bombarded aluminum-27 with alpha particles to form phosphorus:



In the 1930s, scientists began building devices that accelerate particles to high velocities, opening the door to even more possibilities. These devices are generally of two types, the **linear accelerator** and the **cyclotron**.

In a single-stage linear accelerator, a charged particle such as a proton is accelerated in an evacuated tube. The accelerating force is provided by a potential difference (or voltage) between the ends of the tube. In multistage linear accelerators, such as the Stanford Linear Accelerator (SLAC) at Stanford University, a series of tubes of increasing length are connected to a source of alternating voltage, as shown in Figure 19.15 ▶. The voltage alternates in such a way that, as a positively charged particle leaves a particular tube, that tube becomes positively charged, repelling the particle to the next tube. At the same time, the tube that the particle is now approaching becomes negatively charged, pulling the particle toward it. This continues throughout the linear accelerator, allowing the particle to be accelerated to velocities up to 90% of the speed of light. When particles of this speed collide with a target, they produce a shower of subatomic particles that can be studied. For example, researchers using the Stanford Linear Accelerator were awarded the 1990 Nobel Prize in physics for discovering evidence that protons and neutrons were composed of still smaller subatomic particles called quarks.

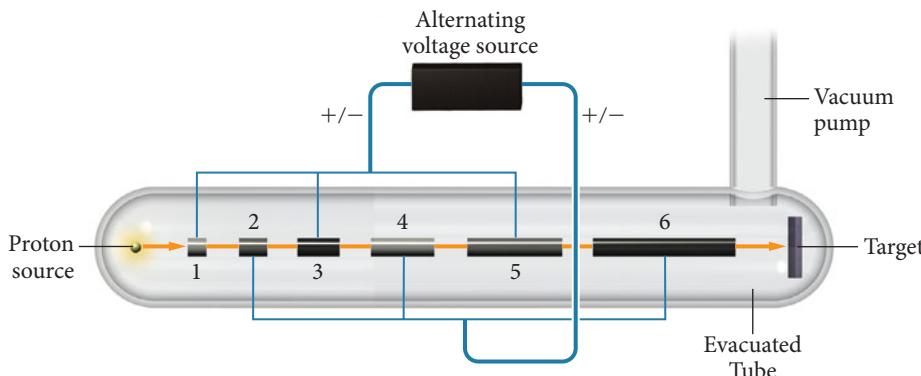
In a cyclotron, a similarly alternating voltage is used to accelerate a charged particle, only this time the alternating voltage is applied between the two semicircular halves of the cyclotron (Figure 19.16 ▷). A charged particle originally in the middle of the two semicircles is accelerated back and forth between them. Additional magnets cause the particle to move in a spiral path. As the charged particle spirals out from the center, it gains speed and eventually exits the cyclotron aimed at the target.

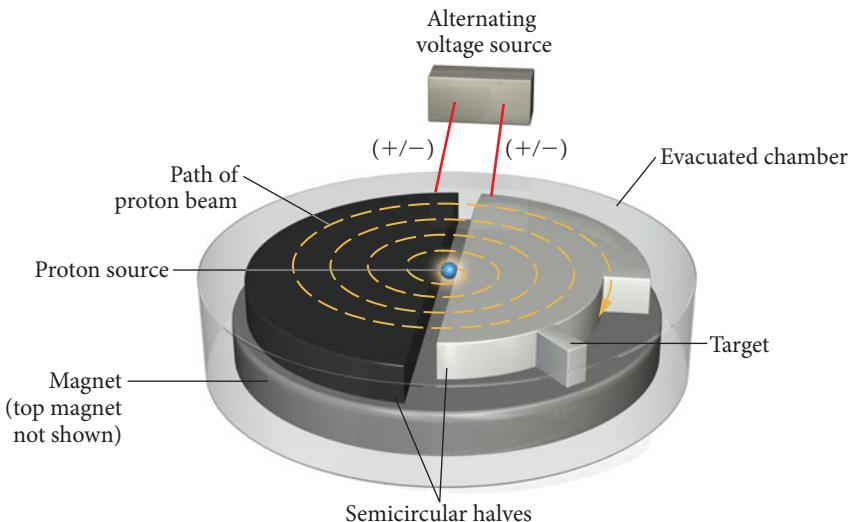


▲ The Joliot-Curies won the 1935 Nobel Prize in Chemistry for their work on nuclear transmutation.

► FIGURE 19.15 The Linear Accelerator

In a multistage linear accelerator, the charge on successive tubes is rapidly alternated in such a way that as a positively charged particle leaves a particular tube, that tube becomes positively charged, repelling the particle toward the next tube. At the same time, the tube that the particle is now approaching becomes negatively charged, pulling the particle toward it. This process repeats through a number of tubes until the particle has been accelerated to a high velocity.





▲ FIGURE 19.16 The Cyclotron In a cyclotron, two semicircular D-shaped structures are subjected to an alternating voltage. A charged particle, starting from a point between the two, is accelerated back and forth between them, while additional magnets cause the particle to move in a spiral path.

With linear accelerators or cyclotrons, all sorts of nuclear transmutations can be achieved. In this way, scientists have made nuclides that don't normally exist in nature. For example, uranium-238 can be made to collide with carbon-12 to form an element with atomic number 98:



This element was named californium (Cf) because it was first produced (by a slightly different nuclear reaction) at the University of California at Berkeley. Many other nuclides with atomic numbers larger than that of uranium have been synthesized since the 1940s. These synthetic elements—called transuranium elements—have been added to the periodic table.



▲ The Stanford Linear Accelerator (top) is located at Stanford University in California. The Fermi National Accelerator Laboratory complex in Batavia, Illinois (bottom), includes two cyclotrons in a figure-8 configuration.

Most synthetic elements are unstable and have very short half-lives. Some exist for only fractions of a second after they are made.

Conceptual Connection 19.4 Nuclear Transformations

Californium-252 is bombarded with a boron-10 nucleus to produce another nuclide and six neutrons. What nuclide forms?

19.11 The Effects of Radiation on Life

As we discussed in Section 19.2, the energy associated with radioactivity can ionize molecules. When radiation ionizes important molecules in living cells, problems can develop. The ingestion of radioactive materials—especially alpha and beta emitters—is particularly dangerous because the radioactivity once inside the body can do even more damage. The effects of radiation can be divided into three different types: acute radiation damage, increased cancer risk, and genetic effects.

Acute Radiation Damage

Acute radiation damage results from exposure to large amounts of radiation in a short period of time. The main sources of this kind of exposure are nuclear bombs and exposed nuclear reactor cores. These high levels of radiation kill large numbers of cells. Rapidly dividing cells, such as those in the immune system and the intestinal lining, are most susceptible. Consequently, people exposed to high levels of radiation have weakened immune systems and a lowered ability to absorb nutrients from food. In milder cases, recovery is possible with time. In more extreme cases, death results, often from infection.

Increased Cancer Risk

Lower doses of radiation over extended periods of time can increase cancer risk. Radiation increases cancer risk because it can damage DNA, the molecules in cells that carry instructions for cell growth and replication. When the DNA within a cell is damaged, the cell normally dies. Occasionally, however, changes in DNA cause cells to grow abnormally and to become cancerous. These cancerous cells grow into tumors that can spread and, in some cases, cause death. Cancer risk increases with increasing radiation exposure. However, cancer is so prevalent and has so many convoluted causes that determining an exact threshold for increased cancer risk from radiation exposure is difficult.

| We explain DNA in more detail in Chapter 21.

Genetic Defects

Another possible effect of radiation exposure is genetic defects in future generations. If radiation damages the DNA of reproductive cells—such as eggs or sperm—then the offspring that develop from those cells may have genetic abnormalities. Genetic defects of this type have been observed in laboratory animals exposed to high levels of radiation. However, such genetic defects—with a clear causal connection to radiation exposure—have yet to be verified in humans, even in studies of Hiroshima survivors.

Measuring Radiation Exposure

We can measure radiation exposure in a number of different ways. One method is to measure the number of decay events to which a person is exposed. The unit used for this type of exposure measurement is the *curie* (Ci), defined as 3.7×10^{10} decay events per second. A person exposed to a curie of radiation from an alpha emitter is bombarded by 3.7×10^{10} alpha particles per second. However, we already know that different kinds of radiation produce different effects. For example, we know that alpha radiation has a much greater ionizing power than beta radiation. Consequently, a certain number of alpha decays occurring within a person's body (due to the ingestion of an alpha emitter) would do more damage than the same number of beta decays. If the alpha emitter and beta emitter were external to the body, however, the radiation from the alpha emitter would largely be stopped by clothing or the skin (due to the low penetrating power of alpha radiation), while the radiation from the beta emitter could penetrate the skin and cause more damage. Consequently, the curie is not an effective measure of how much biological tissue damage the radiation actually does.

A better way to assess radiation exposure is to measure the amount of energy actually absorbed by body tissue. The units used for this type of exposure measurement are the *gray* (Gy), which corresponds to 1 J of energy absorbed per kilogram of body tissue, and the *rad* (for *radiation absorbed dose*), which corresponds to 0.01 Gy.

$$1 \text{ gray (Gy)} = 1 \text{ J/kg body tissue}$$

$$1 \text{ rad} = 0.01 \text{ J/kg body tissue}$$

Although these units measure the actual energy absorbed by bodily tissues, they still do not account for the amount of damage to biological molecules caused by that energy absorption, which differs from one type of radiation to another and from one type of biological tissue to another. For example, when a gamma ray passes through biological tissue, the energy absorbed is spread out over the long distance that the radiation travels through the body, resulting in a low ionization density within the tissue. When an alpha particle passes through biological tissue, in contrast, the energy is absorbed over a much shorter distance, resulting in a much higher ionization density. The higher ionization density results in greater damage, even though the amount of energy absorbed by the tissue might be the same.

Consequently, a correction factor, called the **biological effectiveness factor**, or **RBE** (for *Relative Biological Effectiveness*), is usually multiplied by the dose in rads to obtain the dose in a unit called the **rem** for *roentgen equivalent man*.

$$\text{Dose in rads} \times \text{biological effectiveness factor} = \text{dose in rems}$$

The biological effectiveness factor for alpha radiation, for example, is much higher than that for gamma radiation.

A *roentgen* is defined as the amount of radiation that produces 2.58×10^{-1} C of charge per kg of air.

TABLE 19.4 Exposure by Source for Persons Living in the United States

Source	Dose
Natural Radiation	
A 5-hour jet airplane ride	2.5 mrem/trip (0.5 mrem/hr at 39,000 feet) (whole body dose)
Cosmic radiation from outer space	27 mrem/yr (whole body dose)
Terrestrial radiation	28 mrem/yr (whole body dose)
Natural radionuclides in the body	35 mrem/yr (whole body dose)
Radon gas	200 mrem/yr (lung dose)
Diagnostic Medical Procedures	
Chest X-ray	8 mrem (whole body dose)
Dental X-rays (panoramic)	30 mrem (skin dose)
Dental X-rays (two bitewings)	80 mrem (skin dose)
Mammogram	138 mrem per image
Barium enema (X-ray portion only)	406 mrem (bone marrow dose)
Upper gastrointestinal tract test	244 mrem (X-ray portion only) (bone marrow dose)
Thallium heart scan	500 mrem (whole body dose)
Consumer Products	
Building materials	3.5 mrem/year (whole body dose)
Luminous watches (H-3 and Pm-147)	0.04–0.1 mrem/year (whole body dose)
Tobacco products (to smokers of 30 cigarettes per day)	16,000 mrem/year (bronchial epithelial dose)

Source: Department of Health and Human Services, National Institutes of Health.

On average, each of us is exposed to approximately 310 mrem of radiation per year from natural sources shown in Table 19.4. The majority of this exposure comes from radon, one of the products in the uranium decay series. As you can see from Table 19.4, however, some medical procedures also involve exposure levels similar to those received from natural sources. The increased use of computed tomography (CT) scans over the last decade—which have associated exposures of 200–1600 mrem—has raised some concerns about the overuse of that technology in medicine.

It takes much more than the average natural radiation dose or the dose from a medical diagnostic procedure to produce significant health effects in humans. The first measurable effect, a decreased white blood cell count, occurs at instantaneous exposures of approximately 20 rem (Table 19.5). Exposures of 100 rem produce a definite increase in cancer risk, and exposures of over 500 rem often result in death.

The SI unit that corresponds to the rem is the sievert (Sv). However, the rem is still commonly used in the United States. The conversion factor is 1 rem = 0.01 Sv.

TABLE 19.5 Effects of Instantaneous Radiation Exposure

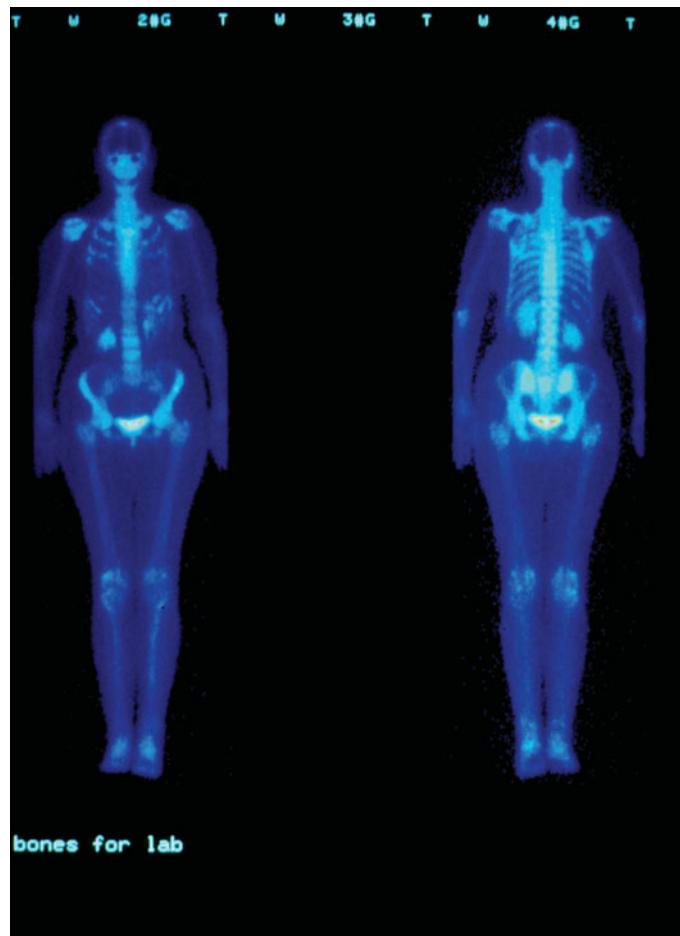
Approximate Dose (rem)	Probable Outcome
20–100	Decreased white blood cell count; possible increase in cancer risk
100–400	Radiation sickness including vomiting and diarrhea; skin lesions; increase in cancer risk
500	Death (often within 2 months)
1000	Death (often within 2 weeks)
2000	Death (within hours)

Conceptual Connection 19.5 Radiation Exposure

Suppose a person ingests equal amounts of two nuclides, both of which are beta emitters (of roughly equal energy). Nuclide A has a half-life of 8.5 hours and Nuclide B has a half-life of 15.0 hours. Both nuclides are eliminated from the body within 24 hours of ingestion. Which of the two nuclides produces the greater radiation exposure?

19.12 Radioactivity in Medicine and Other Applications

Radioactivity is often perceived as dangerous; however, it is also immensely useful to physicians in the diagnosis and treatment of disease and has numerous other valuable applications. The use of radioactivity in medicine can be broadly divided into *diagnostic techniques* (which diagnose disease) and *therapeutic techniques* (which treat disease).



▲ FIGURE 19.17 A Bone Scan These images, front and rear views of the human body, were created by the gamma ray emissions of Tc-99m. Such scans are often used to locate cancer that has metastasized (spread) to the bones from a primary tumor elsewhere.

Diagnosis in Medicine

The use of radioactivity in diagnosis usually involves a **radiotracer**, a radioactive nuclide attached to a compound or introduced into a mixture in order to track the movement of the compound or mixture within the body. Tracers are useful in the diagnosis of disease because of two main factors: (1) the sensitivity with which radioactivity can be detected, and (2) the identical chemical behavior of a radioactive nucleus and its nonradioactive counterpart. For example, the thyroid gland naturally concentrates iodine. When a patient is given small amounts of iodine-131 (a radioactive isotope of iodine), the radioactive iodine accumulates in the thyroid, just as nonradioactive iodine does. However, the radioactive iodine emits radiation, which can then be detected with great sensitivity and used to measure the rate of iodine uptake by the thyroid, and thus to image the gland.

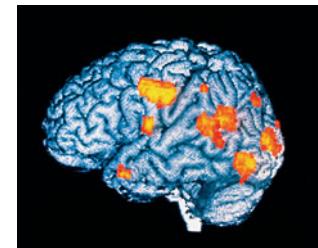
Since different elements are taken up preferentially by different organs or tissues, various radiotracers are used to monitor metabolic activity and image a variety of organs and structures, including the kidneys, heart, brain, gallbladder, bones, and arteries, as shown in Table 19.6. Radiotracers can also be employed to locate infections or cancers within the body. To locate an infection, antibodies are labeled (or tagged) with a radioactive nuclide, such as technetium-99m (where “m” means metastable), and administered to the patient. The tagged antibodies aggregate at the infected site, as described in Section 19.1. Cancerous tumors can be detected because they naturally concentrate phosphorus. When a patient is given phosphorus-32 (a radioactive isotope of phosphorus) or a phosphate compound incorporating another radioactive isotope such as Tc-99m, the tumors concentrate the radioactive substance and become sources of radioactivity that can be detected (Figure 19.17 ◀).

A specialized imaging technique known as **positron emission tomography (PET)** employs positron-emitting nuclides, such as fluorine-18, synthesized in cyclotrons. The fluorine-18 is attached to a metabolically active substance such as glucose and administered to the patient. As the glucose travels through the bloodstream and to the heart and brain, it carries the radioactive fluorine, which decays with a half-life of just under 2 hours. When a fluorine-18 nuclide decays, it emits a positron that immediately combines with any

TABLE 19.6 Common Radiotracers

Nuclide	Type of Emission	Half-Life	Part of Body Studied
Technetium-99m	Gamma (primarily)	6.01 hours	Various organs, bones
Iodine-131	Beta	8.0 days	Thyroid
Iron-59	Beta	44.5 days	Blood, spleen
Thallium-201	Electron capture	3.05 days	Heart
Fluorine-18	Positron emission	1.83 hours	PET studies of heart, brain
Phosphorus-32	Beta	14.3 days	Tumors in various organs

nearby electrons. Since a positron and an electron are antiparticles, they annihilate one other, producing two gamma rays that travel in exactly opposing directions. The gamma rays can be detected by an array of detectors that can locate the point of origin of the rays with great accuracy. The result is a set of highly detailed images that show both the rate of glucose metabolism and structural features of the imaged organ (Figure 19.18 ▶).



▲ FIGURE 19.18 A PET Scan The colored areas indicate regions of high metabolic activity in the brain of a schizophrenic patient experiencing hallucinations.

Radiotherapy in Medicine

Because radiation kills cells and is particularly effective at killing rapidly dividing cells, it is often used as a therapy for cancer (cancer cells reproduce much faster than normal cells). Gamma rays are focused on internal tumors to kill them. The gamma ray beam is usually moved in a circular path around the tumor (Figure 19.19 ▼), maximizing the exposure of the tumor while minimizing the exposure of the surrounding healthy tissue. Nonetheless, cancer patients receiving such treatment usually develop the symptoms of radiation sickness, which include vomiting, skin burns, and hair loss.

You may wonder why radiation—which is known to cause cancer—is also used to treat cancer. The answer lies in risk analysis. A cancer patient is normally exposed to radiation doses of about 100 rem. Such a dose increases cancer risk by about 1%. However, if the patient has a 100% chance of dying from the cancer that he already has, such a risk becomes acceptable, especially since there is a significant chance of curing the cancer.



▲ FIGURE 19.19 Radiotherapy for Cancer This treatment involves exposing a malignant tumor to gamma rays generated by nuclides such as cobalt-60. The beam is moved in a circular pattern around the tumor to maximize exposure of the tumor to radiation while minimizing the exposure of healthy tissues.

Other Applications

Radioactivity is often used to kill microorganisms. For example, physicians use radiation to sterilize medical devices that are to be surgically implanted. The radiation kills bacteria that might otherwise lead to infection. Similarly, radiation is used to kill bacteria and parasites in foods. Like the pasteurization of milk, the irradiation of foods makes them safer to consume and gives them a longer shelf life (Figure 19.20 ▶). The irradiation of raw meat and poultry kills *E. coli* and *Salmonella*, bacteria that can lead to serious illness and even death when consumed. The irradiation of food does not, however, make the food itself radioactive, nor does it decrease the nutritional value of the food. In the United States, the irradiation of many different types of foods—including beef, poultry, potatoes, flour, and fruit—has been approved by the U.S. Food and Drug Administration (FDA) and the U.S. Department of Agriculture (USDA).

Radioactivity is also used to control the populations of harmful insects. For example, fruit flies can be raised in large numbers in captivity and sterilized with radiation. When these fruit flies are released, they mate with wild fruit flies but do not produce offspring. The efforts of the wild fruit flies, which might otherwise lead to reproduction, are wasted and the next generation of flies is smaller than it would otherwise have been. Similar strategies have been employed to control the populations of disease-carrying mosquitoes.



◀ FIGURE 19.20 Irradiation of Food Irradiation kills microbes that cause food to decay, allowing for longer and safer storage. The food is not made radioactive and its properties are unchanged in the process. These strawberries were picked at the same time, but those on the bottom were irradiated before storage.

CHAPTER IN REVIEW

Self Assessment Quiz

- Q1.** What daughter nuclide forms when polonium-214 undergoes alpha decay?
 a) $^{218}_{86}\text{Rn}$ b) $^{214}_{85}\text{At}$ c) $^{214}_{83}\text{Bi}$ d) $^{210}_{82}\text{Pb}$
- Q2.** Which nuclear equation accurately represents the beta decay of Xe-133?
 a) $^{133}_{54}\text{Xe} \rightarrow ^{133}_{55}\text{Cs} + {}_0^-e$
 b) $^{133}_{54}\text{Xe} \rightarrow ^{133}_{53}\text{I} + {}_0^-e$
 c) $^{133}_{54}\text{Xe} + {}_0^-e \rightarrow ^{133}_{53}\text{I}$
 d) $^{133}_{54}\text{Xe} \rightarrow ^{129}_{52}\text{Cs} + {}_2^4\text{He}$
- Q3.** Which nuclide is most likely to undergo beta decay?
 a) Si-22 b) Rb-91
 c) Ar-35 d) Co-52
- Q4.** Which form of radioactive decay would you be most likely to detect if it were happening in the room next to the one you are currently in?
 a) alpha b) beta
 c) gamma d) positron emission
- Q5.** The chart below shows the mass of a decaying nuclide versus time. What is the half-life of the decay?
-
- | Time (min) | Mass (g) |
|------------|----------|
| 0 | 25 |
| 20 | 17 |
| 40 | 11 |
| 60 | 7 |
| 80 | 5 |
| 100 | 3.5 |
| 120 | 2.5 |
- a) 15 min b) 25 min
 c) 35 min d) 70 min
- Q6.** Iron-59 is a beta emitter with a half-life of 44.5 days. If a sample initially contains 132 mg of iron-59, how much iron-59 is left in the sample after 265 days?
 a) 0.00 mg b) 2.13 mg
 c) 33.2 mg d) 66.0 mg
- Q7.** An artifact has a carbon-14 decay rate of 8.55 disintegrations per minute per gram of carbon ($8.55 \text{ dis/min} \cdot \text{g C}$). Living organisms have carbon-14 decay rate of 15.3 $\text{dis/min} \cdot \text{g C}$. How old is the artifact? (The half-life of carbon-14 is 5730 yr.)
 a) $4.81 \times 10^3 \text{ yr}$ b) $2.10 \times 10^3 \text{ yr}$
 c) $3.20 \times 10^3 \text{ yr}$ d) $1.21 \times 10^{-4} \text{ yr}$
- Q8.** An igneous rock contains a Pb-206/U-238 mass ratio of 0.372. How old is the rock? (U-238 decays into Pb-206 with a half-life of $4.5 \times 10^9 \text{ yr}$.)
 a) $4.50 \times 10^9 \text{ yr}$ b) $6.42 \times 10^9 \text{ yr}$
 c) $2.05 \times 10^9 \text{ yr}$ d) $2.32 \times 10^9 \text{ yr}$
- Q9.** Calculate the nuclear binding energy per nucleon for cobalt-59, the only stable isotope of cobalt. The mass of cobalt-59 is 58.933198 amu. (The mass of H_1^1 is 1.00783 amu, and the mass of a neutron is 1.00866 amu.)
 a) 517.3 MeV b) 8.768 MeV
 c) 19.16 MeV d) $1.011 \times 10^{-5} \text{ MeV}$
- Q10.** Which problem is not associated with nuclear power generation?
 a) danger of overheated nuclear core
 b) waste disposal
 c) global warming
 d) none of the above (All of the above are problems associated with nuclear power generation.)

Answers: 1. (d) 2. (a) 3. (b) 4. (c) 5. (c) 6. (b) 7. (a) 8. (d) 9. (b) 10. (c)

Key Terms

Section 19.1

radioactivity (911)
 radioactive (912)

Section 19.2

phosphorescence (912)

Section 19.3

nuclide (913)
 alpha (α) decay (914)

alpha (α) particle (914)

nuclear equation (914)

ionizing power (915)

penetrating power (915)

beta (β) decay (915)

beta (β) particle (915)

gamma (γ) ray emission (915)

gamma (γ) ray (915)

positron emission (916)

positron (916)

electron capture (916)

Section 19.4

strong force (918)

nucleons (918)

magic numbers (920)

Section 19.5

film-badge dosimeter (920)

Geiger-Müller counter (920)
scintillation counter (920)

Section 19.6

radiometric dating (924)
radiocarbon dating (924)

Section 19.7

nuclear fission (928)
chain reaction (929)
critical mass (929)

Section 19.8

mass defect (933)
nuclear binding energy (933)

Section 19.9

nuclear fusion (935)

Section 19.10

transmutation (936)
linear accelerator (936)
cyclotron (936)

Section 19.11

biological effectiveness factor (RBE) (938)
rem (938)

Section 19.12

radiotracer (940)
positron emission tomography (PET) (940)

Key Concepts

Diagnosing Appendicitis (19.1)

- ▶ Radioactivity is the emission of subatomic particles or energetic electromagnetic radiation by the nuclei of certain atoms.
- ▶ Because some of these emissions can pass through matter, radioactivity is useful in medicine and many other areas of study.

The Discovery of Radioactivity (19.2)

- ▶ Radioactivity was discovered by Antoine-Henri Becquerel when he found that uranium causes a photographic exposure in the absence of light.
- ▶ Marie Skłodowska Curie later determined that this phenomenon was not unique to uranium, and she began calling the rays that produced the exposure radioactivity. Curie also discovered two new elements, polonium and radium.

Types of Radioactivity (19.3)

- ▶ The major types of natural radioactivity are alpha (α) decay, beta (β) decay, gamma (γ) ray emission, and positron emission.
- ▶ Alpha radiation is helium nuclei. Beta particles are electrons. Gamma rays are electromagnetic radiation of very high energy. Positrons are the antiparticles of electrons.
- ▶ A nucleus may absorb one of its orbital electrons in a process called electron capture.
- ▶ We can represent each radioactive process with a nuclear equation that illustrates how the parent nuclide changes into the daughter nuclide. In a nuclear equation, although the specific types of atoms may not balance, the atomic numbers and mass numbers must.
- ▶ Each type of radioactivity has a different ionizing and penetrating power. These values are inversely related; a particle with a higher ionizing power has a lower penetrating power. Alpha particles are the most massive and they have the highest ionizing power, followed by beta particles and positrons, which are equivalent in their ionizing power. Gamma rays have the lowest ionizing power.

The Valley of Stability: Predicting the Type of Radioactivity (19.4)

- ▶ The stability of a nucleus, and therefore the probability that it will undergo radioactive decay, depends largely on two factors. The first is the ratio of neutrons to protons (N/Z), because neutrons provide a strong force that overcomes the electromagnetic repulsions between the positive protons. This ratio is one for smaller elements, but becomes greater than one for larger elements. The second factor related to nuclei stability is a concept known as magic numbers; certain numbers of nucleons are more stable than others.

Detecting Radioactivity (19.5)

- ▶ Radiation detectors are used to determine the quantity of radioactivity in an area or sample.

- ▶ Film-badge dosimeters utilize photographic film for that purpose; such detectors do not provide an instantaneous response.
- ▶ Two detectors that instantly register the amount of radiation are the Geiger-Müller counter, which uses the ionization of argon by radiation to produce an electrical signal, and the scintillation counter, which uses the emission of light induced by radiation.

The Kinetics of Radioactive Decay and Radiometric Dating (19.6)

- ▶ All radioactive elements decay according to first-order kinetics (Chapter 13); the half-life equation and the integrated rate law for radioactive decay are derived from the first-order rate laws.
- ▶ The kinetics of radioactive decay is used to date objects and artifacts. The age of materials that were once part of living organisms is measured by carbon-14 dating. The age of ancient rocks and even Earth itself is determined by uranium/lead dating.

The Discovery of Fission: The Atomic Bomb and Nuclear Power (19.7)

- ▶ Fission is the splitting of an atom, such as uranium-235, into two atoms of lesser atomic weight.
- ▶ Because the fission of one uranium-235 atom releases enormous amounts of energy and produces neutrons that can split other uranium-235 atoms, the energy from these collective reactions can be harnessed in an atomic bomb or nuclear reactor.
- ▶ Nuclear power produces no air pollution and requires little mass to release lots of energy; however, there is always a danger of accidents, and it is difficult to dispose of nuclear waste.

Converting Mass to Energy: Mass Defect and Nuclear Binding Energy (19.8)

- ▶ In a nuclear fission reaction, mass is converted into energy.
- ▶ The difference in mass between a nuclide and the individual protons and neutrons that compose it is called the mass defect, and the corresponding energy, calculated from Einstein's equation $E = mc^2$, is the nuclear binding energy.
- ▶ The stability of a nucleus is determined by the binding energy per nucleon, which increases up to mass number 60 and then decreases.

Nuclear Fusion: The Power of the Sun (19.9)

- ▶ Stars produce their energy by a process that is the opposite of fission: nuclear fusion, the combination of two light nuclei to form a heavier one.
- ▶ Modern nuclear weapons employ fusion. Although fusion has been examined as a possible method to produce electricity, experiments with hydrogen fusion have been more costly than productive.

Nuclear Transmutation and Transuranium Elements (19.10)

- Nuclear transmutation, the changing of one element to another element, has been used to create the transuranium elements, elements with atomic numbers greater than that of uranium.
- Two devices are most commonly used to accelerate particles to the high speeds necessary for transmutation reactions: the linear accelerator and the cyclotron. Both use alternating voltage to propel particles by electromagnetic forces.

The Effects of Radiation on Life (19.11)

- The effects of radiation can be grouped into three categories. Acute radiation damage is caused by a large exposure to radiation for a short period of time. Lower radiation exposures may result

in increased cancer risk because of damage to DNA. Genetic defects are caused by damage to the DNA of reproductive cells.

- The most effective unit of measurement for the amount of radiation absorbed is the rem, which takes into account the different penetrating and ionizing powers of the various types of radiation.

Radioactivity in Medicine (19.12)

- Radioactivity is central to the diagnosis of medical problems by means of radiotracers and positron emission tomography (PET). Both of these techniques can provide data about the appearance and metabolic activity of an organ, or help locate a tumor.
- Radiation is also used to treat cancer because it kills cells. Radiation can also be used to kill bacteria in foods and to control harmful insect populations.

Key Equations and Relationships

The First-Order Rate Law (19.6)

$$\text{Rate} = kN$$

The Half-Life Equation (19.6)

$$t_{1/2} = \frac{0.693}{k} \quad k = \text{rate constant}$$

The Integrated Rate Law (19.6)

$$\ln \frac{N_t}{N_0} = -kt \quad N_t = \text{number of radioactive nuclei at time } t$$

N_0 = initial number of radioactive nuclei

Einstein's Energy-Mass Equation (19.8)

$$E = mc^2$$

Key Learning Outcomes

Chapter Objectives	Assessment
Writing Nuclear Equations for Alpha Decay (19.3) 	Example 19.1 For Practice 19.1 Exercises 31–36
Writing Nuclear Equations for Beta Decay, Positron Emission, and Electron Capture (19.3)	Example 19.2 For Practice 19.2 For More Practice 19.2 Exercises 31–36
Predicting the Type of Radioactive Decay (19.4)	Example 19.3 For Practice 19.3 Exercises 41, 42
Using Radioactive Decay Kinetics (19.6)	Example 19.4 For Practice 19.4 Exercises 45–52
Using Radiocarbon Dating (19.6) 	Example 19.5 For Practice 19.5 Exercises 53, 54
Using Uranium/Lead Dating to Estimate the Age of a Rock (19.6)	Example 19.6 For Practice 19.6 Exercises 55, 56
Determining the Mass Defect and Nuclear Binding Energy (19.8)	Example 19.7 For Practice 19.7 Exercises 65–72

EXERCISES

Review Questions

1. What is radioactivity? Who discovered it? How was it discovered?
2. Explain Marie Curie's role in the discovery of radioactivity.
3. Define A , Z , and X in the following notation used to specify a nuclide: ${}^A_Z X$.
4. Use the notation from Question 3 to write symbols for a proton, a neutron, and an electron.
5. What is an alpha particle? What happens to the mass number and atomic number of a nuclide that emits an alpha particle?
6. What is a beta particle? What happens to the mass number and atomic number of a nuclide that emits a beta particle?
7. What is a gamma ray? What happens to the mass number and atomic number of a nuclide that emits a gamma ray?
8. What is a positron? What happens to the mass number and atomic number of a nuclide that emits a positron?
9. Describe the process of electron capture. What happens to the mass number and atomic number of a nuclide that undergoes electron capture?
10. Rank alpha particles, beta particles, positrons, and gamma rays in terms of: (a) increasing ionizing power; (b) increasing penetrating power.
11. Explain why the ratio of neutrons to protons (N/Z) is important in determining nuclear stability. How can you use the N/Z ratio of a nuclide to predict the kind of radioactive decay that it might undergo?
12. What are magic numbers? How are they important in determining the stability of a nuclide?
13. Describe the basic way that each device detects radioactivity: (a) film-badge dosimeter; (b) Geiger-Müller counter; and (c) scintillation counter.
14. Explain the concept of half-life with respect to radioactive nuclides. What rate law is characteristic of radioactivity?
15. Explain the main concepts behind the technique of radiocarbon dating. How can radiocarbon dating be corrected for changes in atmospheric concentrations of C-14? What range of ages can be reliably determined by C-14 dating?
16. How is the uranium to lead ratio in a rock used to estimate its age? How does this dating technique provide an estimate for Earth's age? How old is Earth according to this dating method?
17. Describe fission. Include the concepts of chain reaction and critical mass in your description. How and by whom was fission discovered? Explain how fission can be used to generate electricity.
18. What was the Manhattan Project? Briefly describe its development and culmination.
19. Describe the advantages and disadvantages of using fission to generate electricity.
20. The products of a nuclear reaction usually have a different mass than the reactants. Why?
21. Explain the concepts of mass defect and nuclear binding energy. At what mass number does the nuclear binding energy per nucleon peak? What is the significance of this?
22. What is fusion? Why can fusion and fission both produce energy? Explain.
23. What are some of the problems associated with using fusion to generate electricity?
24. Explain transmutation and provide one or two examples.
25. How does a linear accelerator work? For what purpose is it used?
26. Explain the basic principles of cyclotron function.
27. How does radiation affect living organisms?
28. Explain why different kinds of radiation affect biological tissues differently, even though the amount of radiation exposure may be the same.
29. Explain the significance of the biological effectiveness factor in measuring radiation exposure. What types of radiation would you expect to have the highest biological effectiveness factor?
30. Describe some of the medical uses, both in diagnosis and in treatment of disease, of radioactivity.

Problems by Topic

Radioactive Decay and Nuclide Stability

31. Write a nuclear equation for the indicated decay of each nuclide:
 - U-234 (alpha)
 - Th-230 (alpha)
 - Pb-214 (beta)
 - N-13 (positron emission)
 - Cr-51 (electron capture)
32. Write a nuclear equation for the indicated decay of each nuclide:
 - Po-210 (alpha)
 - Ac-227 (beta)
 - Tl-207 (beta)
 - O-15 (positron emission)
 - Pd-103 (electron capture)
33. Write a partial decay series for Th-232 undergoing the sequential decays: α , β , β , α .

34. Write a partial decay series for Rn-220 undergoing the sequential decays: α , β , β , α .
35. Fill in the missing particles in each nuclear equation.
 - ${}_{\text{ }} \longrightarrow {}^{217}_{85}\text{At} + {}^4_2\text{He}$
 - ${}^{241}_{94}\text{Pu} \longrightarrow {}^{241}_{95}\text{Am} + \text{ }_{\text{ }}$
 - ${}^{19}_{11}\text{Na} \longrightarrow {}^{19}_{10}\text{Ne} + \text{ }_{\text{ }}$
 - ${}^{75}_{34}\text{Se} + \text{ }_{\text{ }} \longrightarrow {}^{75}_{33}\text{As}$
36. Fill in the missing particles in each nuclear equation.
 - ${}^{241}_{95}\text{Am} \longrightarrow {}^{237}_{93}\text{Np} + \text{ }_{\text{ }}$
 - ${}_{\text{ }} \longrightarrow {}^{233}_{92}\text{U} + {}^0_{-1}\text{e}$
 - ${}^{237}_{93}\text{Np} \longrightarrow \text{ }_{\text{ }} + {}^4_2\text{He}$
 - ${}^{75}_{35}\text{Br} \longrightarrow \text{ }_{\text{ }} + {}^0_{+1}\text{e}$

- 37.** Determine whether or not each nuclide is likely to be stable. State your reasons.
- Mg-26
 - Ne-25
 - Co-51
 - Te-124
- 38.** Determine whether or not each nuclide is likely to be stable. State your reasons.
- Ti-48
 - Cr-63
 - Sn-102
 - Y-88
- 39.** The first six elements of the first transition series have the following number of stable isotopes:

Element	Number of Stable Isotopes
Sc	1
Ti	5
V	1
Cr	3
Mn	1
Fe	4

Explain why Sc, V, and Mn each has only one stable isotope while the other elements have several.

- 40.** Neon and magnesium each has three stable isotopes while sodium and aluminum each has only one. Explain why this might be so.
- 41.** Predict a likely mode of decay for each unstable nuclide.
- Mo-109
 - Ru-90
 - P-27
 - Rn-196
- 42.** Predict a likely mode of decay for each unstable nuclide.
- Sb-132
 - Te-139
 - Fr-202
 - Ba-123
- 43.** Which one of each pair of nuclides would you expect to have the longer half-life?
- Cs-113 or Cs-125
 - Fe-62 or Fe-70
- 44.** Which one of each pair of nuclides would you expect to have the longer half-life?
- Cs-149 or Cs-139
 - Fe-45 or Fe-52

The Kinetics of Radioactive Decay and Radiometric Dating

- 45.** One of the nuclides in spent nuclear fuel is U-235, an alpha emitter with a half-life of 703 million years. How long will take for the amount of U-235 to reach 10.0% of its initial amount?
- 46.** A patient is given 0.050 mg of technetium-99m, a radioactive isotope with a half-life of about 6.0 hours. How long does it take for the radioactive isotope to decay to 1.0×10^{-3} mg? (Assume no excretion of the nuclide from the body.)
- 47.** A radioactive sample contains 1.55 g of an isotope with a half-life of 3.8 days. What mass of the isotope remains after 5.5 days? (Assume no excretion of the nuclide from the body.)
- 48.** At 8:00 A.M., a patient receives a 58 mg dose of I-131 to obtain an image of her thyroid. If the nuclide has a half-life of 8 days, what mass of the nuclide remains in the patient at 5:00 P.M. the next day?
- 49.** A sample of F-18 has an initial decay rate of 1.5×10^5 /s. How long will it take for the decay rate to fall to 2.5×10^3 /s? (F-18 has a half-life of 1.83 hours.)
- 50.** A sample of Tl-201 has an initial decay rate of 5.88×10^4 /s. How long will it take for the decay rate to fall to 287/s? (Tl-201 has a half-life of 3.042 days.)
- 51.** A wooden boat discovered just south of the Great Pyramid in Egypt has a carbon-14/carbon-12 ratio that is 72.5% of that found in living organisms. How old is the boat?
- 52.** A layer of peat beneath the glacial sediments of the last ice age has a carbon-14/carbon-12 ratio that is 22.8% of that found in living organisms. How long ago was this ice age?
- 53.** An ancient skull has a carbon-14 decay rate of 0.85 disintegrations per minute per gram of carbon (0.85 dis/min · g C). How old is the skull? (Assume that living organisms have a carbon-14 decay rate of 15.3 dis/min · g C and that carbon-14 has a half-life of 5730 yr.)
- 54.** A mammoth skeleton has a carbon-14 decay rate of 0.48 disintegrations per minute per gram of carbon (0.48 dis/min · g C). When did the mammoth live? (Assume that living organisms have a carbon-14 decay rate of 15.3 dis/min · g C and that carbon-14 has a half-life of 5730 yr.)
- 55.** A rock from Australia contains 0.438 g of Pb-206 to every 1.00 g of U-238. Assuming that the rock did not contain any Pb-206 at the time of its formation, how old is the rock?
- 56.** A meteor has a Pb-206:U-238 mass ratio of 0.855:1.00. What is the age of the meteor? (Assume that the meteor did not contain any Pb-206 at the time of its formation.)

Fission, Fusion, and Transmutation

- 57.** Write the nuclear reaction for the neutron-induced fission of U-235 to form Xe-144 and Sr-90. How many neutrons are produced in the reaction?
- 58.** Write the nuclear reaction for the neutron-induced fission of U-235 to produce Te-137 and Zr-97. How many neutrons are produced in the reaction?
- 59.** Write the nuclear equation for the fusion of two H-2 atoms to form He-3 and one neutron.
- 60.** Write the nuclear equation for the fusion of H-3 with H-1 to form He-4.
- 61.** A breeder nuclear reactor is a reactor in which nonfissionable (nonfissile) U-238 is converted into fissionable (fissile) Pu-239. The process involves bombardment of U-238 by neutrons to form U-239, which then undergoes two sequential beta decays. Write nuclear equations for this process.
- 62.** Write the series of nuclear equations to represent the bombardment of Al-27 with a neutron to form a product that subsequently undergoes an alpha decay followed by a beta decay.
- 63.** Rutherfordium-257 was synthesized by bombarding Cf-249 with C-12. Write the nuclear equation for this reaction.
- 64.** Element 107, now named bohrium, was synthesized by German researchers by colliding bismuth-209 with chromium-54 to form a bohrium isotope and one neutron. Write the nuclear equation to represent this reaction.

Energetics of Nuclear Reactions, Mass Defect, and Nuclear Binding Energy

65. If 1.0 g of matter is converted to energy, how much energy is formed?
66. A typical home uses approximately 1.0×10^3 kWh of energy per month. If the energy came from a nuclear reaction, what mass would have to be converted to energy per year to meet the energy needs of the home?
67. Calculate the mass defect and nuclear binding energy per nucleon of each nuclide.
- O-16 (atomic mass = 15.994915 amu)
 - Ni-58 (atomic mass = 57.935346 amu)
 - Xe-129 (atomic mass = 128.904780 amu)
68. Calculate the mass defect and nuclear binding energy per nucleon of each nuclide.
- Li-7 (atomic mass = 7.016003 amu)
 - Ti-48 (atomic mass = 47.947947 amu)
 - Ag-107 (atomic mass = 106.905092 amu)
69. Calculate the quantity of energy produced per gram of U-235 (atomic mass = 235.043922 amu) for the neutron-induced fission of U-235 to form Xe-144 (atomic mass = 143.9385 amu) and Sr-90 (atomic mass = 89.907738 amu) (discussed in Problem 57).
70. Calculate the quantity of energy produced per mole of U-235 (atomic mass = 235.043922 amu) for the neutron-induced fission of U-235 to produce Te-137 (atomic mass = 136.9253 amu) and Zr-97 (atomic mass = 96.910950 amu) (discussed in Problem 58).

71. Calculate the quantity of energy produced per gram of reactant for the fusion of two H-2 (atomic mass = 2.014102 amu) atoms to form He-3 (atomic mass = 3.016029 amu) and one neutron (discussed in Problem 59).

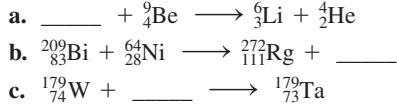
72. Calculate the quantity of energy produced per gram of reactant for the fusion of H-3 (atomic mass = 3.016049 amu) with H-1 (atomic mass = 1.007825 amu) to form He-4 (atomic mass = 4.002603 amu) (discussed in Problem 60).

Effects and Applications of Radioactivity

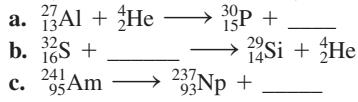
73. A 75 kg human is exposed to 32.8 rad of radiation. How much energy is absorbed by the person's body? Compare this energy to the amount of energy absorbed by the person's body if they jumped from a chair to the floor (assume that the chair is 0.50 m from the ground and that all of the energy from the fall is absorbed by the person).
74. If a 55-gram laboratory mouse is exposed to 20.5 rad of radiation, how much energy is absorbed by the mouse's body?
75. PET studies require fluorine-18, which is produced in a cyclotron and decays with a half-life of 1.83 hours. Assuming that the F-18 can be transported at 60.0 miles/hour, how close must the hospital be to the cyclotron if 65% of the F-18 produced makes it to the hospital?
76. Suppose a patient is given 155 mg of I-131, a beta emitter with a half-life of 8.0 days. Assuming that none of the I-131 is eliminated from the person's body in the first 4.0 hours of treatment, what is the exposure (in Ci) during those first four hours?

Cumulative Problems

77. Complete each nuclear equation and calculate the energy change (in J/mol of reactant) associated with each. (Be-9 = 9.012182 amu, Bi-209 = 208.980384 amu, He-4 = 4.002603 amu, Li-6 = 6.015122 amu, Ni-64 = 63.927969 amu, Rg-272 = 272.1535 amu, Ta-179 = 178.94593 amu, and W-179 = 178.94707 amu).



78. Complete each nuclear equation and calculate the energy change (in J/mol of reactant) associated with each. (Al-27 = 26.981538 amu, Am-241 = 241.056822 amu, He-4 = 4.002603 amu, Np-237 = 237.048166 amu, P-30 = 29.981801 amu, S-32 = 31.972071 amu, and Si-29 = 28.976495 amu).



79. Write the nuclear equation for the most likely mode of decay for each unstable nuclide:

- Ru-114
- Ra-216
- Zn-58
- Ne-31

80. Write the nuclear equation for the most likely mode of decay for each unstable nuclide:

- Kr-74
- Th-221
- Ar-44
- Nb-85

81. Bismuth-210 is a beta emitter with a half-life of 5.0 days. If a sample contains 1.2 g of Bi-210 (atomic mass = 209.984105 amu), how many beta emissions occur in 13.5 days? If a person's body intercepts 5.5% of those emissions, to what dose of radiation (in Ci) is the person exposed?

82. Polonium-218 is an alpha emitter with a half-life of 3.0 minutes. If a sample contains 55 mg of Po-218 (atomic mass = 218.008965 amu), how many alpha emissions occur in 25.0 minutes? If the polonium is ingested by a person, to what dose of radiation (in Ci) is the person exposed?

83. Radium-226 (atomic mass = 226.025402 amu) decays to radon-224 (a radioactive gas) with a half-life of 1.6×10^3 years. What volume of radon gas (at 25.0 °C and 1.0 atm) does 25.0 g of radium produce in 5.0 days? (Report your answer to two significant digits.)

84. In one of the neutron-induced fission reactions of U-235 (atomic mass = 235.043922 amu), the products are Ba-140 and Kr-93 (a radioactive gas). What volume of Kr-93 (at 25.0 °C and 1.0 atm) is produced when 1.00 g of U-235 undergoes this fission reaction?

85. When a positron and an electron annihilate one another, the resulting mass is completely converted to energy. Calculate the energy associated with this process in kJ/mol.

86. A typical nuclear reactor produces about 1.0 MW of power per day. What is the minimum rate of mass loss required to produce this much energy?

87. Find the binding energy in an atom of ${}^3\text{He}$, which has a mass of 3.016030 amu.

88. The overall hydrogen burning reaction in stars can be represented as the conversion of four protons to one α particle. Use the data for the mass of H-1 and He-4 to calculate the energy released by this process.
89. The nuclide ^{247}Es can be made by bombardment of ^{238}U in a reaction that emits five neutrons. Identify the bombarding particle.
90. The nuclide ^6Li reacts with ^2H to form two identical particles. Identify the particles.
91. The half-life of ^{238}U is 4.5×10^9 yr. A sample of rock of mass 1.6 g produces 29 dis/s. Assuming all the radioactivity is due to ^{238}U , find the percent by mass of ^{238}U in the rock.
92. The half-life of ^{232}Th is 1.4×10^{10} yr. Find the number of disintegrations per hour emitted by 1.0 mol of ^{232}Th in 1 minute.
93. A 1.50 L gas sample at 745 mm Hg and 25.0 °C contains 3.55% radon-220 by volume. Radon-220 is an alpha-emitter with a half-life of 55.6 s. How many alpha particles are emitted by the gas sample in 5.00 minutes?
94. A 228 mL sample of an aqueous solution contains 2.35% MgCl_2 by mass. Exactly one-half of the magnesium ions are
- Mg-28, a beta emitter with a half-life of 21 hours. What is the decay rate of Mg-28 in the solution after 4.00 days? (Assume a density of 1.02 g/mL for the solution.)
95. When a positron and an electron collide and annihilate each other, two photons of equal energy are produced. Find the wavelength of these photons.
96. The half-life of ^{235}U , an alpha emitter, is 7.1×10^8 yr. Calculate the number of alpha particles emitted by 1.0 mg of this nuclide in 1.0 minute.
97. Given that the energy released in the fusion of two deuterons to a ^3He and a neutron is 3.3 MeV, and in the fusion to tritium and a proton it is 4.0 MeV, calculate the energy change for the process $^3\text{He} + ^1\text{n} \longrightarrow ^3\text{H} + ^1\text{p}$. Suggest an explanation for why this process occurs at much lower temperatures than either of the first two.
98. The nuclide ^{18}F decays by both electron capture and β^+ decay. Find the difference in the energy released by these two processes. The atomic masses are $^{18}\text{F} = 18.000950$ and $^{18}\text{O} = 17.9991598$.

Challenge Problems

99. The space shuttle carries about 72,500 kg of solid aluminum fuel, which is oxidized with ammonium perchlorate according to the reaction shown here:
- $$10 \text{ Al}(s) + 6 \text{ NH}_4\text{ClO}_4(s) \longrightarrow 4 \text{ Al}_2\text{O}_3(s) + 2 \text{ AlCl}_3(s) + 12 \text{ H}_2\text{O}(g) + 3 \text{ N}_2(g)$$
- The space shuttle also carries about 608,000 kg of oxygen (which reacts with hydrogen to form gaseous water).
- Assuming that aluminum and oxygen are the limiting reactants, determine the total energy produced by these fuels. (ΔH_f° for solid ammonium perchlorate is -295 kJ/mol .)
 - Suppose that a future space shuttle is powered by matter-antimatter annihilation. The matter could be normal hydrogen (containing a proton and an electron) and the antimatter could be antihydrogen (containing an antiproton and a positron). What mass of antimatter is required to produce the energy equivalent of the aluminum and oxygen fuel currently carried on the space shuttle?
100. Suppose that an 85.0-gram laboratory animal ingests 10.0 mg of a substance that contained 2.55% by mass Pu-239, an alpha emitter with a half-life of 24,110 years.
- What is the animal's initial radiation exposure in curies?
 - If all of the energy from the emitted alpha particles is absorbed by the animal's tissues, and if the energy of each
- emission is $7.77 \times 10^{-12} \text{ J}$, what is the dose in rads to the animal in the first 4.0 hours following the ingestion of the radioactive material? Assuming a biological effectiveness factor of 20, what is the 4.0-hour dose in rems?
101. In addition to the natural radioactive decay series that begins with U-238 and ends with Pb-206, there are natural radioactive decay series that begin with U-235 and Th-232. Both of these series end with nuclides of Pb. Predict the likely end product of each series and the number of α decay steps that occur.
102. The hydride of an unstable nuclide of a Group IIA metal, $\text{MH}_2(s)$, decays by α -emission. A 0.025 mol sample of the hydride is placed in an evacuated 2.0 L container at 298 K. After 82 minutes, the pressure in the container is 0.55 atm. Find the half-life of the nuclide.
103. The nuclide ^{38}Cl decays by beta emission with a half-life of 40.0 min. A sample of 0.40 mol of H^{38}Cl is placed in a 6.24 L container. After 80.0 min the pressure is 1650 mmHg. What is the temperature of the container?
104. When BF_3 is bombarded with neutrons, the boron undergoes an α decay, but the F is unaffected. A 0.20 mol sample of BF_3 contained in a 3.0 L container at 298 K is bombarded with neutrons until half of the BF_3 has reacted. What is the pressure in the container at 298 K?

Conceptual Problems

105. Closely examine the diagram representing the beta decay of fluorine-21 and draw in the missing nucleus.
-
106. Approximately how many half-lives must pass for the amount of radioactivity in a substance to decrease to below 1% of its initial level?
107. A person is exposed for 3 days to identical amounts of two different nuclides that emit positrons of roughly equal energy. The half-life of nuclide A is 18.5 days and the half-life of nuclide B is 255 days. Which of the two nuclides poses the greater health risk?

- 108.** Identical amounts of two different nuclides, an alpha emitter and a gamma emitter, with roughly equal half-lives are spilled in a building adjacent to your bedroom. Which of the two nuclides poses the greater health threat to you while you sleep in your bed? If you accidentally wander into the building and ingest equal amounts of the two nuclides, which one poses the greater health threat?
- 109.** Drugstores in many areas now carry tablets, under such trade names as Iosat and NoRad, designed to be taken in the event of an accident at a nuclear power plant or a terrorist attack that releases radioactive material. These tablets contain potassium

iodide (KI). Can you explain the nature of the protection that they provide? (*Hint:* see the label in the photo.)



Answers to Conceptual Connections

Alpha and Beta Decay

- 19.1** (c) The arrow labeled *x* represents a decrease of two neutrons and two protons, indicative of alpha decay. The arrow labeled *y* represents a decrease of one neutron and an increase of one proton, indicative of beta decay.

Half-Life

- 19.2** (b) The half-life is the time it takes for the number of nuclei to decay to one-half of their original number.

Half-Life and the Amount of Radioactive Sample

- 19.3** (b) 0.10 mol. The sample loses one-half of the number of moles per half-life; so over the course of four half-lives, the amount falls to 0.10 mol.

Nuclear Transformations

- 19.4** Lawrencium-256

Radiation Exposure

- 19.5** Nuclide A. Because nuclide A has a shorter half-life, more of the nuclides will decay, and therefore produce radiation, before they exit the body.

20

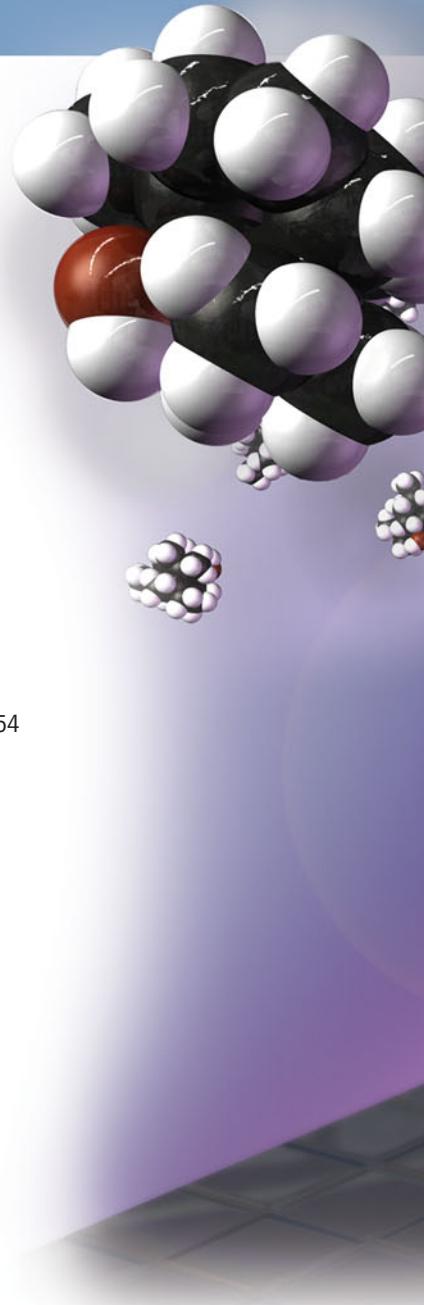
Organic Chemistry

Organic chemistry just now is enough to drive one mad. It gives one the impression of a primeval, tropical forest full of the most remarkable things....

—Friedrich Wöhler (1800–1882)

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ORGANIC CHEMISTRY IS THE STUDY of carbon-containing compounds. Carbon is unique in the sheer number of compounds that it forms. Millions of organic compounds are known, and researchers discover new ones every day. Carbon is also unique in the diversity of compounds that it forms. In most cases, a fixed number of carbon atoms can combine with a fixed number of atoms of another element to form many different compounds. For example, 10 carbon atoms and 22 hydrogen atoms can form 75 distinctly different compounds. With carbon as the backbone, nature can take the same combination of atoms and bond them together in slightly different ways to produce a huge variety of substances. It is not surprising that life is based on the chemistry of carbon because life needs diversity to exist, and organic chemistry is nothing if not diverse. In this chapter, we peer into Friedrich Wöhler's "primeval tropical forest" (see chapter-opening quotation) and discover the most remarkable things.



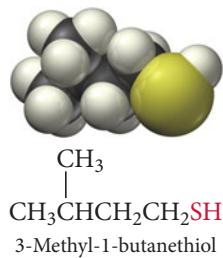
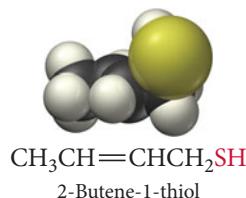


20.1 Fragrances and Odors

Have you ever ridden an elevator with someone wearing too much perfume? Or found yourself too close to a skunk? Or caught a whiff of rotting fish? What causes these fragrances and odors? When we inhale certain molecules called odorants, they bind with olfactory receptors in our noses. This interaction sends a nerve signal to the brain that we experience as a smell. Some smells, such as that of perfume, are pleasant (when not overdone). Other smells, such as that of the skunk or rotting fish, are unpleasant. Our sense of smell helps us identify food, people, and other organisms, and it alerts us to dangers such as polluted air or spoiled food. Smell (olfaction) is one way we probe the environment around us.

Odorants, if they are to reach our noses, must be volatile. However, many volatile substances have no scent at all. Nitrogen, oxygen, water, and carbon dioxide molecules, for example, are constantly passing through our noses, yet they produce no smell because

About half of all men's colognes contain at least some patchouli alcohol ($C_{15}H_{26}O$), an organic compound (pictured here) derived from the patchouli plant. Patchouli alcohol has a pungent, musty, earthy fragrance.



▲ The smell of skunk is due primarily to the molecules shown here.

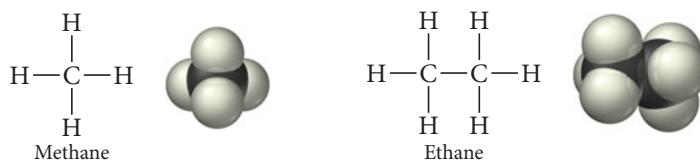
they do not bind to olfactory receptors. Most common smells are caused by **organic molecules**, molecules containing carbon combined with several other elements such as hydrogen, nitrogen, oxygen, and sulfur. Organic molecules are responsible for the smells of roses, vanilla, cinnamon, almond, jasmine, body odor, and rotting fish. When you wander into a rose garden, you experience the sweet smell caused in part by geraniol, an organic compound emitted by roses. Men's colognes often contain patchouli alcohol, an earthy-smelling organic compound extracted from the patchouli plant. If you have been in the vicinity of skunk spray (or have been unfortunate enough to be sprayed yourself), you are familiar with the unpleasant smell of 2-butene-1-thiol and 3-methyl-1-butanethiol, two particularly odiferous compounds present in the secretion that skunks use to defend themselves.

The study of compounds containing carbon combined with one or more of the elements mentioned previously (hydrogen, nitrogen, oxygen, and sulfur), including their properties and their reactions, is known as **organic chemistry**. Besides composing much of what we smell, organic compounds are prevalent in foods, drugs, petroleum products, and pesticides. Organic chemistry is also the basis for living organisms. Life has evolved based on carbon-containing compounds, making organic chemistry of utmost importance to any person interested in understanding living organisms.

20.2 Carbon: Why It Is Unique

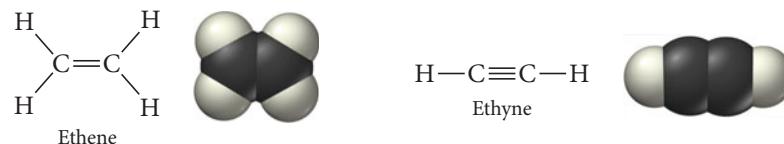
Why did life evolve based on the chemistry of carbon? Why is life not based on some other element? The answer may not be simple, but we know that life—in order to exist—must entail complexity, and carbon chemistry is clearly complex. The number of compounds containing carbon is greater than the number of compounds containing all of the other elements combined. The reasons for carbon's unique and versatile behavior include its ability to form four covalent bonds, its ability to form double and triple bonds, and its tendency to *catenate* (that is, to form chains).

Carbon's Tendency to Form Four Covalent Bonds Carbon—with its four valence electrons—forms four covalent bonds. Consider the Lewis structure and space-filling models of two simple carbon compounds, methane and ethane:



The geometry about a carbon atom forming four single bonds is tetrahedral, as shown in the figure for methane. Carbon's ability to form four bonds, and to form those bonds with a number of different elements, results in the potential to form many different compounds. As you learn to draw structures for organic compounds, always remember to draw carbon with four bonds.

Carbon's Ability to Form Double and Triple Bonds Carbon atoms also form double bonds (trigonal planar geometry) and triple bonds (linear geometry), adding even more diversity to the number of compounds that carbon forms.



In contrast, silicon (the element in the periodic table with properties closest to that of carbon) does not readily form double or triple bonds because the greater size of silicon atoms results in a Si—Si bond that is too long for much overlap between nonhybridized *p* orbitals.



Chemistry in Your Day

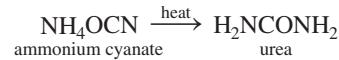
Vitalism and the Perceived Difference between Organic and Inorganic

By the end of the eighteenth century, chemists had learned that compounds could be broadly categorized as either organic or inorganic. Organic compounds come from living things while inorganic compounds come from the nonliving things on Earth. Sugar—obtained from sugarcane or the sugar beet—is a common example of an organic compound. Salt—mined from the ground or extracted from ocean water—is a common example of an inorganic compound.

Organic and inorganic compounds are different, not only in their origin, but also in their properties. Organic compounds are easily decomposed. Sugar, for example, readily decomposes into carbon and water when heated. (Think of the last time you burned something sugary in a pan or in the oven.) Inorganic compounds are more difficult to decompose. Salt decomposes only when heated to very high temperatures. Even more curious to these early chemists was their inability to synthesize a single organic compound in the laboratory. Although they were able to synthesize many inorganic compounds, despite concerted efforts, they were not able to synthesize any organic compounds.

The origin and properties of organic compounds led early chemists to postulate that organic compounds were unique to living organisms. They hypothesized that living organisms contained a *vital force*—a mystical or supernatural power—that allowed them to produce organic compounds. They thought that producing an organic compound outside of a living organism was impossible because the vital force was not present. This belief—which became known as *vitalism*—explained why no chemist had succeeded in synthesizing an organic compound in the laboratory.

An experiment performed in 1828 by German chemist Friedrich Wöhler (1800–1882) marked the beginning of the end of vitalism. Wöhler heated ammonium cyanate (an inorganic compound) and formed urea (an organic compound).

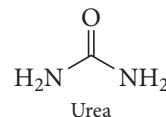


Urea was a known organic compound that had previously been isolated only from urine. Although it was not realized at the time, Wöhler's simple experiment was a key step in opening all of life to scientific investigation. He showed that the compounds composing living organisms—like all compounds—follow scientific laws and can be studied and understood. Today, known organic compounds number in the millions, and modern organic chemistry is a vast field that produces substances as diverse as drugs, petroleum products, and plastics.

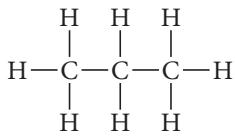


Friedrich Wöhler

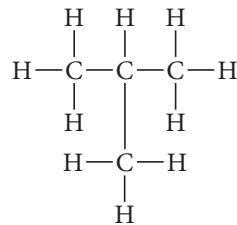
► The synthesis of urea in 1828 by German chemist Friedrich Wöhler marked the beginning of the end for vitalism.



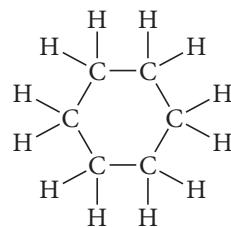
Carbon's Tendency to Catenate Carbon, more than any other element, can bond to itself to form chain, branched, and ring structures.



Propane



Isobutane



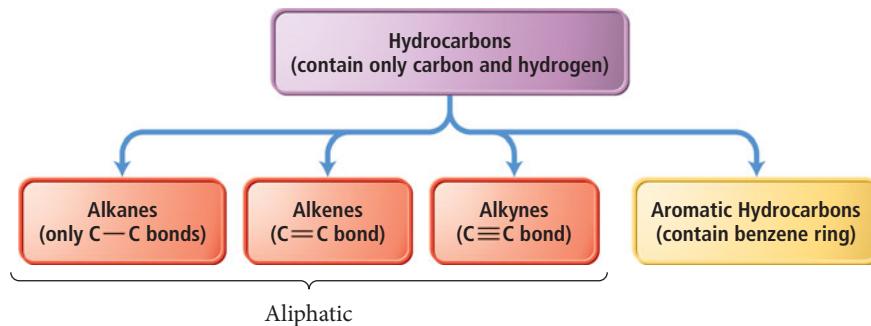
Cyclohexane

Although other elements can form chains, none surpasses carbon at this ability. Silicon, for example, can form chains with itself. However, silicon's affinity for oxygen (the Si—O bond is stronger than the Si—Si bond) coupled with the prevalence of oxygen in our atmosphere means that silicon–silicon chains are readily oxidized to form silicates (the silicon–oxygen compounds that compose a significant proportion of minerals). By contrast, the C—C bond (347 kJ/mol) and the C—O bond (359 kJ/mol) are nearly the same strength, allowing carbon chains to exist relatively peacefully in an oxygen-rich environment. Silicon's affinity for oxygen robs it of the rich diversity that catenation provides to carbon.

20.3 Hydrocarbons: Compounds Containing Only Carbon and Hydrogen

Hydrocarbons—compounds that contain only carbon and hydrogen—are the simplest organic compounds. However, because of the uniqueness of carbon, many different kinds of hydrocarbons exist. We use hydrocarbons as fuels. Candle wax, oil, gasoline, LP gas, and natural gas are all composed of hydrocarbons. Hydrocarbons are also the starting materials in the synthesis of many different consumer products including fabrics, soaps, dyes, cosmetics, drugs, plastic, and rubber.

As shown in Figure 20.1 ▶, we can classify hydrocarbons into four different types: **alkanes**, **alkenes**, **alkynes**, and **aromatic hydrocarbons**. Alkanes, alkenes, and alkynes—also called **aliphatic hydrocarbons**—are differentiated based on the kinds of bonds between carbon atoms. (We discuss aromatic hydrocarbons in detail in Section 20.7.) As shown in Table 20.1, alkanes have only single bonds between carbon atoms, alkenes have a double bond, and alkynes have a triple bond.



► FIGURE 20.1 Four Types of Hydrocarbons

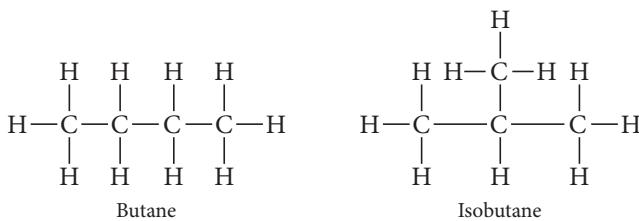
TABLE 20.1 Alkanes, Alkenes, Alkynes

Type of Hydrocarbon	Type of Bonds	Generic Formula*	Example
Alkane	All single	C_nH_{2n+2}	$\begin{array}{c} H & H \\ & \\ H-C & -C-H \\ & \\ H & H \end{array}$ Ethane
Alkenes	One (or more) double	C_nH_{2n}	$\begin{array}{c} H & & H \\ & C = C & \\ H & & H \end{array}$ Ethene
Alkynes	One (or more) triple	C_nH_{2n-2}	$H-C\equiv C-H$ Ethyne

* n is the number of carbon atoms. These formulas apply only to noncyclic structures containing no more than one multiple bond.

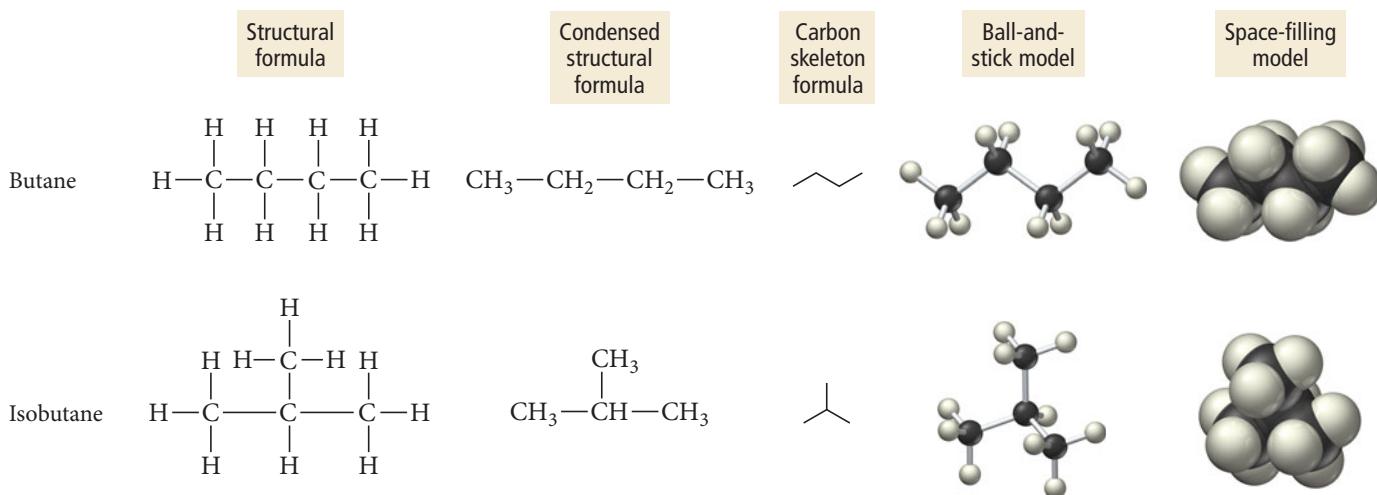
Drawing Hydrocarbon Structures

Throughout this book, we have relied primarily on molecular formulas as the simplest way to represent compounds. In organic chemistry, however, molecular formulas are insufficient because, as we have already discussed, the same atoms can bond together in different ways to form different compounds. For example, consider an alkane with 4 carbon atoms and 10 hydrogen atoms. Two different structures, named butane and isobutane, are possible:



Butane and isobutane are **structural isomers**, molecules with the same molecular formula but different structures. Because of their different structures, they have different properties—indeed they are different compounds. Isomerism is ubiquitous in organic chemistry. Butane has 2 structural isomers. Pentane (C_5H_{12}) has 3, hexane (C_6H_{14}) has 5, and decane ($C_{10}H_{22}$) has 75!

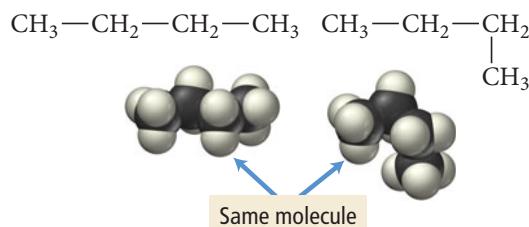
We represent the structure of a particular hydrocarbon with a **structural formula**, a formula that shows not only the numbers of each kind of atoms, but also how the atoms are bonded together. Organic chemists use several different kinds of structural formulas. For example, we can represent butane and isobutane in each of the following ways:



The structural formula shows all of the carbon and hydrogen atoms in the molecule and how they are bonded together. The *condensed structural formula* groups the hydrogen atoms with the carbon atom to which they are bonded. Condensed structural formulas may show some of the bonds (as the previous examples do) or none at all. The condensed structural formula for butane can also be written as $CH_3CH_2CH_2CH_3$. The *carbon skeleton formula* (also called a *line formula*) shows the carbon–carbon bonds only as lines. Each end or bend of a line represents a carbon atom bonded to as many hydrogen atoms as necessary to form a total of four bonds. Carbon skeleton formulas allow us to draw complex structures quickly.

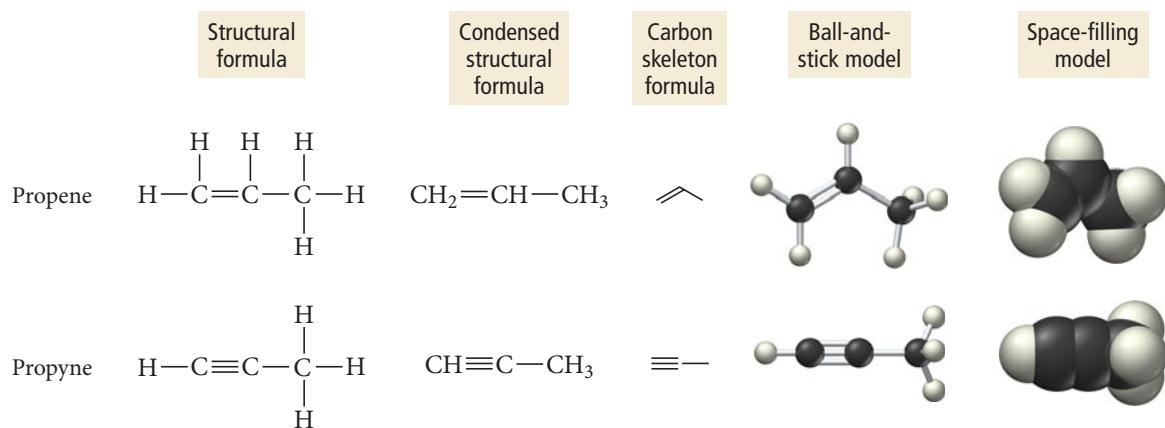
A carbon skeleton formula is called a *line formula* because it uses lines to represent a molecule.

Note that structural formulas are generally not three-dimensional representations of the molecule—as space-filling or ball-and-stick models are—but rather two-dimensional representations that show how atoms are bonded together. As such, the most important feature of a structural formula is the *connectivity* of the atoms, not the exact way the formula is drawn. For example, consider the two condensed structural formulas for butane and the corresponding space-filling models below them:



Since rotation about single bonds is relatively unhindered at room temperature, the two structural formulas are identical, even though they are drawn differently.

We represent double and triple bonds in structural formulas with double or triple lines. For example, we draw the structural formulas for C_3H_6 (propene) and C_3H_4 (propyne) as follows:



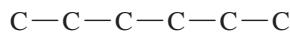
The kind of structural formula we use depends on how much information we want to portray. Example 20.1 illustrates how to write structural formulas for a compound.

EXAMPLE 20.1 Writing Structural Formulas for Hydrocarbons

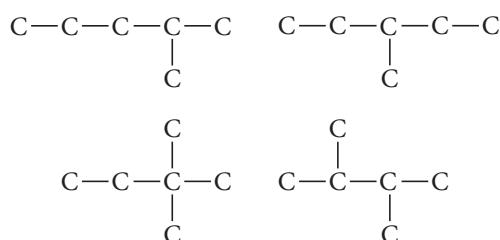
Write the structural formulas and carbon skeleton formulas for the five isomers of C_6H_{14} (hexane).

SOLUTION

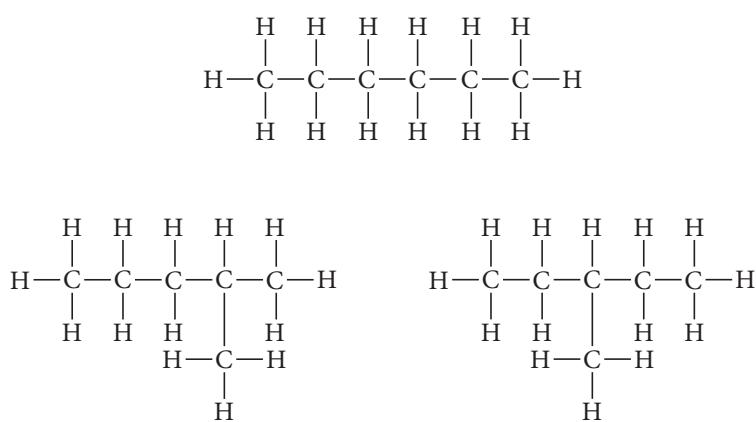
To start, draw the carbon backbone of the straight-chain isomer.

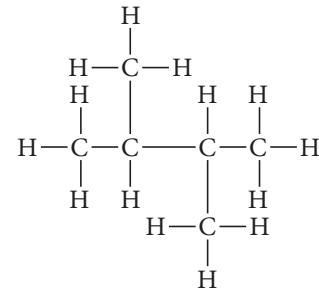
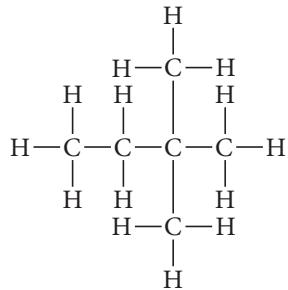


Next, determine the carbon backbone structure of the other isomers by arranging the carbon atoms in four other unique ways.

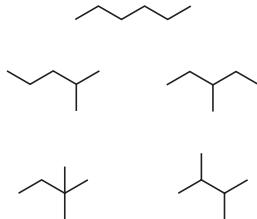


Fill in all the hydrogen atoms so that each carbon forms four bonds.





Write the carbon skeleton formulas by using lines to represent each carbon–carbon bond. Remember that each end or bend represents a carbon atom.

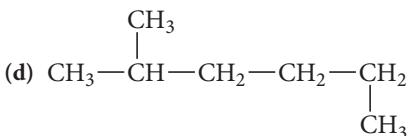
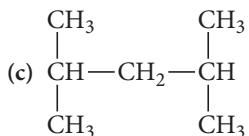
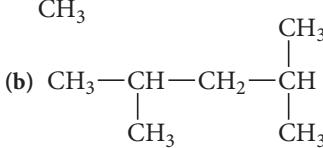
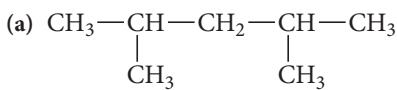


FOR PRACTICE 20.1

Write the structural formulas and carbon skeleton formulas for the three isomers of C_5H_{12} (pentane).

Conceptual Connection 20.1 Organic Structures

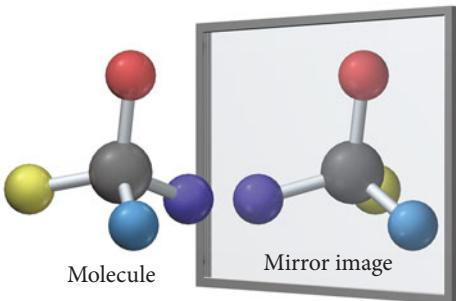
Which structure is an *isomer* of $\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{CH}}}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{CH}}}-\text{CH}_3$ (and not just the same structure)?



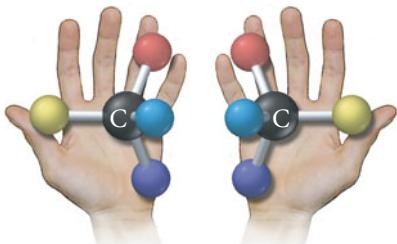
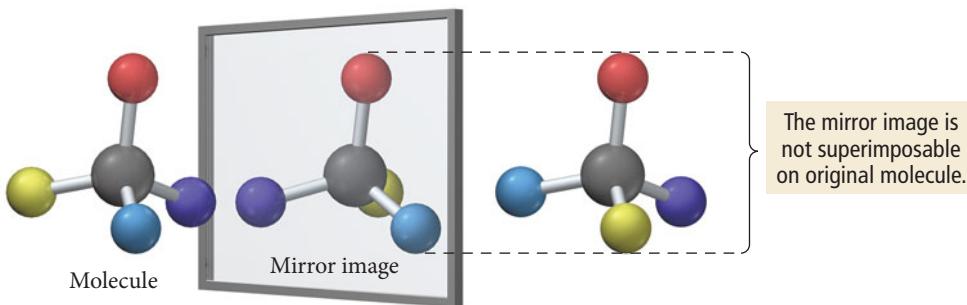
Stereoisomerism and Optical Isomerism

Stereoisomers are molecules in which the atoms have the same connectivity but a different spatial arrangement. We can categorize stereoisomers into two types: geometric (or cis–trans) isomers and optical isomers. We discuss geometric isomers in Section 20.5.

Optical isomers are two molecules that are nonsuperimposable mirror images of one another. Consider the molecule shown here with its mirror image.



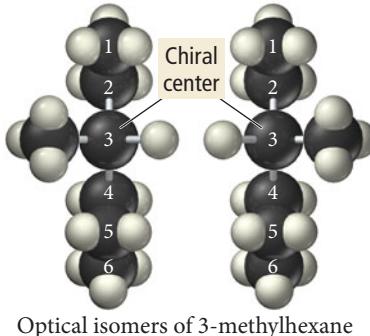
The molecule cannot be superimposed onto its mirror image. If we swing the mirror image around to try to superimpose the two, we find that there is no way to get all four substituent atoms to align together. (A substituent is an atom or group of atoms that is substituted for a hydrogen atom in an organic compound.)



▲ FIGURE 20.2 Mirror Images The left and right hand are nonsuperimposable mirror images, just as are optical isomers.

Optical isomers are similar to your right and left hands (Figure 20.2 ▲). The two are mirror images of one another, but you cannot superimpose one on the other. For this reason, a right-handed glove does not fit on your left hand and vice versa.

Any carbon atom with four different substituents in a tetrahedral arrangement exhibits its optical isomerism. Consider 3-methylhexane:

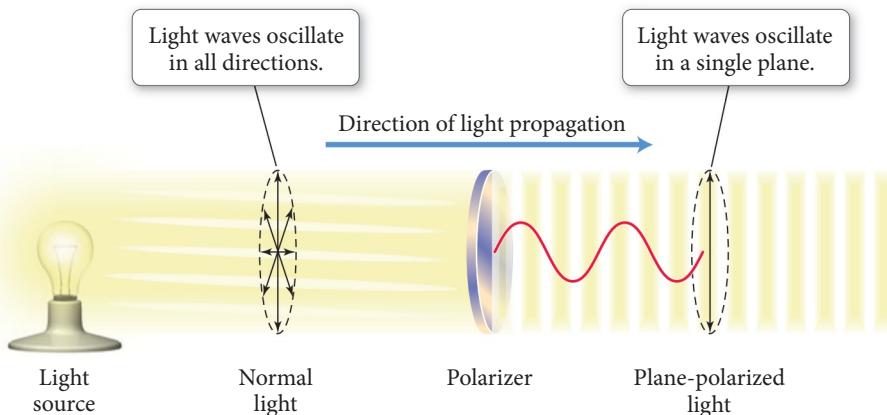


The molecules shown here are nonsuperimposable mirror images and are optical isomers of one other. Optical isomers are also called **enantiomers**. Any molecule, such as 3-methylhexane, that exhibits optical isomerism is said to be **chiral**, from the Greek word *cheir*, which means “hand.” Optical isomerism is important, not only to organic chemistry, but also to biology and biochemistry. Most biological molecules are chiral and usually only one or the other enantiomer is active in biological systems. For example, glucose, the primary fuel of cells, is chiral. Only one of the enantiomers of glucose has that familiar sweet taste and only that enantiomer can fuel our cellular functioning; the other enantiomer is not even metabolized by the body.

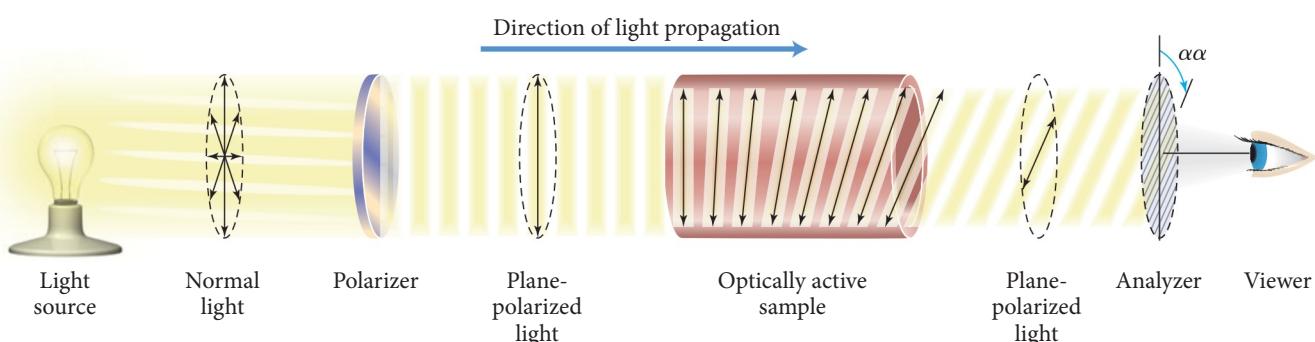
Some of the physical and chemical properties of enantiomers are indistinguishable from one another. For example, both of the optical isomers of 3-methylhexane have identical freezing points, melting points, and densities. However, the properties of enantiomers differ from one another in two important ways: (1) in the direction in which they rotate polarized light and (2) in their chemical behavior in a chiral environment.

Rotation of Polarized Light *Plane-polarized light* is light that is made up of electric field waves that oscillate in only one plane as shown in Figure 20.3 ►. When a beam of plane-polarized light is directed through a sample containing only one of two optical isomers, the plane of polarization of the light is rotated as shown in Figure 20.4 ►. One of the two optical isomers rotates the polarization of the light clockwise and is called the **dextrorotatory** isomer (or the *d* isomer). The other isomer rotates the polarization of the light counterclockwise and is called the **levorotatory** isomer (or the *l* isomer). An equimolar mixture of both optical isomers does not rotate the polarization of light at all and is called a **racemic mixture**.

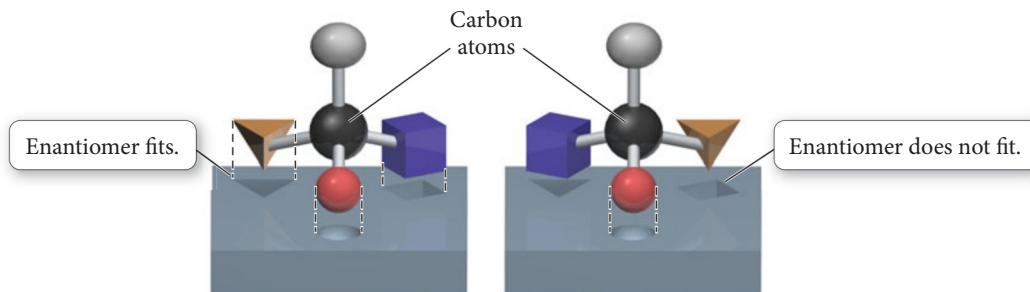
Dextrorotatory means turning clockwise or to the right. Levorotatory means turning counterclockwise or to the left.

**◀ FIGURE 20.3 Plane-Polarized Light**

The electric field of plane-polarized light oscillates in one plane.

**▲ FIGURE 20.4 Rotation of Plane-Polarized Light** Plane-polarized light rotates as it passes through a sample containing only one of two optical isomers.

Chemical Behavior in a Chiral Environment Optical isomers also exhibit different chemical behavior when they are in a chiral environment (a chiral environment is one that is not superimposable on its mirror image). Enzymes are large biological molecules that catalyze reactions in living organisms and provide chiral environments. Consider the following simplified picture of two enantiomers in a chiral environment:



One of the enantiomers fits the template, but the other does not, no matter how it is rotated. In this way, an enzyme is able to catalyze the reaction of one enantiomer because that particular enantiomer fits the “template.” As we have already seen, most biological molecules are chiral and usually only one or the other enantiomer is active in biological systems.

Conceptual Connection 20.2 Optical Isomers

Which molecule exhibits optical isomerism?

- (a) $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{Cl} \\ | \\ \text{Br} \end{array}$ (b) $\begin{array}{c} \text{H} & \text{H} \\ | & | \\ \text{Br}-\text{C} & -\text{C}-\text{H} \\ | & | \\ \text{Cl} & \text{H} \end{array}$ (c) $\begin{array}{c} \text{H} & \text{H} \\ | & | \\ \text{Br}-\text{C} & -\text{C}-\text{Cl} \\ | & | \\ \text{H} & \text{H} \end{array}$ (d) $\begin{array}{c} \text{H} & \text{Cl} \\ | & | \\ \text{Br}-\text{C} & -\text{C}-\text{Cl} \\ | & | \\ \text{H} & \text{H} \end{array}$

20.4 Alkanes: Saturated Hydrocarbons

Alkanes (hydrocarbons containing only single bonds) are often referred to as **saturated hydrocarbons** because they are saturated (loaded to capacity) with hydrogen. The simplest hydrocarbons are methane (CH_4), the main component of natural gas; ethane (C_2H_6), a minority component in natural gas; and propane (C_3H_8), the main component of liquid petroleum (LP) gas.

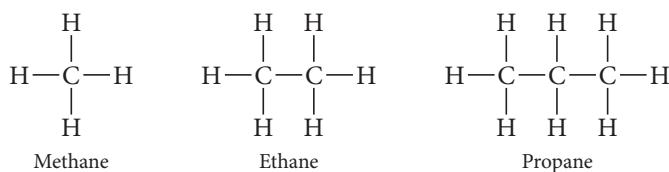
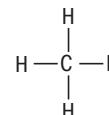
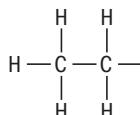
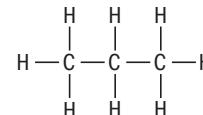
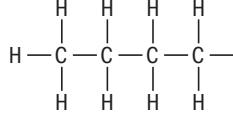
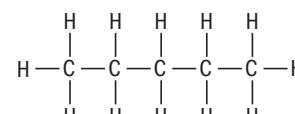


TABLE 20.2 *n*-Alkane Boiling Points

<i>n</i> -Alkane	Boiling Point (°C)
Methane	−161.5
Ethane	−88.6
Propane	−42.1
<i>n</i> -Butane	−0.5
<i>n</i> -Pentane	36.0
<i>n</i> -Hexane	68.7
<i>n</i> -Heptane	98.5
<i>n</i> -Octane	125.6

Alkanes containing four or more carbon atoms may be straight or branched (as we have already seen). The straight-chain isomers are often called normal alkanes, or *n*-alkanes. As the number of carbon atoms increases in the *n*-alkanes, so does their boiling point (as shown in Table 20.2). The increase is due to the increasing dispersion force with increasing molar mass (see Section 11.3). Methane, ethane, propane, and *n*-butane are all gases at room temperature, but the next *n*-alkane in the series, pentane, is a liquid at room temperature. Pentane is a component of gasoline. Table 20.3 summarizes the *n*-alkanes through decane, which contains ten carbon atoms. Like pentane, hexane through decane are all components of gasoline. Table 20.4 summarizes the uses of hydrocarbons.

TABLE 20.3 *n*-Alkanes

<i>n</i>	Name	Molecular Formula $\text{C}_n\text{H}_{2n+2}$	Structural Formula	Condensed Structural Formula
1	Methane	CH_4		CH_4
2	Ethane	C_2H_6		CH_3CH_3
3	Propane	C_3H_8		$\text{CH}_3\text{CH}_2\text{CH}_3$
4	<i>n</i> -Butane	C_4H_{10}		$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
5	<i>n</i> -Pentane	C_5H_{12}		$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

(Continued)

TABLE 20.3 *n*-Alkanes (Continued)

6	<i>n</i> -Hexane	C ₆ H ₁₄		CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃
7	<i>n</i> -Heptane	C ₇ H ₁₆		CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃
8	<i>n</i> -Octane	C ₈ H ₁₈		CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃
9	<i>n</i> -Nonane	C ₉ H ₂₀		CH ₃ CH ₂ CH ₃
10	<i>n</i> -Decane	C ₁₀ H ₂₂		CH ₃ CH ₂ CH ₃

TABLE 20.4 Uses of Hydrocarbons

Number of Carbon Atoms	State	Major Uses
1–4	Gas	Heating fuel, cooking fuel
5–7	Low-boiling liquids	Solvents, gasoline
6–18	Liquids	Gasoline
12–24	Liquids	Jet fuel, portable-stove fuel
18–50	High-boiling liquids	Diesel fuel, lubricants, heating oil
50+	Solids	Petroleum jelly, paraffin wax

Naming Alkanes

Many organic compounds have common names that we can learn only through familiarity. Because of the sheer number of organic compounds, however, we need a systematic method of nomenclature. In this book, we adopt the nomenclature system recommended by the IUPAC (International Union of Pure and Applied Chemistry), which is used throughout the world. In this system, the longest continuous chain of carbon atoms—called the base chain—determines the base name of the compound. The root of the base name depends on the number of carbon atoms in the base chain, as shown in Table 20.5. Base names for alkanes always have the ending *-ane*. Groups of carbon atoms branching off the base chain are alkyl groups and are named as substituents. Remember that a *substituent* is an atom or group of atoms that has been substituted for a hydrogen atom in an organic compound. Common alkyl groups are shown in Table 20.6.

TABLE 20.5 Prefixes for Base Names of Alkane Chains

Number of Carbon Atoms	Prefix
1	meth-
2	eth-
3	prop-
4	but-
5	pent-
6	hex-
7	hept-
8	oct-
9	non-
10	dec-

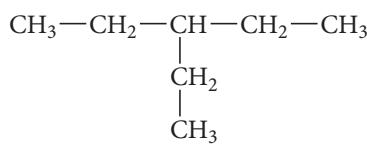
TABLE 20.6 Common Alkyl Groups

Condensed Structural Formula	Name	Condensed Structural Formula	Name
—CH ₃	Methyl	—CH(CH ₃) ₂	Isopropyl
—CH ₂ CH ₃	Ethyl	—CH ₂ CH(CH ₃) ₂	Isobutyl
—CH ₂ CH ₂ CH ₃	Propyl	—CH(CH ₂ CH ₃) ₂	sec-Butyl
—CH ₂ CH ₂ CH ₂ CH ₃	Butyl	—C(CH ₃) ₃	tert-Butyl

The procedure in Examples 20.2 and 20.3 will allow you to systematically name many alkanes. The procedure is presented in the left column and two examples of applying the procedure are shown in the center and right columns.

PROCEDURE FOR...**Naming Alkanes****EXAMPLE 20.2****Naming Alkanes**

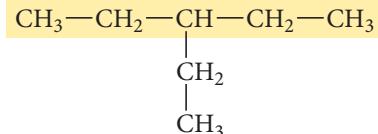
Name this alkane.



- Count the number of carbon atoms in the longest continuous carbon chain to determine the base name of the compound. Locate the prefix corresponding to this number of atoms in Table 20.5 and add the ending *-ane* to form the base name.

SOLUTION

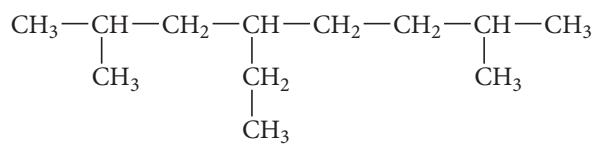
This compound has five carbon atoms in its longest continuous chain.



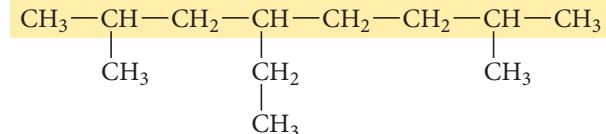
The correct prefix from Table 20.5 is *pent-*. The base name is pentane.

EXAMPLE 20.3**Naming Alkanes**

Name this alkane.

**SOLUTION**

This compound has eight carbon atoms in its longest continuous chain.



The correct prefix from Table 20.5 is *oct-*. The base name is octane.



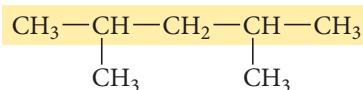
<p>2. Consider every branch from the base chain to be a substituent. Name each substituent according to Table 20.6.</p>	<p>This compound has one substituent named <i>ethyl</i>.</p> $\begin{array}{ccccccc} \text{CH}_3 & -\text{CH}_2 & -\text{CH} & -\text{CH}_2 & -\text{CH}_3 \\ & & & & \\ & & \text{CH}_2 & & \\ & & & & \\ & & \text{CH}_3 & & \\ \text{ethyl} \quad \nearrow & & & & & & \end{array}$	<p>This compound has one substituent named <i>ethyl</i> and two named <i>methyl</i>.</p> $\begin{array}{ccccccccc} \text{CH}_3 & -\text{CH} & -\text{CH}_2 & -\text{CH} & -\text{CH}_2 & -\text{CH}_2 & -\text{CH} & -\text{CH}_3 \\ & & & & & & & \\ & \text{CH}_3 & & \text{CH}_2 & & & \text{CH}_3 & \\ & & & & & & & \\ & & & \text{CH}_3 & & & & \\ & & & & \text{ethyl} \quad \nearrow & & & \text{CH}_3 \\ & & & & & & & \\ & & & & & & & \text{methyl} \quad \nearrow & \end{array}$
<p>3. Beginning with the end closest to the branching, number the base chain and assign a number to each substituent. (If two substituents occur at equal distances from each end, go to the next substituent to determine from which end to start numbering.)</p>	<p>Number the base chain as follows:</p> $\begin{array}{ccccc} \textcolor{red}{1} & \textcolor{red}{2} & \textcolor{red}{3} & \textcolor{red}{4} & \textcolor{red}{5} \\ \text{CH}_3 & -\text{CH}_2 & -\text{CH} & -\text{CH}_2 & -\text{CH}_3 \\ & & & & \\ & & \text{CH}_2 & & \\ & & & & \\ & & \text{CH}_3 & & \end{array}$ <p>Assign the number 3 to the ethyl substituent.</p>	<p>Number the base chain as follows:</p> $\begin{array}{cccccccc} \textcolor{red}{1} & \textcolor{red}{2} & \textcolor{red}{3} & \textcolor{red}{4} & \textcolor{red}{5} & \textcolor{red}{6} & \textcolor{red}{7} & \textcolor{red}{8} \\ \text{CH}_3 & -\text{CH} & -\text{CH}_2 & -\text{CH} & -\text{CH}_2 & -\text{CH}_2 & -\text{CH} & -\text{CH}_3 \\ & & & & & & & \\ & \text{CH}_3 & & \text{CH}_2 & & & \text{CH}_3 & \\ & & & & & & & \\ & & & \text{CH}_3 & & & & \end{array}$ <p>Assign the number 4 to the ethyl substituent and the numbers 2 and 7 to the two methyl substituents.</p>
<p>4. Write the name of the compound in the following format: (substituent number)- (substituent name) (base name)</p> <p>If there are two or more substituents, give each one a number and list them alphabetically with hyphens between words and numbers.</p>	<p>The name of the compound is: 3-ethylpentane</p>	<p>The basic form of the name of the compound is: 4-ethyl-2,7-methyloctane</p> <p>List ethyl before methyl because substituents are listed in alphabetical order.</p>
<p>5. If a compound has two or more identical substituents, indicate the number of identical substituents with the prefix <i>di-</i> (2), <i>tri-</i> (3), or <i>tetra-</i> (4) before the substituent's name. Separate the numbers indicating the positions of the substituents relative to each other with a comma. Do not take the prefixes into account when alphabetizing.</p>	<p>Does not apply to this compound.</p>	<p>This compound has two methyl substituents; therefore, the name of the compound is: 4-ethyl-2,7-dimethyloctane</p>
<p>FOR PRACTICE 20.2 Name this alkane.</p> $\text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ <p style="text-align: center;">CH_3</p>		<p>FOR PRACTICE 20.3 Name this alkane.</p> $\text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_3$ <p style="text-align: center;">$\text{CH}_3 \quad \text{CH}_3$</p>

EXAMPLE 20.4 Naming Alkanes

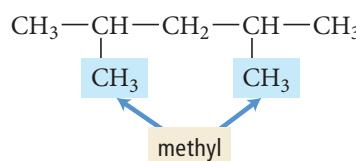
Name this alkane. $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\underset{\text{CH}_3}{\text{CH}_2}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$

SOLUTION

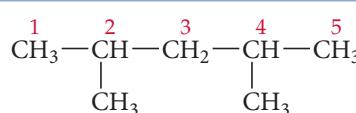
1. The longest continuous carbon chain has five atoms. Therefore, the base name is pentane.



2. This compound has two substituents, both of which are named methyl.



3. Since both substituents are equidistant from the ends, it does not matter from which end you start numbering.



- 4, 5. Use the general form for the name:

(substituent number)-(substituent name)(base name)

Because this compound contains two identical substituents, step 5 from the naming procedure applies and you use the prefix *di-*. Indicate the position of each substituent with a number separated by a comma.

2,4-dimethylpentane

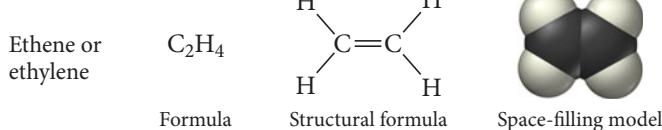
FOR PRACTICE 20.4

Name this alkane. $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\underset{\text{CH}_3}{\text{CH}_2}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}-\text{CH}_3$

The general formulas shown here for alkenes and alkynes assume only one multiple bond.

20.5 Alkenes and Alkynes

Alkenes are hydrocarbons containing at least one double bond between carbon atoms. Alkynes contain at least one triple bond. Because of the double or triple bond, alkenes and alkynes have fewer hydrogen atoms than the corresponding alkanes and are therefore called **unsaturated hydrocarbons** because they are not loaded to capacity with hydrogen. Recall that noncyclic alkenes have the formula C_nH_{2n} and noncyclic alkynes have the formula C_nH_{2n-2} . The simplest alkene is ethene (C_2H_4), also called ethylene.



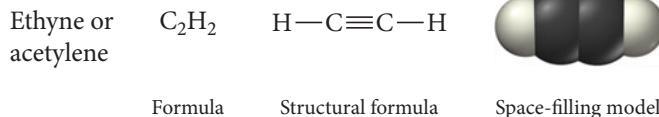
The geometry about each carbon atom in ethene is trigonal planar (see Example 10.8 for the valence bond model of ethene), making ethene a flat, rigid molecule. Ethene is a ripening agent in fruit such as bananas. When a banana within a cluster of bananas begins to ripen, it emits ethene. The ethene then causes other bananas in the cluster to ripen. Banana farmers usually pick bananas green for ease of shipping. When the bananas arrive at their destination, they are often “gassed” with ethene to initiate ripening. Table 20.7 lists the names and structures of several other alkenes. Most of them do not have familiar uses except their presence as minority components in fuels.

TABLE 20.7 Alkenes

<i>n</i>	Name	Molecular Formula C_nH_{2n}	Structural Formula	Condensed Structural Formula
2	Ethene	C_2H_4	<pre> H H C = C H H </pre>	$CH_2 = CH_2$
3	Propene	C_3H_6	<pre> H H C = C - C - H H H </pre>	$CH_2 = CHCH_3$
4	1-Butene*	C_4H_8	<pre> H H H C = C - C - C - H H H </pre>	$CH_2 = CHCH_2CH_3$
5	1-Pentene*	C_5H_{10}	<pre> H H H H C = C - C - C - C - H H H H </pre>	$CH_2 = CHCH_2CH_2CH_3$
6	1-Hexene*	C_6H_{12}	<pre> H H H H H C = C - C - C - C - C - H H H H </pre>	$CH_2 = CHCH_2CH_2CH_2CH_3$

* These alkenes have one or more isomers depending on the position of the double bond. The isomers shown here have the double bond in the 1 position, meaning the first carbon–carbon bond of the chain.

The simplest alkyne is ethyne, C_2H_2 , also known as acetylene.



The geometry about each carbon atom in ethyne is linear, making ethyne a linear molecule. Ethyne (or acetylene) is commonly used as fuel for welding torches. The names and structures of several other alkynes are shown in Table 20.8. Like alkenes, the alkynes do not have familiar uses other than their presence as minority components of gasoline.



Naming Alkenes and Alkynes

We name alkenes and alkynes in the same way we name alkanes with the following exceptions:

- The base chain is the longest continuous carbon chain *that contains the double or triple bond*.
- The base name has the ending *-ene* for alkenes and *-yne* for alkynes.
- We number the base chain to give the double or triple bond the lowest possible number.
- We insert a number indicating the position of the double or triple bond (lowest possible number) just before the base name.

▲ Welding torches burn ethyne in pure oxygen to produce the very hot flame needed for melting metals.

For example, the alkene and alkyne shown here are 2-methyl-2-pentene and 1-butyne:

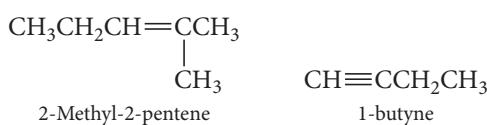


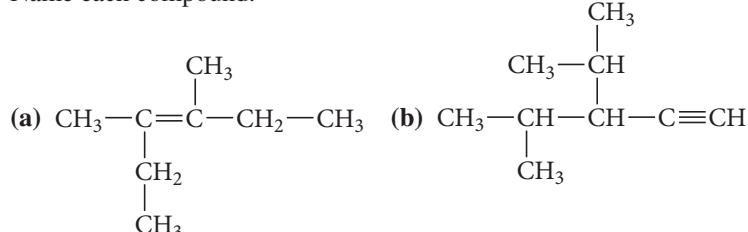
TABLE 20.8 Alkynes

<i>n</i>	Name	Molecular Formula C_nH_{2n-2}	Structural Formula	Condensed Structural Formula
2	Ethyne	C_2H_2	H—C≡C—H	$CH \equiv CH$
3	Propyne	C_3H_4	H—C≡C—C(H) H	$CH \equiv CCH_3$
4	1-Butyne*	C_4H_6	H—C≡C—C(H) H H	$CH \equiv CCH_2CH_3$
5	1-Pentyne*	C_5H_8	H—C≡C—C(H) H H H	$CH \equiv CCH_2CH_2CH_3$
6	1-Hexyne*	C_6H_{10}	H—C≡C—C(H) H H H H	$CH \equiv CCH_2CH_2CH_2CH_3$

* These alkynes have one or more isomers depending on the position of the triple bond. The isomers shown here have the triple bond in the 1 position, meaning the first carbon–carbon bond of the chain.

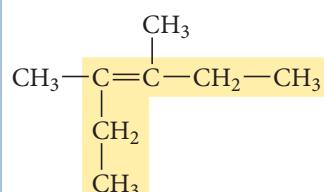
EXAMPLE 20.5 Naming Alkenes and Alkynes

Name each compound.

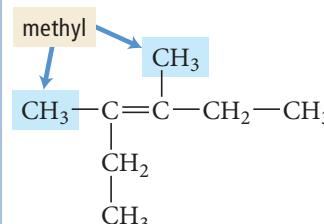


SOLUTION

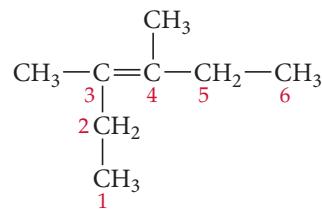
- (a) 1. The longest continuous carbon chain containing the double bond has six carbon atoms. The base name is therefore *hexene*.



2. The two substituents are both methyl.



3. One of the exceptions listed previously states that, in naming alkenes, you should number the chain so that the *double bond* has the lowest number. In this case, the double bond is equidistant from the ends. Assign the double bond the number 3. The two methyl groups are then at positions 3 and 4.



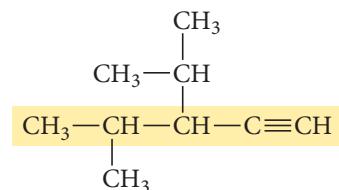
4, 5. Use the general form for the name:

(substituent number)-(substituent name)(base name)

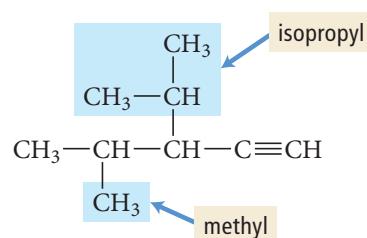
Because this compound contains two identical substituents, step 5 of the naming procedure applies. Use the prefix *di-*. In addition, indicate the position of each substituent with a number separated by a comma. Because this compound is an alkene, specify the position of the double bond, isolated by hyphens, just before the base name.

- (b)** 1. The longest continuous carbon chain containing the triple bond is five carbon atoms long; therefore, the base name is *pentyne*.

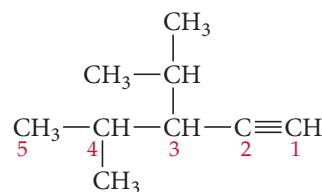
3,4-dimethyl-3-hexene



2. There are two substituents; one is a methyl group and the other an isopropyl group.



3. Number the base chain, giving the triple bond the lowest number (1). Assign the isopropyl and methyl groups the numbers 3 and 4, respectively.



4. Use the general form for the name:

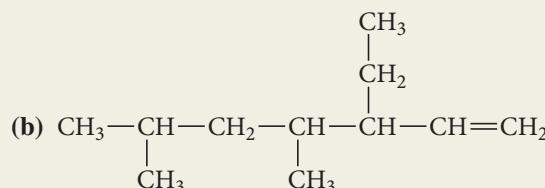
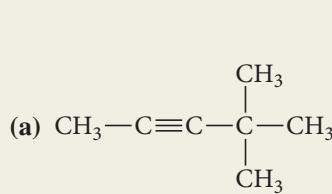
(substituent number)-(substituent name)(base name)

Since there are two substituents, list both of them in alphabetical order. Since this compound is an alkyne, specify the position of the triple bond with a number isolated by hyphens just before the base name.

3-isopropyl-4-methyl-1-pentyne

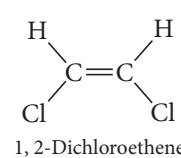
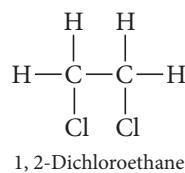
FOR PRACTICE 20.5

Name each compound.

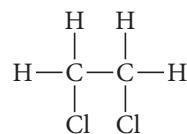
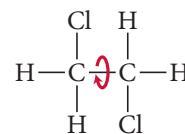


Geometric (Cis–Trans) Isomerism in Alkenes

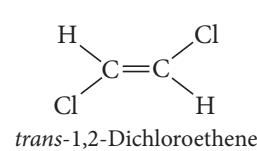
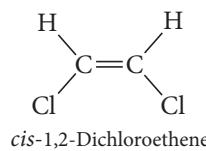
A major difference between a single bond and a double bond is the degree to which rotation occurs about the bond. As discussed in Section 10.7, rotation about a double bond is highly restricted due to the overlap between unhybridized *p* orbitals on the adjacent carbon atoms. Consider the difference between 1,2-dichloroethane and 1,2-dichloroethene:



The hybridization of the carbon atoms in 1,2-dichloroethane is sp^3 , resulting in relatively free rotation about the sigma single bond. Consequently, the two structures are identical at room temperature because they quickly interconvert.



In contrast, rotation about the double bond (sigma + pi) in 1,2-dichloroethene is restricted, so at room temperature, 1,2-dichloroethene exists in two isomeric forms.

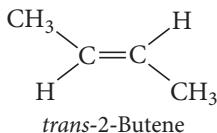
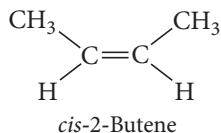


These two forms of 1,2-dichloroethene are different compounds with different properties as shown in Table 20.9. This kind of isomerism is a type of stereoisomerism (see Section 20.3) called **geometric** (or **cis–trans**) **isomerism**. We distinguish between the two isomers with the designations *cis* (meaning “same side”) and *trans* (meaning “opposite sides”). Cis–trans isomerism is common in alkenes. As another example,

TABLE 20.9 Physical Properties of *cis*- and *trans*-1,2-Dichloroethene

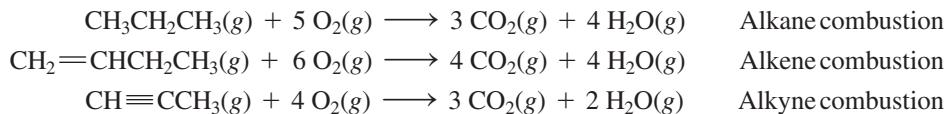
Name	Structure	Space-filling Model	Density (g/mL)	Melting Point (°C)	Boiling Point (°C)
<i>cis</i> -1,2-Dichloroethene	$\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{Cl} - \text{C} = & \text{C} - \text{Cl} \\ & \end{array}$		1.284	−80.5	60.1
<i>trans</i> -1,2-Dichloroethene	$\begin{array}{c} \text{H} & \text{Cl} \\ & \\ \text{Cl} - \text{C} = & \text{C} - \text{H} \\ & \end{array}$		1.257	−49.4	47.5

consider *cis*- and *trans*-2-butene. Like the two isomers of 1,2-dichloroethene, these two isomers have different physical properties. For example, *cis*-2-butene boils at 3.7 °C, and *trans*-2-butene boils at 0.9 °C.



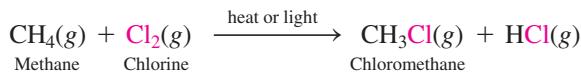
20.6 Hydrocarbon Reactions

One of the most common hydrocarbon reactions is combustion, the burning of hydrocarbons in the presence of oxygen. Hydrocarbon combustion reactions are highly exothermic and are commonly used to warm homes and buildings, to generate electricity, and to power the engines of cars, ships, and airplanes. It is not an exaggeration to say that hydrocarbon combustion makes our current way of life possible. Approximately 90% of energy produced in the United States is generated by hydrocarbon combustion. Alkanes, alkenes, and alkynes all undergo combustion. In a combustion reaction, the hydrocarbon reacts with oxygen to form carbon dioxide and water.

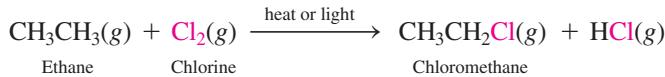


Reactions of Alkanes

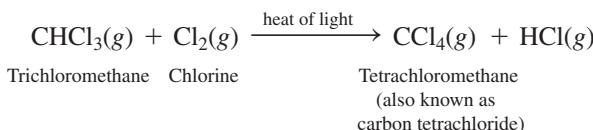
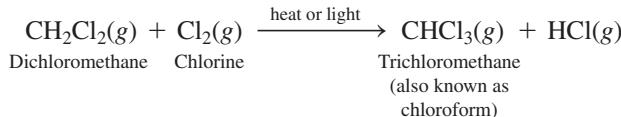
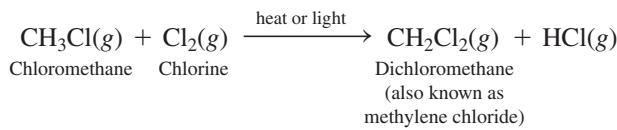
In addition to combustion reactions, alkanes also undergo *substitution* reactions, in which one or more hydrogen atoms on an alkane are replaced by one or more other atoms. The most common substitution reaction is halogen substitution (also referred to as halogenation). For example, methane can react with chlorine gas in the presence of heat or light to form chloromethane.



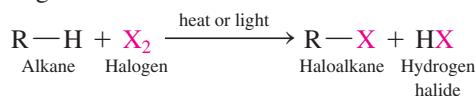
Ethane reacts with chlorine gas to form chloroethane.



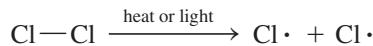
Multiple halogenation reactions can occur because halogens can replace more than one of the hydrogen atoms on an alkane. For example, chloromethane can react with chlorine and the product of that reaction can react again (and so on).



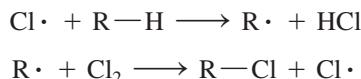
The general form for halogen substitution reactions is:



Notice that the halogenation of hydrocarbons requires initiation with heat or light, which causes the chlorine–chlorine bond to break.



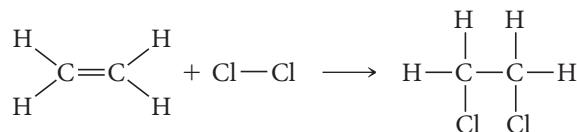
The resulting chlorine atoms are *free radicals* (see Section 9.9), as the dot that represents each chlorine atom's unpaired electron indicates. Chlorine radicals are highly reactive and attack the C–H bond in hydrocarbons. The subsequent reaction proceeds by this mechanism:



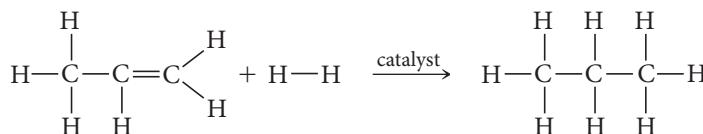
Notice that a chlorine free radical is produced as a product of the last step. This free radical can go on to react again, unless it encounters another chlorine free radical, in which case it reacts with it to re-form Cl_2 .

Reactions of Alkenes and Alkynes

Alkenes and alkynes undergo addition reactions in which molecules add across (on either side of) the multiple bond. For example, ethene reacts with chlorine gas to form dichloroethane.

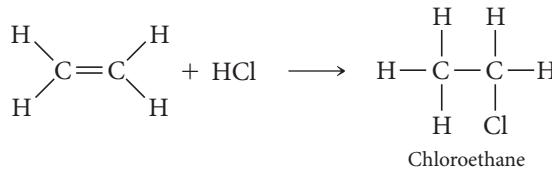


The addition of chlorine converts the carbon–carbon double bond into a single bond because each carbon atom bonds to a chlorine atom. Alkenes and alkynes can also add hydrogen in hydrogenation reactions. For example, in the presence of an appropriate catalyst, propene reacts with hydrogen gas to form propane.



Hydrogenation reactions convert unsaturated hydrocarbons into saturated hydrocarbons. For example, hydrogenation reactions convert unsaturated vegetable oils into saturated fats. Most vegetable oils are unsaturated because their carbon chains contain double bonds. The double bonds put bends into the carbon chains that result in less efficient packing of molecules; thus vegetable oils are liquids at room temperature while saturated fats are solids at room temperature. When food manufacturers add hydrogen to the double bonds of vegetable oil, the unsaturated fat is converted into a saturated fat, turning the liquid oil into a solid at room temperature. The words “partially hydrogenated vegetable oil” on a label indicate a food product that contains saturated fats made via hydrogenation reactions.

Alkenes can also add unsymmetrical reagents across the double bond. For example, ethene reacts with hydrogen chloride to form chloroethane.

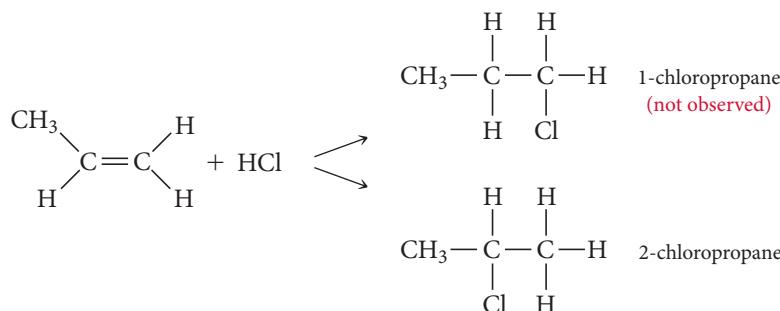


We often indicate the presence of a catalyst by adding a label over the reaction arrow.



▲ Partially hydrogenated vegetable oil is a saturated fat that is made by hydrogenating unsaturated fats.

If the alkene itself is also unsymmetrical, then the addition of an unsymmetrical reagent leads to the potential for two different products. For example, when HCl reacts with propene, two products are possible:



When this reaction is carried out in the lab, however, only the 2-chloropropane forms. We can predict the product of the addition of an unsymmetrical reagent to an unsymmetrical alkene with Markovnikov's rule, which states the following:

When a polar reagent is added to an unsymmetrical alkene, the positive end (the least electronegative part) of the reagent adds to the carbon atom that has the most hydrogen atoms.

In most reactions of this type, the positive end of the reagent is hydrogen; therefore, the hydrogen atom bonds to the carbon atom that already contains the most hydrogen atoms.

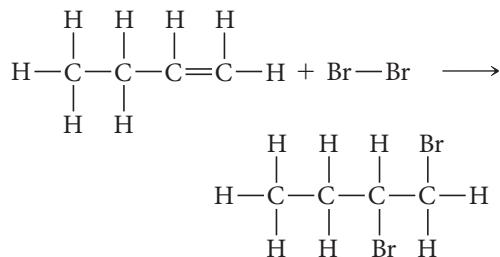
EXAMPLE 20.6 Alkene Addition Reactions

Determine the products of the reactions.

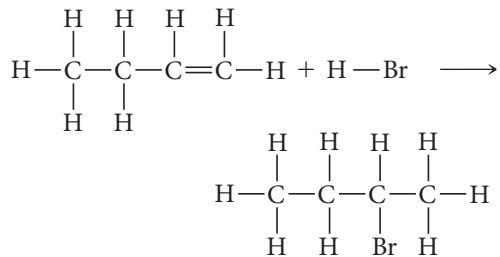


SOLUTION

- (a) The reaction of 1-butene with bromine is an example of a symmetric addition. The bromine adds across the double bond and each carbon forms a single bond to a bromine atom.

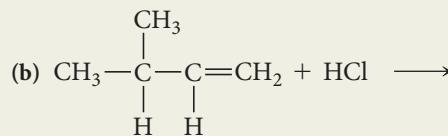
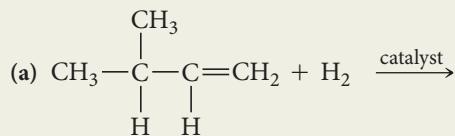


- (b) The reaction of 1-butene with hydrogen bromide is an example of an unsymmetrical addition. Apply Markovnikov's rule to determine which carbon the hydrogen bonds with and which carbon the bromine atom bonds with. Markovnikov's rule predicts that the hydrogen bonds to the end carbon in this case.



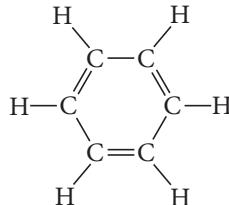
FOR PRACTICE 20.6

Determine the products of the reactions.

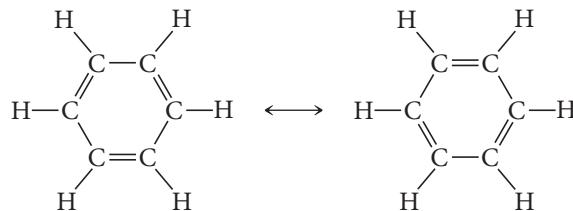


20.7 Aromatic Hydrocarbons

As you might imagine, determining the structure of organic compounds has not always been easy. During the mid-1800s chemists were working to determine the structure of a particularly stable organic compound named benzene (C_6H_6). In 1865, Friedrich August Kekulé (1829–1896) had a dream in which he envisioned chains of carbon atoms as snakes. The snakes danced before him, and one of them twisted around and bit its tail. Based on that vision, Kekulé proposed the following structure for benzene:

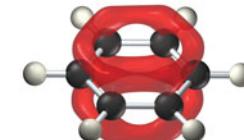


This structure has alternating single and double bonds. When we examine the carbon–carbon bond lengths in benzene, however, we find that all the bonds are the same length, which indicates that the following resonance structures are a more accurate representation of benzene:



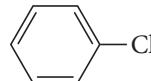
Recall from Section 9.8 that the actual structure of a molecule represented by resonance structures is intermediate between the two resonance structures and is called a *resonance hybrid*.

The true structure of benzene is a hybrid of the two resonance structures. We often represent benzene with the following carbon skeletal formula (or line formula):

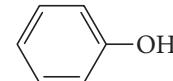


The ring represents the delocalized π electrons that occupy the molecular orbital shown superimposed on the ball-and-stick model. When drawing benzene rings, either by themselves or as parts of other compounds, organic chemists use either this diagram or just one of the resonance structures with alternating double bonds. Both representations indicate the same thing—a benzene ring.

The benzene ring structure occurs in many organic compounds. An atom or group of atoms can be substituted for one or more of the six hydrogen atoms on the ring to form compounds referred to as substituted benzenes, such as chlorobenzene and phenol.



Chlorobenzene

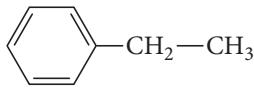


Phenol

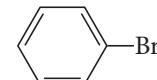
Because many compounds containing benzene rings have pleasant aromas, benzene rings are also called *aromatic rings*, and compounds containing them are called *aromatic compounds*. Aromatic compounds are responsible for the pleasant smells of cinnamon, vanilla, and jasmine.

Naming Aromatic Hydrocarbons

Monosubstituted benzenes—benzenes in which only one of the hydrogen atoms has been substituted—are often named as derivatives of benzene.



Ethylbenzene

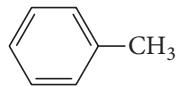


Bromobenzene

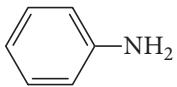
These names take the general form:

(name of substituent)benzene

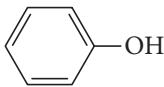
However, many monosubstituted benzenes have names that can only be learned through familiarity. Some common ones are shown here.



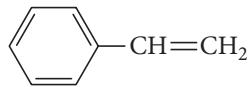
Toluene



Aniline

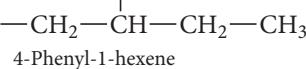
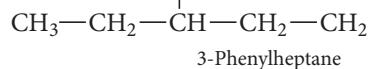


Phenol

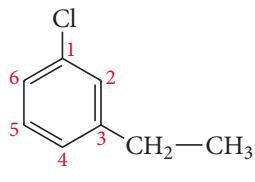


Styrene

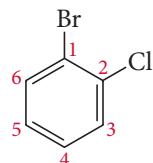
Some substituted benzenes, especially those with large substituents, are named by treating the benzene ring as the substituent. In these cases, the benzene substituent is referred to as a **phenyl group**.



Disubstituted benzenes—benzenes in which two hydrogen atoms have been substituted—are numbered and the substituents are listed alphabetically. We determine the order of numbering on the ring by the alphabetical order of the substituents.

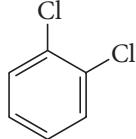


1-Chloro-3-ethylbenzene

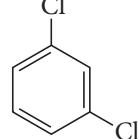


1-Bromo-2-chlorobenzene

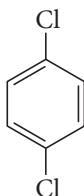
When the two substituents are identical, we use the prefix *di*-.



1,2-Dichlorobenzene

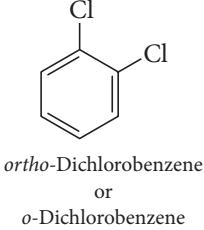


1,3-Dichlorobenzene

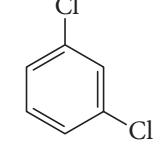


1,4-Dichlorobenzene

Also in common use, in place of numbering, are the prefixes *ortho* (1,2 disubstituted), *meta* (1,3 disubstituted), and *para* (1,4 disubstituted).



ortho-Dichlorobenzene
or
o-Dichlorobenzene



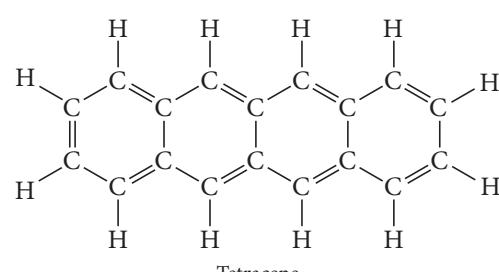
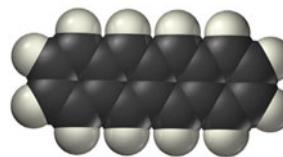
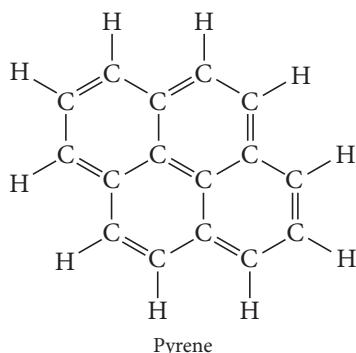
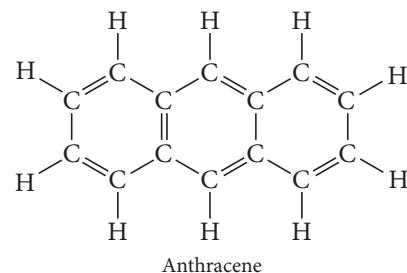
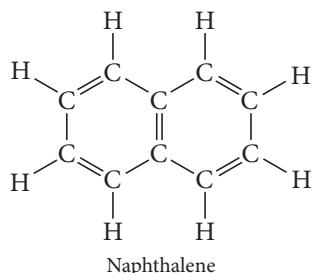
meta-Dichlorobenzene
or
m-Dichlorobenzene



para-Dichlorobenzene
or
p-Dichlorobenzene

Compounds containing fused aromatic rings are called polycyclic aromatic hydrocarbons. Some common examples (shown in Figure 20.5 ▶) include naphthalene, the substance that composes mothballs, and pyrene, a carcinogen found in cigarette smoke.

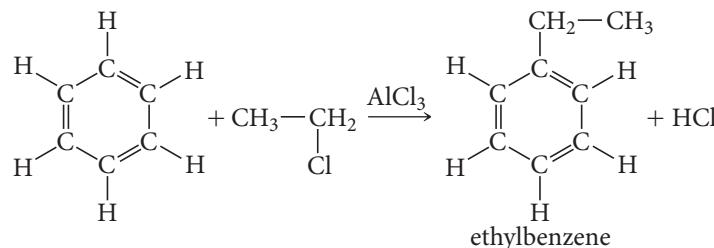
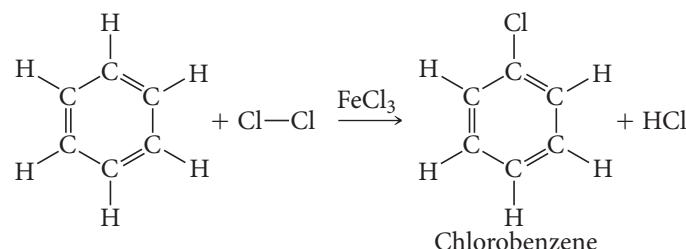
► FIGURE 20.5 Polycyclic aromatic compounds The structures of some common polycyclic aromatic compounds contain fused rings.



Reactions of Aromatic Compounds

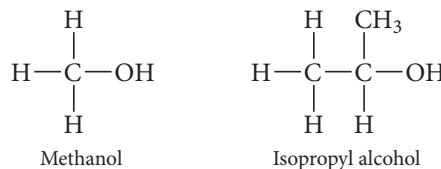
The substances shown over the arrows are catalysts needed to increase the rate of the reaction.

We might expect benzene to react similarly to the alkenes, readily undergoing addition reactions across its double bonds. However, because of electron delocalization around the ring and the resulting greater stability, benzene does not typically undergo addition reactions. Instead, benzene undergoes substitution reactions in which the hydrogen atoms are replaced by other atoms or groups of atoms as shown in the following examples:



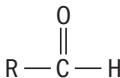
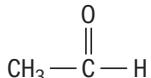
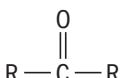
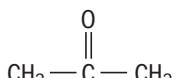
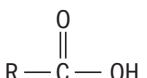
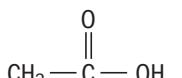
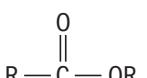
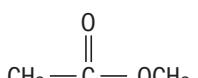
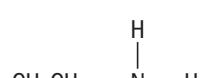
20.8 Functional Groups

Most other families of organic compounds are hydrocarbons with a *functional group*—a characteristic atom or group of atoms—inserted into the hydrocarbon. A group of organic compounds that all have the same functional group is a *family*. For example, the members of the family of alcohols each have an —OH functional group and the general formula R—OH, where R represents a hydrocarbon group. (That is, we refer to the hydrocarbon group as an “R group.”) Some specific examples include methanol and isopropyl alcohol (also known as rubbing alcohol).



The presence of a functional group in a hydrocarbon alters the properties of the compound significantly. For example, methane is a nonpolar gas. By contrast, methanol—methane with an —OH group substituted for one of the hydrogen atoms—is a polar, hydrogen-bonded liquid at room temperature. Although each member of a family is unique and different, their common functional group causes some similarities in both their physical and chemical properties. Table 20.10 lists some common functional groups, their general formulas, and an example of each.

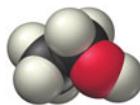
TABLE 20.10 Some Common Functional Groups

Family	General Formula*	Condensed General Formula	Example	Name
Alcohols	R—OH	ROH	CH ₃ CH ₂ OH	Ethanol (ethyl alcohol)
Ethers	R—O—R	ROR	CH ₃ OCH ₃	Dimethyl ether
Aldehydes		RCHO		Ethanal (acetaldehyde)
Ketones		RCOR		Propanone (acetone)
Carboxylic acids		RCOOH		Ethanoic acid (acetic acid)
Esters		RCOOR		Methyl acetate
Amines		R ₃ N		Ethylamine

*In ethers, ketones, esters, and amines, the R groups may be the same or different.

20.9 Alcohols

As we discussed in Section 20.8, **alcohols** are organic compounds containing the —OH functional group, or **hydroxyl group**, and they have the general formula R—OH. In addition to methanol and isopropyl alcohol, ethanol and 1-butanol (shown here) are also common alcohols.



$\text{CH}_3\text{—CH}_2\text{—OH}$
Ethanol

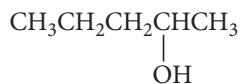


$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—OH}$
1-Butanol

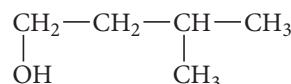
Naming Alcohols

The names of alcohols are like the names of alkanes with the following differences:

- The base chain is the longest continuous carbon chain that contains the —OH functional group.
- The base name has the ending *-ol*.
- We number the base chain to assign the —OH group the lowest possible number.
- We insert a number indicating the position of the —OH group just before the base name. For example:



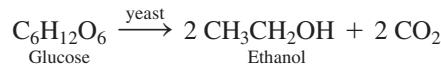
2-Pentanol



3-Methyl-1-butanol

About Alcohols

The familiar alcohol in alcoholic beverages, ethanol, is most commonly formed by the yeast fermentation of sugars, such as glucose, from fruits and grains.



Alcoholic beverages contain ethanol, water, and a few other components that impart flavor and color. Beer usually contains 3–6% ethanol. Wine contains about 12–14% ethanol, and spirits—beverages like whiskey, rum, or tequila—range from 40% to 80% ethanol, depending on their *proof*. The proof of an alcoholic beverage is twice the percentage of its ethanol content, so an 80-proof whiskey contains 40% ethanol. Ethanol is used as a gasoline additive because it increases the octane rating of gasoline and fosters its complete combustion, reducing the levels of certain pollutants such as carbon monoxide and the precursors of ozone.

Isopropyl alcohol (or 2-propanol) is available at any drug store under the name of rubbing alcohol. It is commonly used as a disinfectant for wounds and to sterilize medical instruments. Isopropyl alcohol should never be consumed internally, as it is highly toxic. Four ounces of isopropyl alcohol can cause death. A third common alcohol is methanol, also called wood alcohol. Methanol is commonly used as a laboratory solvent and as a fuel additive. Like isopropyl alcohol, methanol is toxic and should never be consumed.

Alcohol Reactions

Alcohols undergo a number of reactions including substitution, elimination (or dehydration), and oxidation. Alcohols also react with active metals to form strong bases.

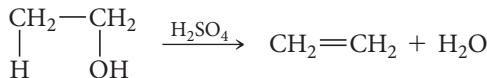
Substitution Alcohols react with acids such as HBr to form halogenated hydrocarbons:



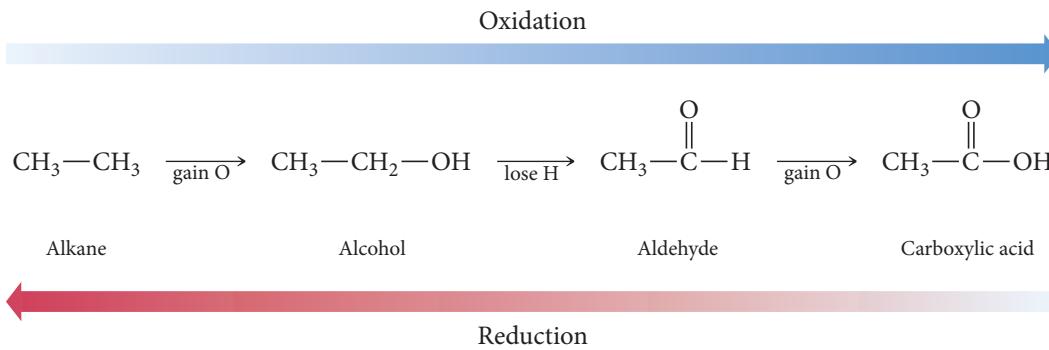
In these reactions, the halogen replaces the hydroxyl group on the alcohol. For example, ethanol reacts with hydrobromic acid to form bromoethane and water:



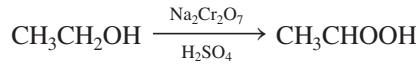
Elimination (or Dehydration) In the presence of concentrated acids such as H_2SO_4 , alcohols react and eliminate water, forming an alkene. For example, ethanol eliminates water to form ethene according to the reaction:



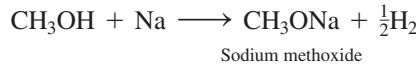
Oxidation In organic chemistry, we think of oxidation and reduction in terms of the changes to the carbon atoms in the molecule. Thus, oxidation is the gaining of oxygen or the losing of hydrogen by a carbon atom. Reduction is the loss of oxygen or the gaining of hydrogen by a carbon atom. We can draw a series showing relative states of oxidation:



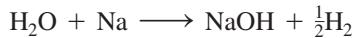
In this view, an alcohol is a partially oxidized hydrocarbon; it can be further oxidized to form an aldehyde or carboxylic acid, or it can be reduced to form a hydrocarbon (but this is rare). For example, ethanol can be oxidized to acetic acid according to the reaction:



Reaction with Active Metals Alcohols react with active metals, such as sodium, much as water does. For example, methanol reacts with sodium to form *sodium methoxide* and hydrogen gas:



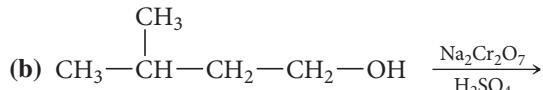
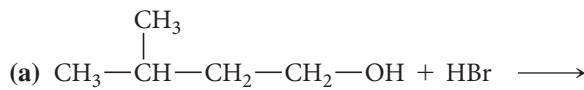
The reaction of water with sodium produces *sodium hydroxide* and hydrogen gas:



In both cases, a strong base forms (OH^- for water and CH_3O^- for methanol).

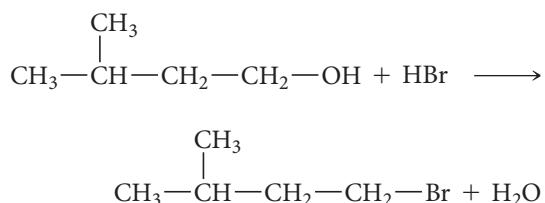
EXAMPLE 20.7 Alcohol Reactions

Determine the type of reaction (substitution, dehydration, oxidation, or reaction with an active metal) that occurs in each case, and write formulas for the products.

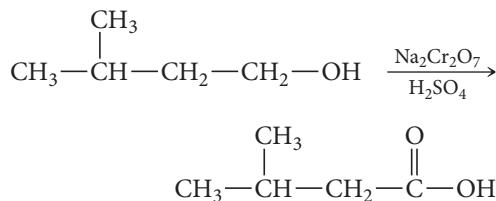


SOLUTION

- (a) An alcohol reacting with an acid is an example of a *substitution reaction*. The product of the substitution reaction is a halogenated hydrocarbon and water.

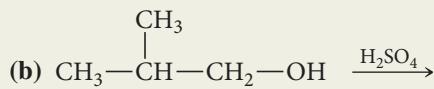


- (b) An alcohol in solution with sodium dichromate and acid undergoes an *oxidation reaction*. The product of the oxidation reaction is a carboxylic acid functional group. (We discuss carboxylic acid functional groups in detail in Section 20.11.)



FOR PRACTICE 20.7

Determine the type of reaction (substitution, dehydration, oxidation, or reaction with an active metal) that occurs in each case, and write formulas for the products.



20.10 Aldehydes and Ketones

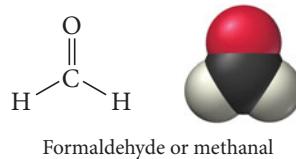
Aldehydes and ketones have the following general formulas:

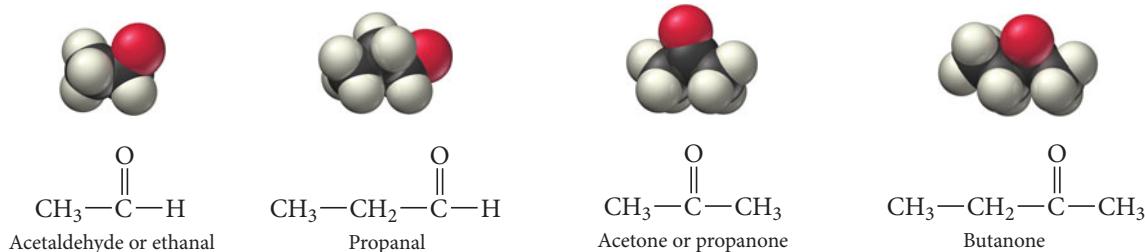


The functional group for both aldehydes and ketones is the **carbonyl group**:



Ketones have an R group attached to both sides of the carbonyl, while aldehydes have one R group and a hydrogen atom. (An exception is formaldehyde, which is an aldehyde with two H atoms bonded to the carbonyl group.)

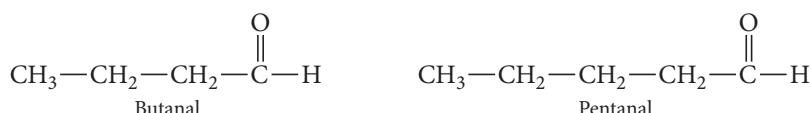


**▲ FIGURE 20.6** Common Aldehydes and Ketones

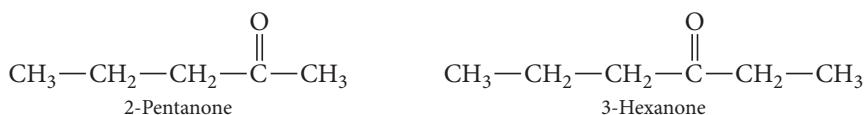
Other common aldehydes and ketones are shown in Figure 20.6 ▲.

Naming Aldehydes and Ketones

Many aldehydes and ketones have common names that we can learn only by becoming familiar with them, but we can systematically name simple aldehydes according to the number of carbon atoms in the longest continuous carbon chain that contains the carbonyl group. We form the base name from the name of the corresponding alkane by dropping the *-e* and adding the ending *-al*.

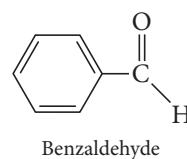
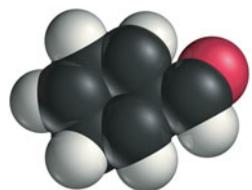
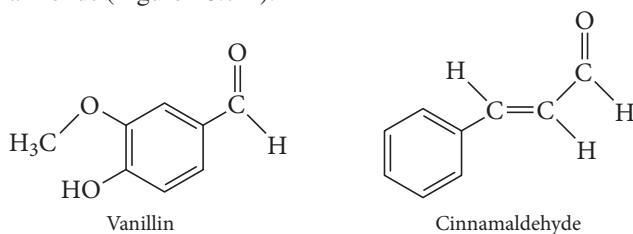


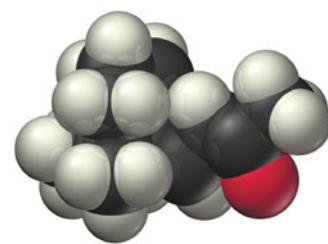
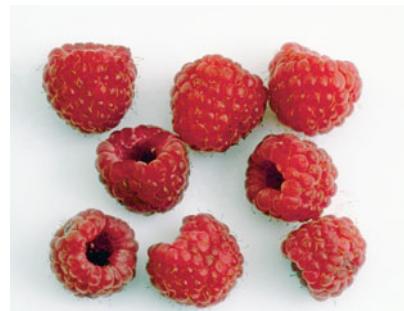
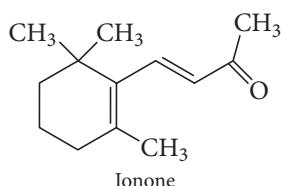
We name simple ketones according to the longest continuous carbon chain containing the carbonyl group, forming the base name from the name of the corresponding alkane by dropping the letter *-e* and adding the ending *-one*. For ketones, we number the chain to give the carbonyl group the lowest possible number.



About Aldehydes and Ketones

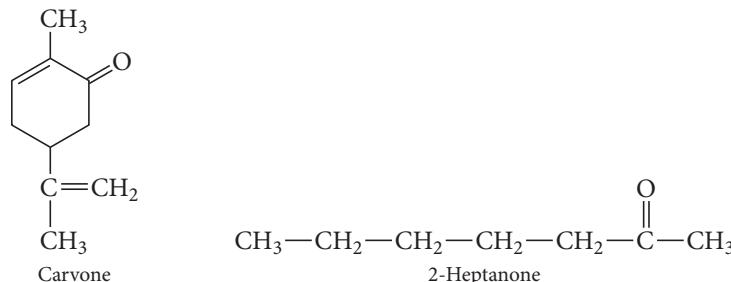
The most familiar aldehyde is probably formaldehyde, shown earlier in this section. Formaldehyde is a gas with a pungent odor. It is often mixed with water to make formalin, a preservative and disinfectant. Formaldehyde is also found in wood smoke, which is one reason that smoking is an effective method of food preservation—the formaldehyde kills bacteria. Aromatic aldehydes, those that also contain an aromatic ring, have pleasant aromas. For example, vanillin causes the smell of vanilla, cinnamaldehyde is the sweet-smelling component of cinnamon, and benzaldehyde accounts for the smell of almonds (Figure 20.7 ▼).

**▲ FIGURE 20.7** The Nutty Aroma of Almonds Benzaldehyde is partly responsible for the smell of almonds.



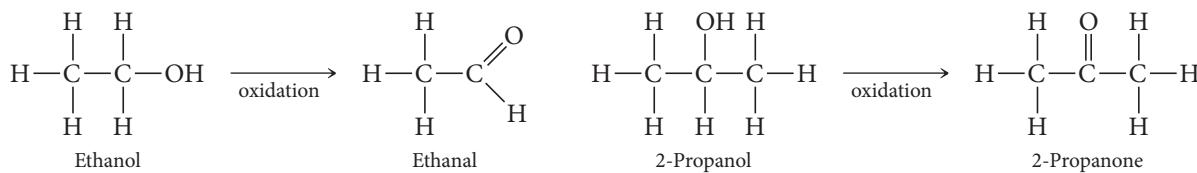
▲ FIGURE 20.8 The Fragrance of Raspberries Ionone is partly responsible for the smell of raspberries.

The most familiar ketone is acetone, the main component of nail polish remover. Other ketones have more pleasant aromas. For example, carvone is largely responsible for the smell of spearmint, 2-heptanone (among other compounds) for the smell of cloves, and ionone for the smell of raspberries (Figure 20.8 ▲).

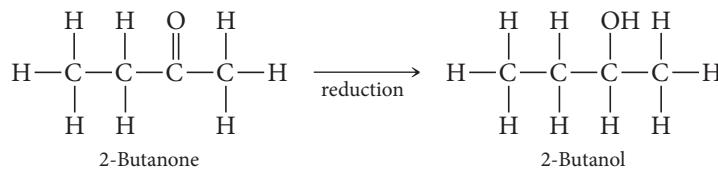


Aldehyde and Ketone Reactions

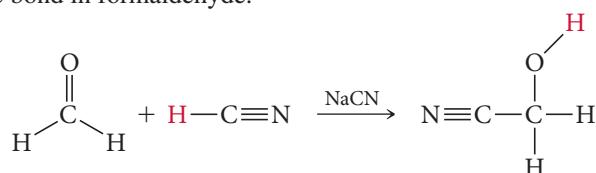
Aldehydes and ketones can be formed by the *oxidation* of alcohols. For example, ethanol can be oxidized to ethanal, and 2-propanol can be oxidized to 2-propanone (or acetone).

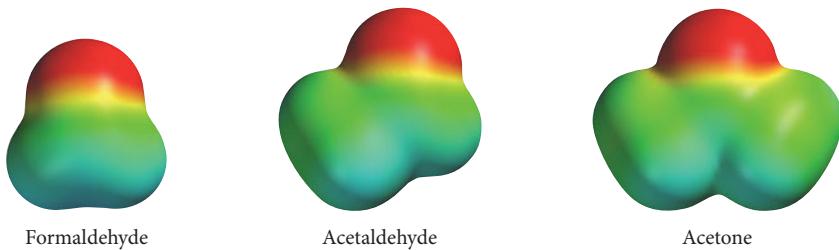


In the reverse reaction, an aldehyde or ketone is reduced to an alcohol. For example, 2-butanone can be reduced to 2-butanol in the presence of a reducing agent.



The carbonyl group in aldehydes and ketones is unsaturated, much like the double bond in an alkene. Because of this feature, the most common reactions of aldehydes and ketones are **addition reactions**. However, in contrast to the carbon–carbon double bond in alkenes, which is nonpolar, the double bond in the carbonyl group is highly polar (Figure 20.9 ►). Consequently, additions across the double bond result in the more electronegative part of the reagent bonding to the carbon atom and the less electronegative part (often hydrogen) bonding to the oxygen atom. For example, HCN adds across the carbonyl double bond in formaldehyde.





◀ FIGURE 20.9 Charge Density Plots of the Carbonyl Group The carbonyl group is highly polar, as shown in these plots of electrostatic potential.

20.11 Carboxylic Acids and Esters

Carboxylic acids and esters have the general formulas:

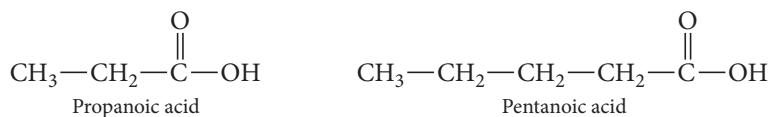


The condensed structural formula for carboxylic acids is RCOOH ; for esters it is RCOOR .

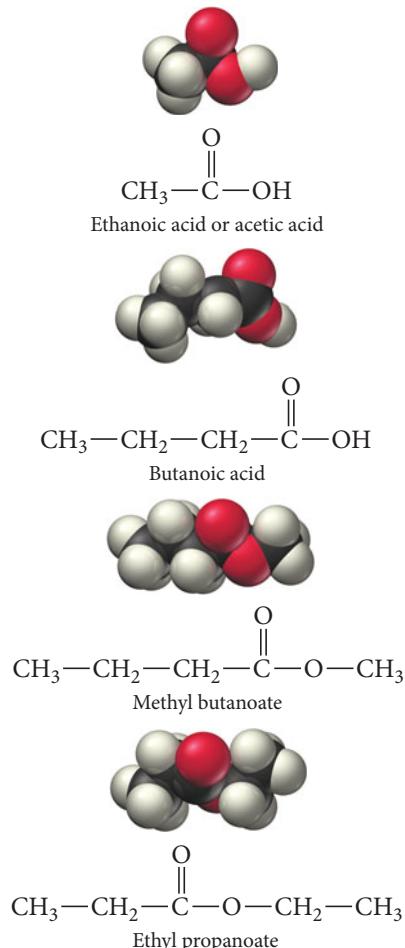
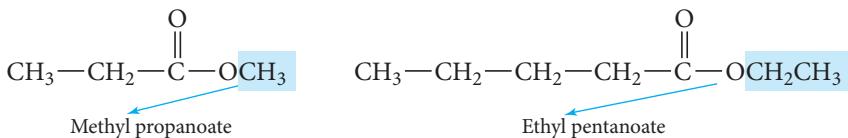
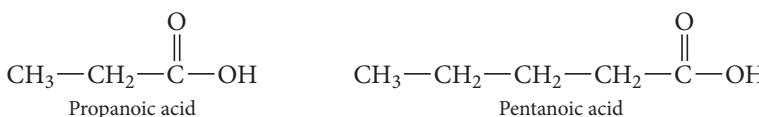
Figure 20.10 ▶ shows the structures of some common carboxylic acids and esters.

Naming Carboxylic Acids and Esters

We systematically name carboxylic acids according to the number of carbon atoms in the longest chain containing the $-\text{COOH}$ functional group. We form the base name by dropping the *-e* from the name of the corresponding alkane and adding the ending *-oic acid*.



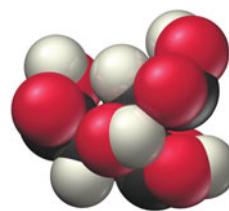
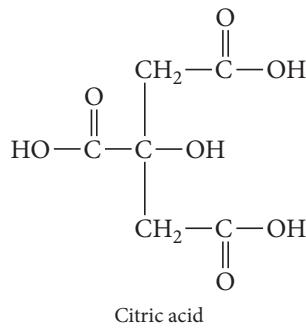
We name esters as if they were derived from a carboxylic acid by replacing the H on the OH with an alkyl group. The R group from the parent acid forms the base name of the compound. We change the *-ic* on the name of the corresponding carboxylic acid to *-ate*, and drop *acid*, naming the R group that replaced the H on the carboxylic acid as an alkyl group with the ending *-yl*, as shown in the following examples:



▲ FIGURE 20.10 Common Carboxylic Acids and Esters

About Carboxylic Acids and Esters

Like all acids, carboxylic acids taste sour. The most familiar carboxylic acid is ethanoic acid, better known by its common name, acetic acid. Acetic acid is the active ingredient in vinegar. It can form by the oxidation of ethanol, which is why wines left open to air become sour. Some yeasts and bacteria also form acetic acid when they metabolize sugars in bread dough. These are added to bread dough to make sourdough bread. Other common carboxylic acids include methanoic acid (formic acid), present in bee stings and

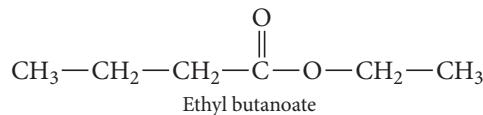
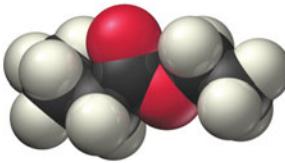


▲ FIGURE 20.11 The Tart Taste of Limes Citric acid is partly responsible for the sour taste of limes.

ant bites; lactic acid, which collects in muscles after intense exercise causing soreness; and citric acid, found in limes, lemons, and oranges (Figure 20.11 ▲).



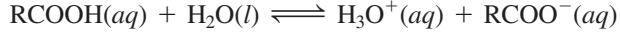
Esters are best known for their sweet smells. Methyl butanoate is largely responsible for the smell and taste of apples, and ethyl butanoate is largely responsible for the smell and taste of pineapples (see Figure 20.12 ▼).



▲ FIGURE 20.12 The Aroma of Pineapple Ethyl butanoate is partly responsible for the aroma of pineapples.

Carboxylic Acid and Ester Reactions

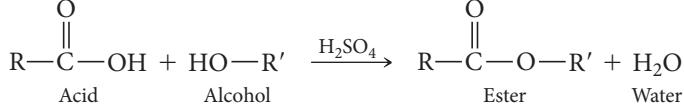
Carboxylic acids act as weak acids in solution.



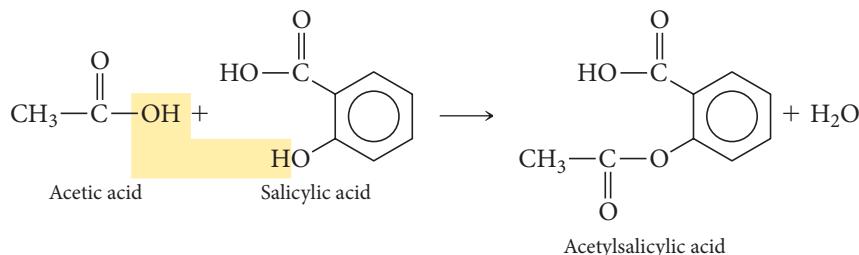
Like all acids, carboxylic acids react with strong bases via neutralization reactions. For example, propanoic acid reacts with sodium hydroxide to form sodium propanoate and water.



A carboxylic acid reacts with an alcohol to form an ester via a **condensation reaction**, a reaction in which two (or more) organic compounds join, often with the loss of water (or some other small molecule).



An important example of this reaction is the formation of acetylsalicylic acid (aspirin) from ethanoic acid (acetic acid) and salicylic acid (originally obtained from the bark of the willow tree).



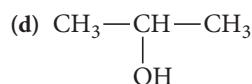
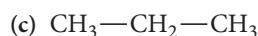
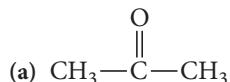
If we subject a carboxylic acid to high temperatures, it undergoes a condensation reaction with itself to form an acid anhydride (anhydride means “without water”).



We can add water to an acid anhydride to reverse the reaction just shown and regenerate the carboxylic acid molecules.

Conceptual Connection 20.3 Oxidation

Arrange the compounds from least oxidized to most oxidized.



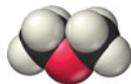
20.12 Ethers

Ethers are organic compounds with the general formula ROR. The two R groups may be identical or they may be different. Some common ethers are shown in Figure 20.13 ▼.

Naming Ethers

Common names for ethers have the format:

(R group 1) (R group 2) ether



$\text{CH}_3-\text{O}-\text{CH}_3$
Dimethyl ether



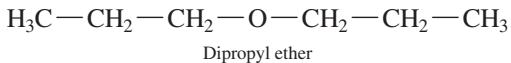
$\text{CH}_3-\text{O}-\text{CH}_2-\text{CH}_3$
Ethyl methyl ether



$\text{CH}_3-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3$
Diethyl ether

▲ FIGURE 20.13 Ethers

If the two R groups differ, we use each of their names in alphabetical order. If the two R groups are the same, we use the prefix *di-*. Some examples include:

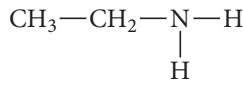
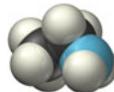


About Ethers

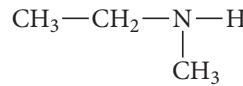
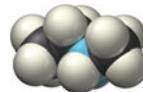
The most common ether is diethyl ether. Diethyl ether is a useful laboratory solvent because it can dissolve many organic compounds and it has a low boiling point (34.6 °C). The low boiling point allows for easy removal of the solvent. Diethyl ether was used as a general anesthetic for many years. When inhaled, diethyl ether depresses the central nervous system, causing unconsciousness and insensitivity to pain. Its use as an anesthetic, however, has decreased in recent years because other compounds have the same anesthetic effect with fewer side effects (such as nausea).

20.13 Amines

The simplest nitrogen-containing compound is ammonia (NH_3). **Amines** are organic compounds containing nitrogen that are derived from ammonia with one or more of the hydrogen atoms replaced by alkyl groups. Like ammonia, amines are weak bases. We systematically name amines according to the hydrocarbon groups attached to the nitrogen and assign the ending *-amine*.

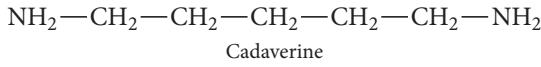
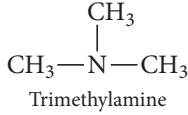


Ethylamine



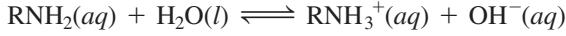
Ethylmethylamine

Amines are most commonly known for their awful odors. When a living organism dies, the bacteria that feast on its proteins emit amines. For example, trimethylamine causes the smell of rotten fish, and cadaverine causes the smell of decaying animal flesh.

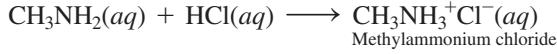


Amine Reactions

Just as carboxylic acids act as weak acids, so amines act as weak bases:



Like all bases, amines react with strong acids to form salts called ammonium salts. For example, methylamine reacts with hydrochloric acid to form methylammonium chloride:



An important amine reaction that we will see again in Chapter 21 is the condensation reaction between a carboxylic acid and an amine.

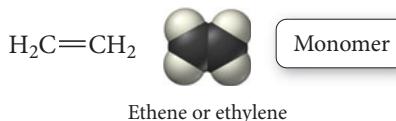


This reaction is responsible for the formation of proteins from amino acids (see Section 21.4).

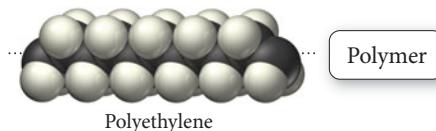
20.14 Polymers

Polymers are long, chainlike molecules composed of repeating units called **monomers**. In Chapter 21, we will learn about natural polymers such as starches, proteins, and DNA, which play important roles in living organisms. In this section, we learn about synthetic polymers, which we encounter daily in plastic products such as PVC tubing, styrofoam coffee cups, nylon rope, and plexiglass windows. Polymer materials are common in our everyday lives, found in everything from computers to toys to packaging materials. Most polymers are durable, partly because of the length of their molecules. In general, the longer the length of a molecule, the greater the intermolecular forces between molecules, and the higher the melting point and boiling point of the substance. Since breaking or tearing a polymeric material involves either overcoming the intermolecular forces between chains, or actually breaking the covalent bonds between monomers, polymers tend to be durable materials.

One of the simplest synthetic polymers is polyethylene. The polyethylene monomer is ethene (also called ethylene).

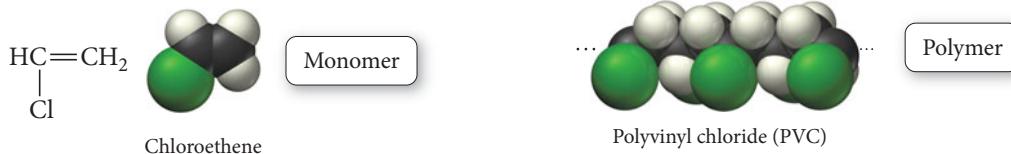
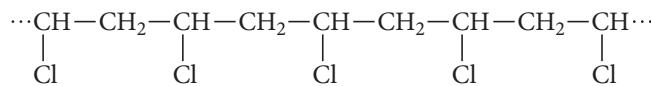


Ethene monomers can react with each other, breaking the double bond between carbons and bonding together to form a long polymer chain.



Polyethylene is the plastic that is used for soda bottles, juice containers, and garbage bags (Figure 20.14 ▶). It is an example of an **addition polymer**, a polymer in which the monomers link together without the elimination of any atoms.

Substituted polyethylenes make up an entire class of polymers. For example, polyvinyl chloride (PVC)—the plastic used to make certain kinds of pipes and plumbing fixtures—is composed of monomers in which a chlorine atom has been substituted for one of the hydrogen atoms in ethene (Figure 20.15 ▶). These monomers (shown here) react to form PVC:



▲ **FIGURE 20.14** Polyethylene Soda and juice bottles are made from polyethylene.



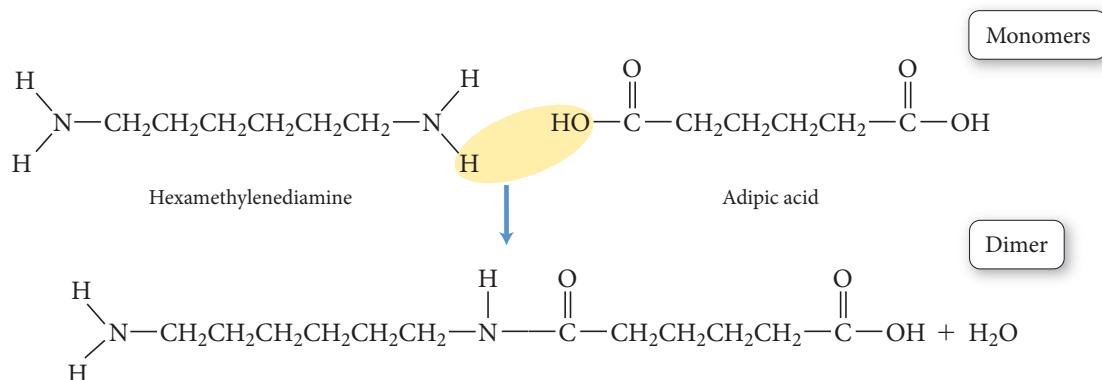
► **FIGURE 20.15** Polyvinyl Chloride Polyvinyl chloride is used for many plastic plumbing supplies, such as pipes and connectors.

TABLE 20.11 Polymers of Commercial Importance

Polymer	Structure	Uses
Addition Polymers		
Polyethylene	$-(\text{CH}_2 - \text{CH}_2)_n$	Films, packaging, bottles
Polypropylene	$\left[\begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \\ \text{CH}_3 \end{array} \right]_n$	Kitchenware, fibers, appliances
Polystyrene	$\left[\begin{array}{c} \text{CH}_2 - \text{CH} \\ \\ \text{C}_6\text{H}_5 \end{array} \right]_n$	Packaging, disposable food containers, insulation
Polyvinyl chloride	$\left[\begin{array}{c} \text{CH}_2 - \text{CH} \\ \\ \text{Cl} \end{array} \right]_n$	Pipe fittings, clear film for meat packaging
Condensation Polymers		
Polyurethane	$\left[\begin{array}{c} \text{C} - \text{NH} - \text{R} - \text{NH} - \text{C} - \text{O} - \text{R}' - \text{O} \\ \qquad \qquad \qquad \\ \text{O} \qquad \qquad \qquad \text{O} \end{array} \right]_n$ R, R' = —CH ₂ —CH ₂ — (for example)	“Foam” furniture stuffing, spray-on insulation, automotive parts, footwear, water-protective coatings
Polyethylene terephthalate (a polyester)	$\left[\begin{array}{c} \text{O} - \text{CH}_2 - \text{CH}_2 - \text{O} - \text{C} - \text{C}_6\text{H}_4 - \text{C} - \text{O} \\ \qquad \qquad \qquad \\ \text{O} \qquad \qquad \qquad \text{O} \end{array} \right]_n$	Tire cord, magnetic tape, apparel, soda bottles
Nylon 6,6	$\left[\begin{array}{c} \text{NH} - (\text{CH}_2)_6 - \text{NH} - \text{C} - (\text{CH}_2)_4 - \text{C} \\ \qquad \qquad \qquad \\ \text{O} \qquad \qquad \qquad \text{O} \end{array} \right]_n$	Home furnishings, apparel, carpet fibers, fish line, polymer blends

Table 20.11 lists several other substituted polyethylene polymers.

Some polymers—called copolymers—consist of two different kinds of monomers. For example, the monomers that compose nylon 6,6 are hexamethylenediamine and adipic acid. These two monomers add together via a condensation reaction as follows:



The product that forms between the reaction of two monomers is called a **dimer**. The polymer (nylon 6,6) forms as the dimer continues to add more monomers. Polymers that eliminate an atom or a small group of atoms during polymerization are called **condensation polymers**. Nylon 6,6 and other similar nylons can be drawn into fibers and used to make consumer products such as panty hose, carpet fibers, and fishing line. Table 20.11 shows other condensation polymers.

CHAPTER IN REVIEW

Self Assessment Quiz

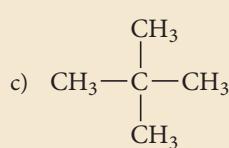
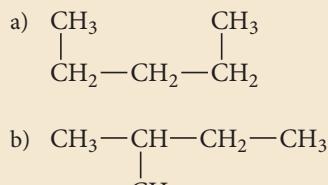
Q1. Which property of carbon is related to its ability to form a large number of compounds?

- a) its tendency to form four covalent bonds
- b) its ability to form double and triple bonds
- c) its tendency to catenate
- d) all of the above

Q2. What is the correct formula for the alkane (nongyclical) containing eight carbon atoms?

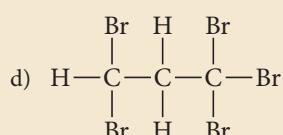
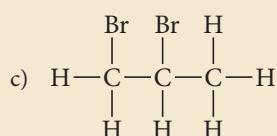
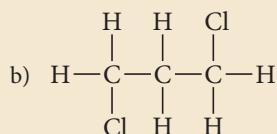
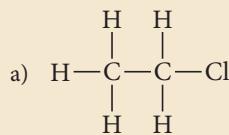
- a) C₈H₁₆
- b) C₈H₁₈
- c) C₈H₁₄
- d) C₈H₈

Q3. Which structure is not an isomer of CH₃CH₂CH₂CH₂CH₃?

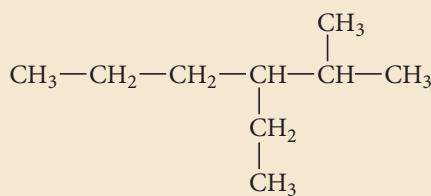


- d) None of the above (all are isomers).

Q4. Which structure can exhibit optical isomerism?

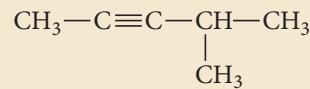


Q5. Name the compound.



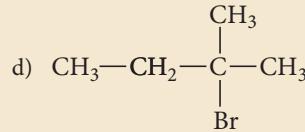
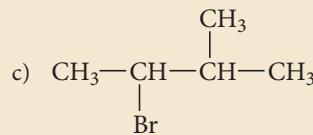
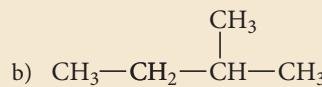
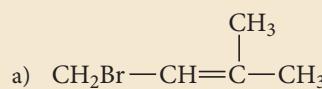
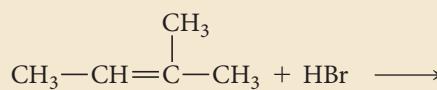
- a) 4-ethyl-5-methylhexane
- b) 3-ethyl-2-methylhexane
- c) 3-ethyl-2-methylnonane
- d) 4-methyl-5ethylhexane

Q6. Name the compound.

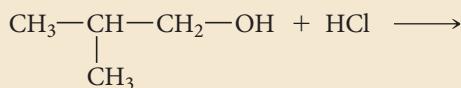


- a) 4-methyl-2-pentyne
- b) 2-methyl-3-pentyne
- c) 2-methyl-3-hexyne
- d) 4-methyl-2-hexyne

Q7. Determine the product of the reaction.

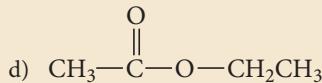
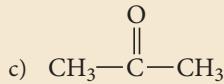
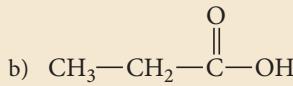


- Q8.** Determine the product of the reaction.

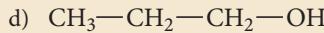
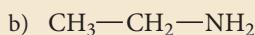
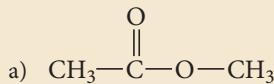


- a) $\text{CH}_3-\underset{\text{Cl}}{\text{CH}}-\text{CH}_3$
- b) $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$
- c) $\text{CH}_3-\underset{\text{CH}_3}{\text{C}}-\text{CH}_2-\text{OH}$
- d) $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{Cl}$

- Q9.** Which compound is an ester?



- Q10.** Which compound is most likely to have a foul odor?



Answers: 1. (d) 2. (b) 3. (a) 4. (c) 5. (b) 6. (a) 7. (d) 8. (d) 9. (d) 10. (b)

Key Terms

Section 20.1

organic molecule (952)
organic chemistry (952)

Section 20.3

alkane (954)
alkene (954)
alkyne (954)
aromatic hydrocarbon (954)
aliphatic hydrocarbon (954)
structural isomers (955)
structural formula (955)
stereoisomers (957)
optical isomers (957)
enantiomers (958)

chiral (958)

dextrorotatory (958)
levorotatory (958)
racemic mixture (958)

Section 20.4

saturated hydrocarbon (960)

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geometric (*cis*–*trans*)
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ether (983)

Section 20.13

amine (984)

Section 20.14

polymer (985)
monomer (985)
addition polymer (985)
dimer (987)
condensation polymer (987)

Key Concepts

Fragrances and Odors (20.1)

► Organic chemistry is the study of organic compounds, which contain carbon (and other elements including hydrogen, oxygen, and nitrogen).

Carbon (20.2)

► Carbon forms more compounds than all the other elements combined for several reasons.

- Carbon's four valence electrons (in conjunction with its size) allow carbon to form four bonds (in the form of single, double, or triple bonds).
- Carbon also has the capacity to catenate, to form long chains, because of the strength of the carbon–carbon bond.

Hydrocarbons (20.3)

- ▶ Organic compounds containing only carbon and hydrogen are called hydrocarbons, the key components of our world's fuels.
- ▶ Hydrocarbons can be divided into four different types: alkanes, alkenes, alkynes, and aromatic hydrocarbons.
- ▶ Stereoisomers are molecules that feature the same atoms bonded in the same order but arranged differently in space. Optical isomerism, a type of stereoisomerism, occurs when two molecules are nonsuperimposable mirror images of one another.

Alkanes (20.4)

- ▶ Alkanes are saturated hydrocarbons—they contain only single bonds and are therefore represented by the generic formula C_nH_{2n+2} . Alkane names always end in *-ane*.

Alkenes and Alkynes (20.5)

- ▶ Alkenes and alkynes are unsaturated hydrocarbons—they contain double bonds (alkenes) or triple bonds (alkynes) and are represented by the generic formulas C_nH_{2n} and C_nH_{2n-2} , respectively.
- ▶ Alkene names end in *-ene* and alkynes end in *-yne*.
- ▶ Because rotation about a double bond is severely restricted, geometric (or cis-trans) isomerism occurs in alkenes.

Hydrocarbon Reactions (20.6)

- ▶ The most common hydrocarbon reaction is probably combustion, in which hydrocarbons react with oxygen to form carbon dioxide and water; this reaction is exothermic and is used to provide most of our society's energy.
- ▶ Alkanes can also undergo substitution reactions, where heat or light causes another atom, commonly a halogen such as bromine, to be substituted for a hydrogen atom.
- ▶ Unsaturated hydrocarbons undergo addition reactions. If the addition reaction is between two unsymmetrical molecules, Markovnikov's rule predicts that the positive end of the polar reagent adds to the carbon with the most hydrogen atoms.

Aromatic Hydrocarbons (20.7)

- ▶ Aromatic hydrocarbons contain six-membered benzene rings represented with alternating single and double bonds that become equivalent through resonance. These compounds are called aromatic because they often produce pleasant fragrances.
- ▶ Because of the stability of the aromatic ring, benzene is more stable than a straight-chain alkene, and it undergoes substitution rather than addition reactions.

Functional Groups (20.8)

- ▶ Characteristic groups of atoms, such as hydroxyl ($—OH$), are called functional groups. Molecules that contain the same functional group have similar chemical and physical properties, and they are referred to as families.

Alcohols (20.9)

- ▶ The family of alcohols contains the $—OH$ group and is named with the suffix *-ol*.
- ▶ Alcohols are commonly used in gasoline, in alcoholic beverages, and in sterilization procedures.

- ▶ Alcohols undergo substitution reactions, in which a substituent such as a halogen replaces the hydroxyl group.
- ▶ Alcohols undergo elimination reactions, in which water is eliminated across a bond to form an alkene, and oxidation or reduction reactions.
- ▶ Alcohols also react with active metals to form alkoxide ions and hydrogen gas.

Aldehydes and Ketones (20.10)

- ▶ Aldehydes and ketones both contain a carbonyl group (a carbon atom double-bonded to oxygen).
- ▶ In aldehydes, the carbonyl group is at the end of a carbon chain, while in ketones it is between two other carbon atoms.
- ▶ Aldehydes are named with the suffix *-al* and ketones with the suffix *-one*.
- ▶ A carbonyl can be formed by the oxidation of an alcohol or reverted to an alcohol by reduction.
- ▶ Like alkenes, carbonyls undergo addition reactions; however, because the carbon–oxygen bond is highly polar, the electronegative component of the reagent always adds to the carbon atom, and the less electronegative part adds to the oxygen.

Carboxylic Acids and Esters (20.11)

- ▶ Carboxylic acids contain a carbonyl group and a hydroxide on the same carbon and are named with the suffix *-oic acid*.
- ▶ Esters contain a carbonyl group bonded to an oxygen atom that is in turn bonded to an R group; they are named with the suffix *-oate*.
- ▶ Carboxylic acids taste sour, such as acetic acid in vinegar, while esters smell sweet.
- ▶ Carboxylic acids react as weak acids but can also form esters through condensation reactions with alcohols.

Ethers (20.12)

- ▶ The family of ethers contains an oxygen atom between two R groups.
- ▶ Ethers are named with the ending *-yl ether*.

Amines (20.13)

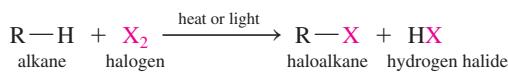
- ▶ Amines are organic compounds that contain nitrogen and are named with the suffix *-amine*.
- ▶ They are known for their terrible odors; the smell of decaying animal flesh is produced by cadaverine.
- ▶ Amines act as weak bases and produce a salt when mixed with a strong acid.
- ▶ The combination of an amine with a carboxylic acid leads to a condensation reaction; this reaction is used by our bodies to produce proteins from amino acids.

Polymers (20.14)

- ▶ Polymers are long, chainlike molecules that consist of repeating units called monomers. They can be natural or synthetic.
- ▶ Polyethylene is an addition polymer, a polymer formed without the elimination of any atoms.
- ▶ Condensation polymers, such as nylon, are formed by the elimination of small groups of atoms.

Key Equations and Relationships

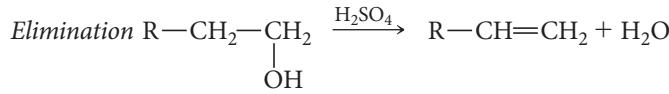
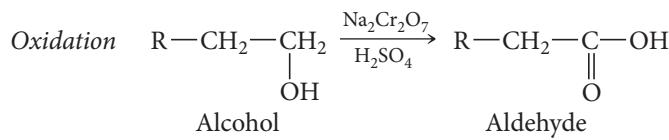
Halogen Substitution Reactions in Alkanes (20.6)



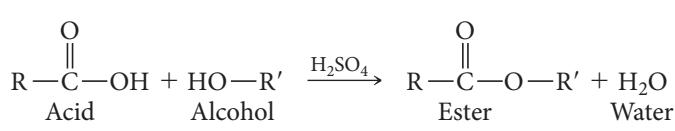
Common Functional Groups (20.8)

Family	General Formula	Condensed General Formula	Example	Name
Alcohols	R — OH	ROH	CH ₃ CH ₂ OH	Ethanol (ethyl alcohol)
Ethers	R — O — R	ROR	CH ₃ OCH ₃	Dimethyl ether
Aldehydes	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R} — \text{C} — \text{H} \end{array}$	RCHO	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C} — \text{C} — \text{H} \end{array}$	Ethanal (acetaldehyde)
Ketones	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R} — \text{C} — \text{R} \end{array}$	RCOR	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C} — \text{C} — \text{CH}_3 \end{array}$	Propanone (acetone)
Carboxylic acids	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R} — \text{C} — \text{OH} \end{array}$	RCOOH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C} — \text{C} — \text{OH} \end{array}$	Acetic acid
Esters	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R} — \text{C} — \text{OR} \end{array}$	RCOOR	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C} — \text{C} — \text{OCH}_3 \end{array}$	Methyl acetate
Amines	$\begin{array}{c} \text{R} \\ \\ \text{R} — \text{N} — \text{R} \end{array}$	R ₃ N	$\begin{array}{c} \text{H} \\ \\ \text{H}_3\text{CH}_2\text{C} — \text{N} — \text{H} \end{array}$	Ethylamine

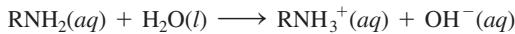
Alcohol Reactions (20.9)



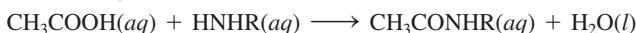
Carboxylic Acid Condensation Reactions (20.11)



Amine Acid-Base Reactions (20.13)



Amine-Carboxylic Acid Condensation Reactions (20.13)



Key Learning Outcomes

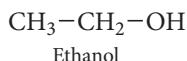
Chapter Objectives	Assessment
Writing Structural Formulas for Hydrocarbons (20.3)	Example 20.1 For Practice 20.1 Exercises 37, 38
Naming Alkanes (20.4)	Examples 20.2, 20.3, 20.4 For Practice 20.2, 20.3, 20.4 Exercises 43, 44
Naming Alkenes and Alkynes (20.5)	Example 20.5 For Practice 20.5 Exercises 53–56



Key Learning Outcomes, continued

Writing Reactions: Addition Reactions (20.6)

Writing Reactions: Alcohols (20.9)



Ethanol

Example 20.6 For Practice 20.6 Exercises 59–62

Example 20.7 For Practice 20.7 Exercises 75, 76

EXERCISES**Review Questions**

1. What kinds of molecules often trigger our sense of smell?
2. What is organic chemistry?
3. What is unique about carbon and carbon-based compounds? Why did life evolve around carbon?
4. Why does carbon form such a large diversity of compounds?
5. Why does silicon exhibit less diversity of compounds than carbon does?
6. Describe the geometry and hybridization about a carbon atom that forms
 - a. four single bonds.
 - b. two single bonds and one double bond.
 - c. one single bond and one triple bond.
7. What are hydrocarbons? What are their main uses?
8. What are the main classifications of hydrocarbons? What are their generic molecular formulas?
9. Explain the differences between a structural formula, a condensed structural formula, a carbon skeleton formula, a ball-and-stick model, and a space-filling model.
10. What are structural isomers? How do the properties of structural isomers differ from one another?
11. What are optical isomers? How do the properties of optical isomers differ from one another?
12. Define each term related to optical isomerism: enantiomers, chiral, dextrorotatory, levorotatory, racemic mixture.
13. What is the difference between saturated and unsaturated hydrocarbons?
14. What are the key differences in the way that alkanes, alkenes, and alkynes are named?
15. Explain geometric isomerism in alkenes. How do the properties of geometric isomers differ from one another?
16. Describe and provide an example of a hydrocarbon combustion reaction.
17. What kinds of reactions are common to alkanes? List an example of each.
18. Describe each kind of reaction.
 - a. substitution reaction
 - b. addition reaction
 - c. elimination reaction
19. What kinds of reactions are common to alkenes? Give an example of each.
20. Explain Markovnikov's rule and give an example of a reaction to which it applies.
21. What is the structure of benzene? What are the different ways in which this structure is represented?
22. What kinds of reactions are common to aromatic compounds? Provide an example of each.
23. What is a functional group? List some examples.
24. What is the generic structure of alcohols? Write the structures of two specific alcohols.
25. Explain oxidation and reduction with respect to organic compounds.
26. What kinds of reactions are common to alcohols? Provide an example of each.
27. What are the generic structures for aldehydes and ketones? Write a structure for a specific aldehyde and ketone.
28. What kind of reactions are common to aldehydes and ketones? List an example of each.
29. What are the generic structures for carboxylic acids and esters? Write a structure for a specific carboxylic acid and ester.
30. What kind of reactions are common to carboxylic acids and esters? Provide an example of each.
31. What is the generic structure of ethers? Write the structures of two specific ethers.
32. What is the generic structure of amines? Write the structures of two specific amines.
33. What is a polymer? What is the difference between a polymer and a copolymer?
34. How do an addition polymer and a condensation polymer differ from each other?

Problems by Topic

Hydrocarbons

35. Based on the molecular formula, determine whether each compound is an alkane, alkene, or alkyne. (Assume that the hydrocarbons are noncyclical and there is no more than one multiple bond.)

- a. C_5H_{12} b. C_3H_6
c. C_7H_{12} d. $\text{C}_{11}\text{H}_{22}$

36. Based on the molecular formula, determine whether each compound is an alkane, alkene, or alkyne. (Assume that the hydrocarbons are noncyclical and there is no more than one multiple bond.)

- a. C_8H_{16} b. C_4H_6
c. C_7H_{16} d. C_2H_2

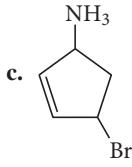
37. Write structural formulas for each of the nine structural isomers of heptane.

38. Write structural formulas for any 6 of the 18 structural isomers of octane.

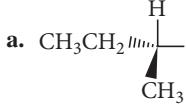
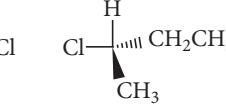
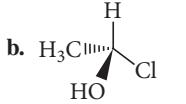
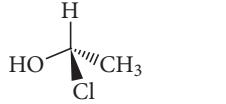
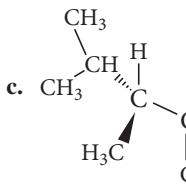
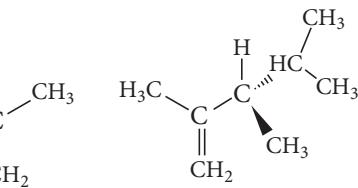
39. Determine whether each compound exhibits optical isomerism.

- a. CCl_4
b. $\text{CH}_3\text{---CH}_2\text{---CH}(\text{CH}_3)\text{---CH}_2\text{---CH}_2\text{---CH}_3$
c. $\text{CH}_3\text{---C}(\text{NH}_2)\text{---Cl}$
d. $\text{CH}_3\text{CHClCH}_3$

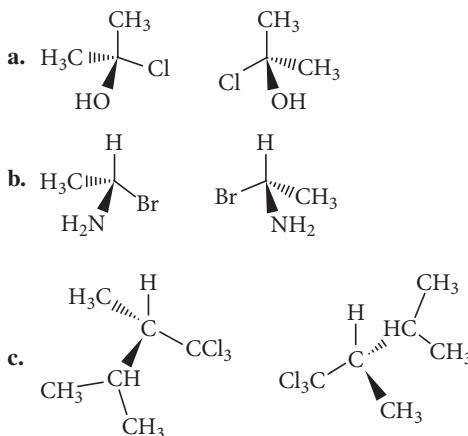
40. Determine whether each compound exhibits optical isomerism.

- a. $\text{CH}_3\text{CH}_2\text{CHClCH}_3$ b. $\text{CH}_3\text{CCl}_2\text{CH}_3$
c. 
d. $\text{CH}_3\text{---C}(\text{CH}_2\text{---CH}_2\text{---CH}_2\text{---OH})\text{---C}(=\text{O})\text{---OH}$

41. Determine whether the molecules in each pair are the same or enantiomers.

- a.  
b.  
c.  

42. Determine whether the molecules in each pair are the same or enantiomers.



Alkanes

43. Name each alkane.

- a. $\text{CH}_3\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---CH}_3$
b. $\text{CH}_3\text{---CH}_2\text{---CH}(\text{CH}_3)\text{---CH}_3$
c. $\text{CH}_3\text{---CH}(\text{CH}_3)\text{---CH}_2\text{---CH}(\text{CH}_3)\text{---CH}_2\text{---CH}_3$
d. $\text{CH}_3\text{---CH}(\text{CH}_3)\text{---CH}_2\text{---CH}(\text{CH}_3)\text{---CH}_2\text{---CH}_3$

44. Name each alkane.

- a. $\text{CH}_3\text{---CH}(\text{CH}_3)\text{---CH}_3$
b. $\text{CH}_3\text{---CH}(\text{CH}_3)\text{---CH}_2\text{---CH}(\text{CH}_3)\text{---CH}_2\text{---CH}_3$
c. $\text{CH}_3\text{---C}(\text{CH}_3\text{---CH}_3)\text{---C}(\text{CH}_3\text{---CH}_3)\text{---CH}_3$
d. $\text{CH}_3\text{---CH}(\text{CH}_3)\text{---CH}_2\text{---CH}(\text{CH}_3)\text{---CH}_2\text{---CH}_2\text{---CH}_3$

45. Draw a structure for each alkane.

- 3-ethylhexane
- 3-ethyl-3-methylpentane
- 2,3-dimethylbutane
- 4,7-diethyl-2,2-dimethylnonane

46. Draw a structure for each alkane.

- 2,2-dimethylpentane
- 3-isopropylheptane
- 4-ethyl-2,2-dimethylhexane
- 4,4-diethyloctane

47. Complete and balance each hydrocarbon combustion reaction.

- $\text{CH}_3\text{CH}_2\text{CH}_3 + \text{O}_2 \longrightarrow$
- $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{O}_2 \longrightarrow$
- $\text{CH}\equiv\text{CH} + \text{O}_2 \longrightarrow$

48. Complete and balance each hydrocarbon combustion reaction.

- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 + \text{O}_2 \longrightarrow$
- $\text{CH}_2=\text{CHCH}_3 + \text{O}_2 \longrightarrow$
- $\text{CH}\equiv\text{CCH}_2\text{CH}_3 + \text{O}_2 \longrightarrow$

49. List all the possible products for each alkane substitution reaction. (Assume monosubstitution.)

- $\text{CH}_3\text{CH}_3 + \text{Br}_2 \longrightarrow$
- $\text{CH}_3\text{CH}_2\text{CH}_3 + \text{Cl}_2 \longrightarrow$
- $\text{CH}_2\text{Cl}_2 + \text{Br}_2 \longrightarrow$
- $\text{CH}_3-\underset{\substack{| \\ \text{CH}_3}}{\text{CH}}-\text{CH}_3 + \text{Cl}_2 \longrightarrow$

50. List all the possible products for each alkane substitution reaction. (Assume monosubstitution.)

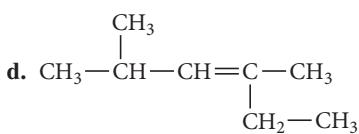
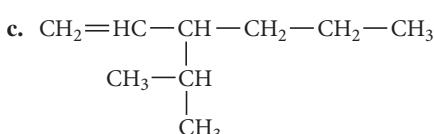
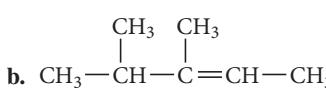
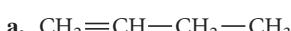
- $\text{CH}_4 + \text{Cl}_2 \longrightarrow$
- $\text{CH}_3\text{CH}_2\text{Br} + \text{Br}_2 \longrightarrow$
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 + \text{Cl}_2 \longrightarrow$
- $\text{CH}_3\text{CHBr}_2 + \text{Br}_2 \longrightarrow$

Alkenes and Alkynes

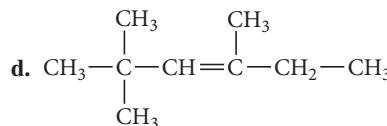
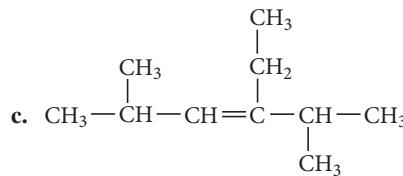
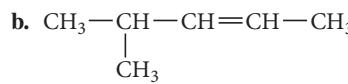
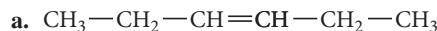
51. Write structural formulas for each of the possible isomers of *n*-hexene that are formed by moving the position of the double bond.

52. Write structural formulas for each of the possible isomers of *n*-pentyne that are formed by moving the position of the triple bond.

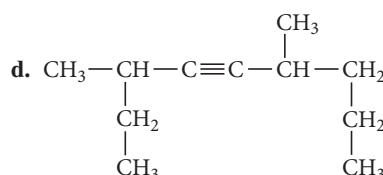
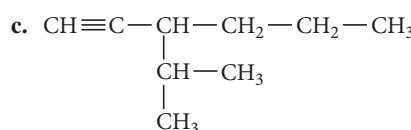
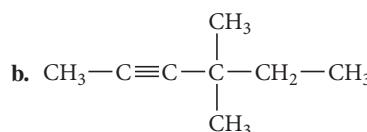
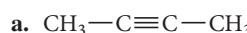
53. Name each alkene.



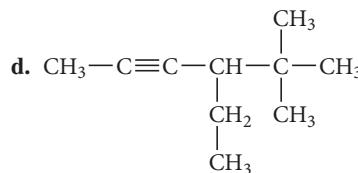
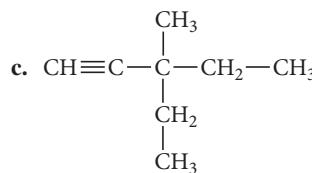
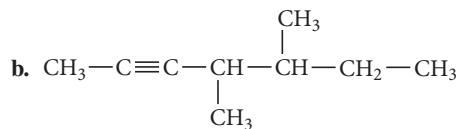
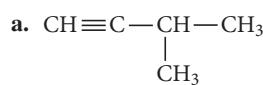
54. Name each alkene.



55. Name each alkyne.



56. Name each alkyne.



57. Draw the correct structure for each compound.

- 4-octyne
- 3-nonen
- 3,3-dimethyl-1-pentyne
- 5-ethyl-3,6-dimethyl-2-heptene

58. Draw the correct structure for each compound.

- 2-hexene
- 1-heptyne
- 4,4-dimethyl-2-hexene
- 3-ethyl-4-methyl-2-pentene

59. List the products of each alkene addition reaction.

- $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3 + \text{Cl}_2 \longrightarrow$
- $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}=\text{CH}-\text{CH}_3 + \text{HBr} \longrightarrow$
- $\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_3 + \text{Br}_2 \longrightarrow$
- $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}=\text{C}-\text{CH}_3 + \text{HCl} \longrightarrow$

60. What are the products of each alkene addition reaction?

- $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}=\text{CH}_2 + \text{Br}_2 \longrightarrow$
- $\text{CH}_2=\text{CH}-\text{CH}_3 + \text{Cl}_2 \longrightarrow$
- $\text{CH}_3-\underset{\text{CH}_3}{\text{C}}-\text{CH}=\text{CH}_2 + \text{HCl} \longrightarrow$
- $\text{CH}_3-\underset{\text{CH}_2-\text{CH}_3}{\text{CH}}-\text{CH}=\text{C}-\text{CH}_3 + \text{HBr} \longrightarrow$

61. Complete each hydrogenation reaction.

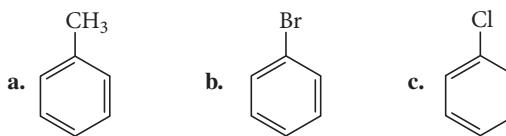
- $\text{CH}_2=\text{CH}-\text{CH}_3 + \text{H}_2 \xrightarrow{\text{catalyst}}$
- $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}=\text{CH}_2 + \text{H}_2 \xrightarrow{\text{catalyst}}$
- $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\underset{\text{CH}_3}{\text{C}}=\text{CH}_2 + \text{H}_2 \xrightarrow{\text{catalyst}}$

62. Complete each hydrogenation reaction.

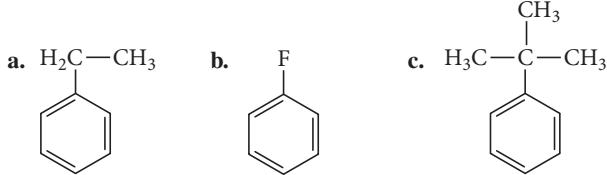
- $\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2 + \text{H}_2 \xrightarrow{\text{catalyst}}$
- $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\underset{\text{CH}_3}{\text{C}}=\text{C}-\text{CH}_3 + \text{H}_2 \xrightarrow{\text{catalyst}}$
- $\text{CH}_3-\text{CH}_2-\underset{\text{CH}_3}{\text{C}}=\text{CH}_2 + \text{H}_2 \xrightarrow{\text{Catalyst}}$

Aromatic Hydrocarbons

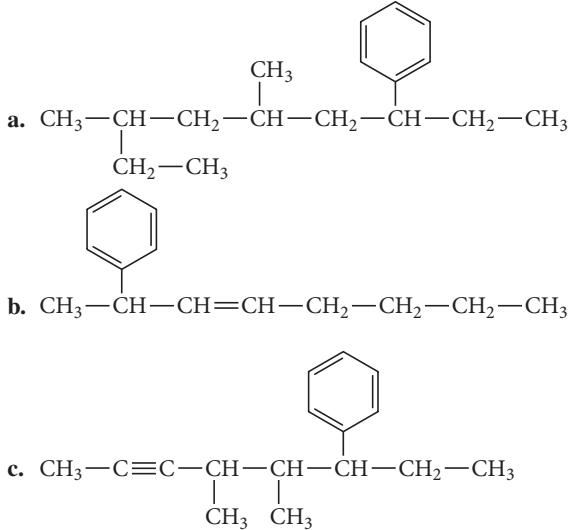
63. Name each monosubstituted benzene.



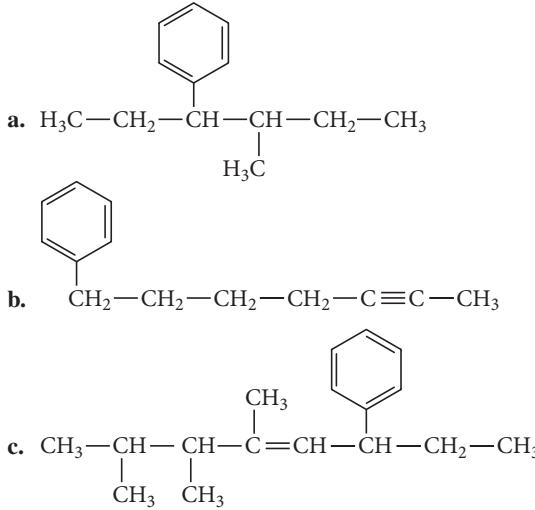
64. Name each monosubstituted benzene.



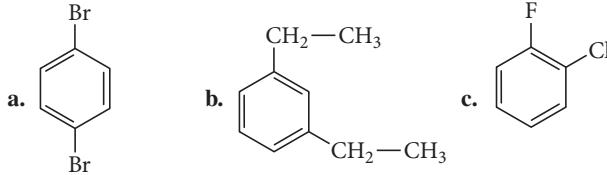
65. Name each compound in which the benzene ring is best treated as a substituent.



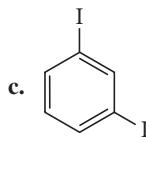
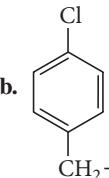
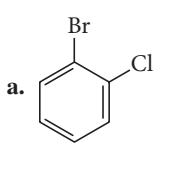
66. Name each compound in which the benzene ring is best treated as a substituent.



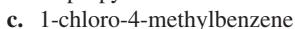
67. Name each disubstituted benzene.



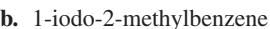
68. Name each disubstituted benzene.



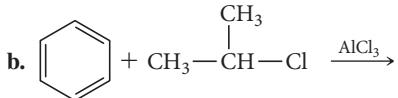
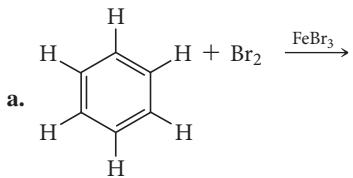
69. Draw the structure for each compound.



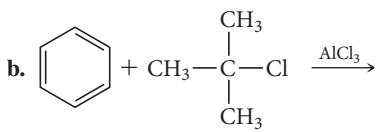
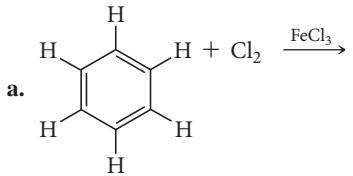
70. Draw the structure for each compound.



71. What are the products of each aromatic substitution reaction?

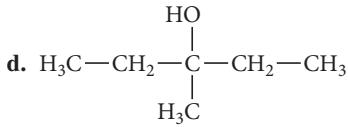
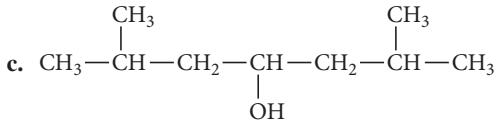
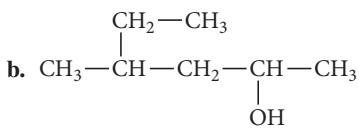
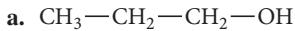


72. What are the products of each aromatic substitution reaction?

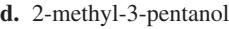
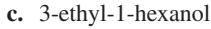
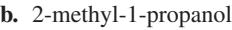
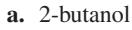


Alcohols

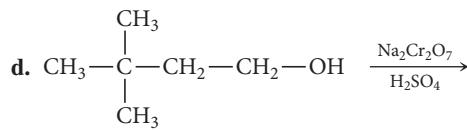
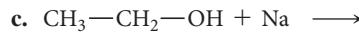
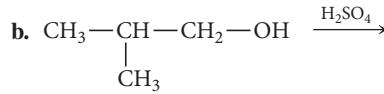
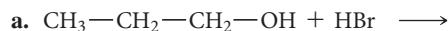
73. Name each alcohol.



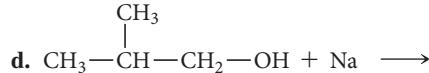
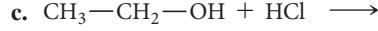
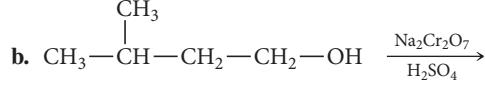
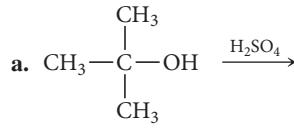
74. Draw the structure for each alcohol.



75. List the products of each alcohol reaction.

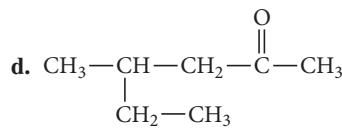
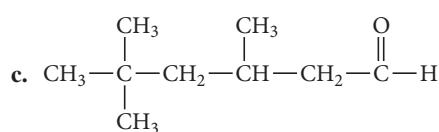
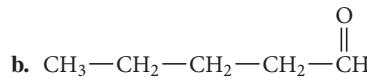
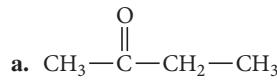


76. List the products of each alcohol reaction.

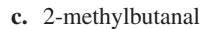


Aldehydes and Ketones

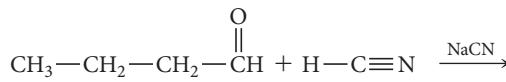
77. Name each aldehyde or ketone.



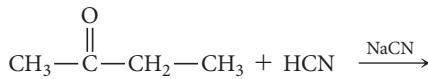
78. Draw the structure of each aldehyde or ketone.



79. Determine the product of the addition reaction.

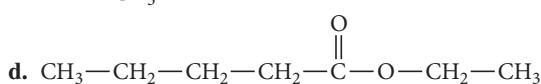
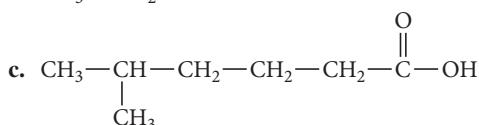
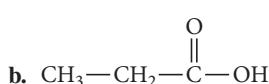
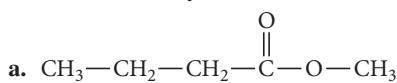


80. Determine the product of the addition reaction.



Carboxylic Acids and Esters

81. Name each carboxylic acid or ester.



82. Draw the structure of each carboxylic acid or ester.

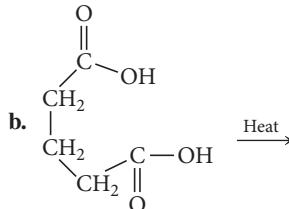
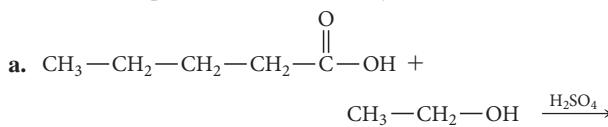
a. pentanoic acid

b. methyl hexanoate

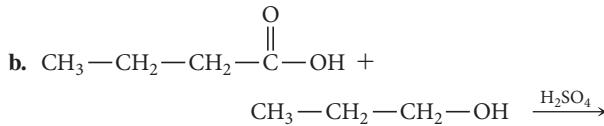
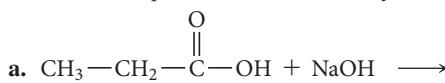
c. 3-ethylheptanoic acid

d. butyl ethanoate

83. Determine the products of each carboxylic acid reaction.



84. Determine the products of each carboxylic acid reaction.



Ethers

85. Name each ether.

a. $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—O—CH}_2\text{—CH}_3$

b. $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—O—CH}_2\text{—CH}_3$

c. $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—O—CH}_2\text{—CH}_2\text{—CH}_3$

d. $\text{CH}_3\text{—CH}_2\text{—O—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_3$

86. Draw the structure for each ether.

a. ethyl propyl ether

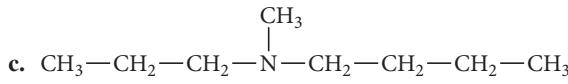
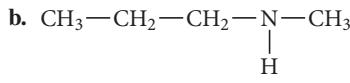
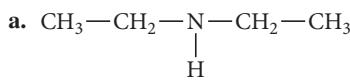
b. dibutyl ether

c. methyl hexyl ether

d. dipentyl ether

Amines

87. Name each amine.



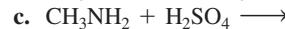
88. Draw the structure for each amine.

a. isopropylamine

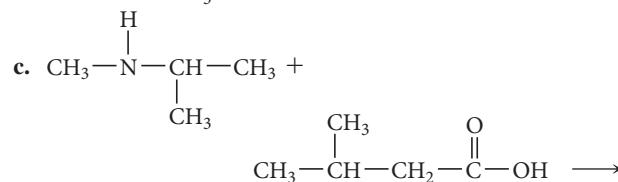
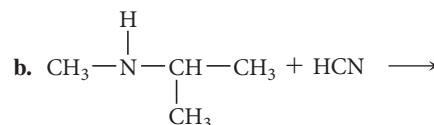
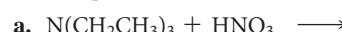
b. triethylamine

c. butylethylamine

89. Classify each amine reaction as acid–base or condensation and list its products.

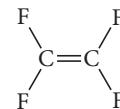


90. List the products of each amine reaction.

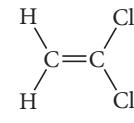


Polymers

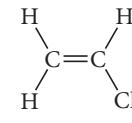
91. Teflon is an addition polymer formed from the monomer shown here. Draw the structure of the polymer.



92. Saran, the polymer used to make saran wrap, is an addition polymer formed from two monomers—vinylidene chloride and vinyl chloride. Draw the structure of the polymer. (Hint: The monomers alternate.)

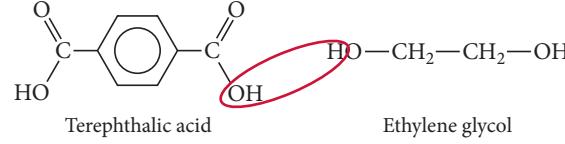


Vinylidene chloride



Vinyl chloride

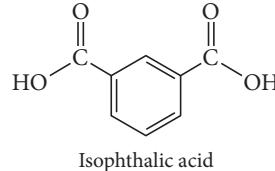
93. One kind of polyester is a condensation copolymer formed from terephthalic acid and ethylene glycol. Draw the structure of the dimer and circle the ester functional group. [Hint: Water (circled) is eliminated when the bond between the monomers forms.]



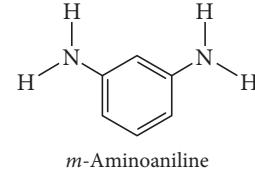
Terephthalic acid

Ethylene glycol

94. Nomex, a condensation copolymer used by firefighters because of its flame-resistant properties, forms from isophthalic acid and *m*-aminoaniline. Draw the structure of the dimer. (Hint: Water is eliminated when the bond between the monomers forms.)



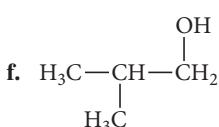
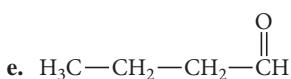
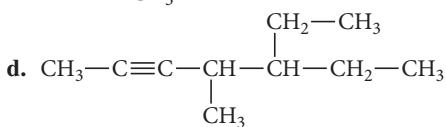
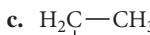
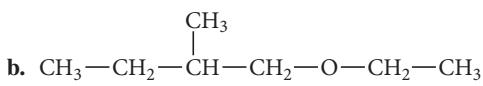
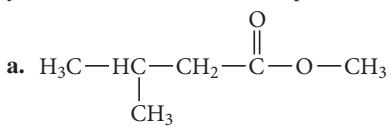
Isophthalic acid



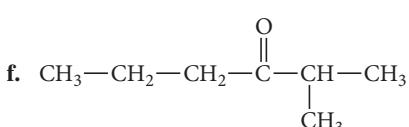
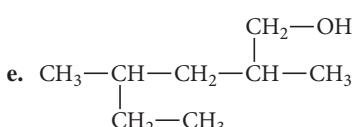
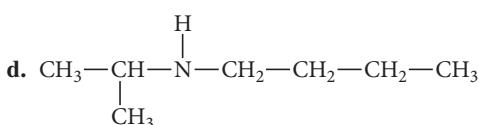
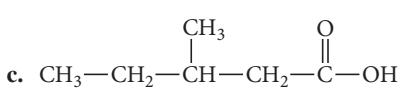
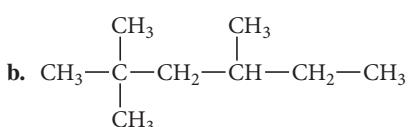
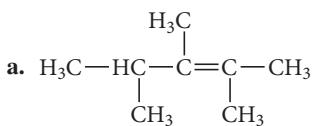
m-Aminoaniline

Cumulative Problems

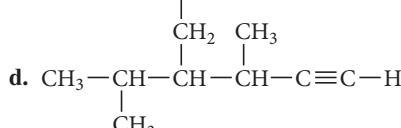
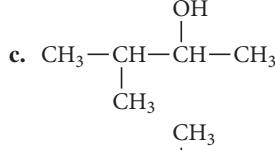
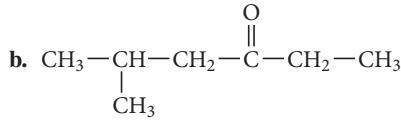
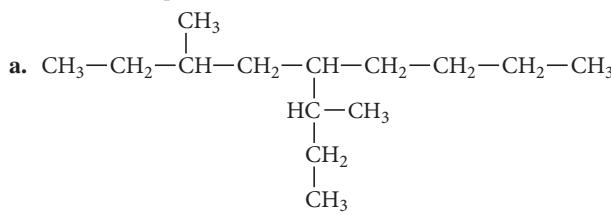
- 95.** Identify each organic compound as an alkane, alkene, alkyne, aromatic hydrocarbon, alcohol, ether, aldehyde, ketone, carboxylic acid, ester, or amine, and provide a name for the compound.



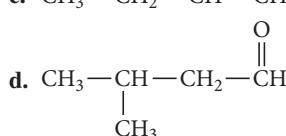
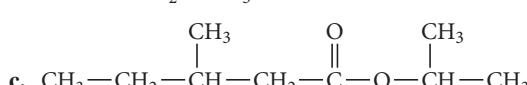
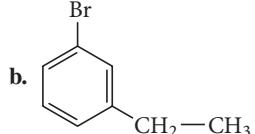
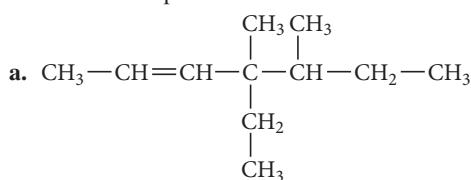
- 96.** Identify each organic compound as an alkane, alkene, alkyne, aromatic hydrocarbon, alcohol, ether, aldehyde, ketone, carboxylic acid, ester, or amine, and provide a name for the compound.



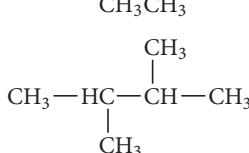
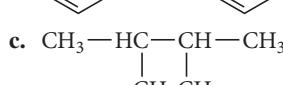
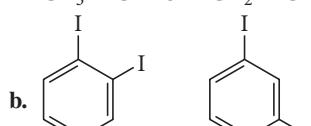
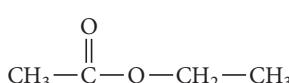
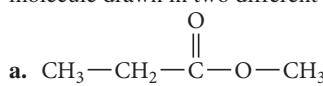
- 97.** Name each compound.



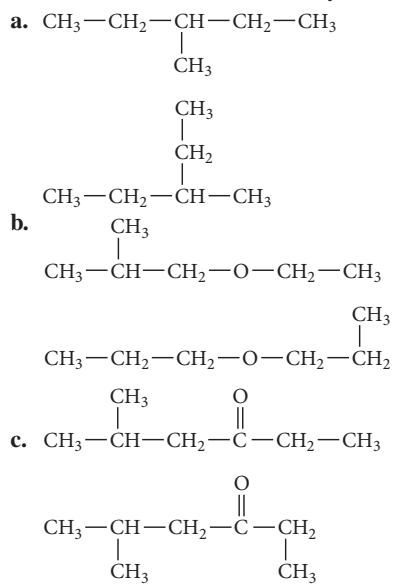
- 98.** Name each compound.



- 99.** Determine whether the two structures are isomers or the same molecule drawn in two different ways.



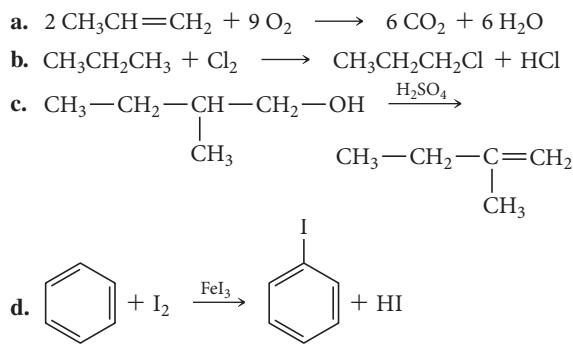
100. Determine whether the two structures are isomers or the same molecule drawn two different ways.



101. What minimum amount of hydrogen gas, in grams, is required to completely hydrogenate 15.5 kg of 2-butene?

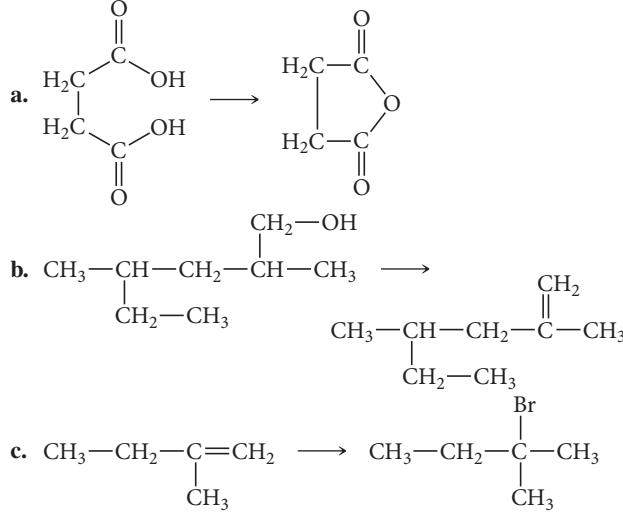
102. How many kilograms of CO_2 does the complete combustion of 3.8 kg of *n*-octane produce?

103. Classify each organic reaction as combustion, alkane substitution, alkene addition or hydrogenation, aromatic substitution, or alcohol substitution, elimination, or oxidation.

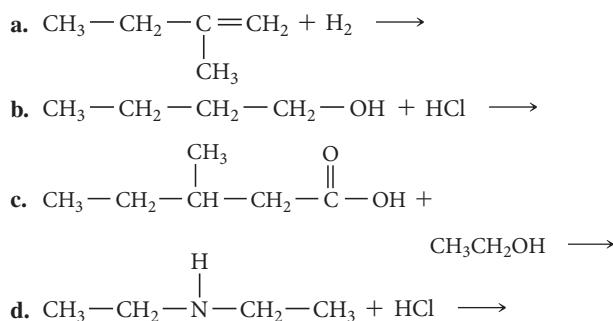


Challenge Problems

111. Determine the one or two steps it takes to get from the starting material to the product using the reactions found in this chapter.



104. Determine the products of each reaction.



105. Draw the structure that corresponds to each name and indicate which structures can exist as stereoisomers.

- a. 3-methyl-1-pentene
b. 3,5-dimethyl-2-hexene
c. 3-propyl-2-hexene

106. Identify the two compounds that display stereoisomerism and draw their structures.

- a. 3-methyl-3-pentanol
b. 2-methyl-2-pentanol
c. 3-methyl-2-pentanol
d. 2-methyl-3-pentanol
e. 2,4-dimethyl-3-pentanol

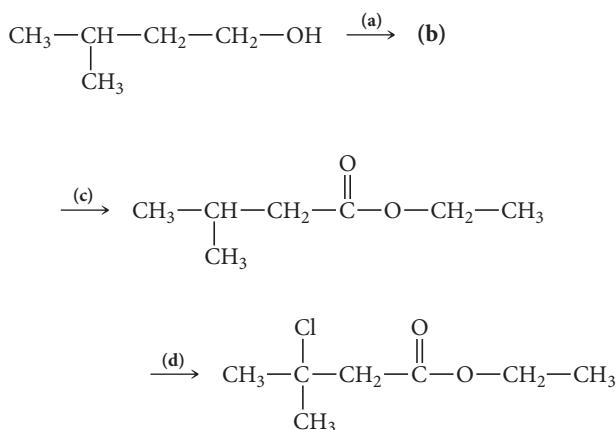
107. There are 11 structures (ignoring stereoisomerism) with the formula $\text{C}_4\text{H}_8\text{O}$ that have no carbon branches. Draw the structures and identify the functional groups in each.

108. There are eight structures with the formula $\text{C}_3\text{H}_7\text{NO}$ in which the O is part of a carbonyl group. Draw the structures and identify the functional groups in each.

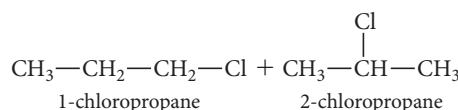
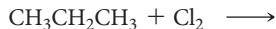
109. Explain why carboxylic acids are much stronger acids than alcohols.

110. The hydrogen at C-1 of 1-butyne is much more acidic than the one at C-1 in 1-butene. Explain.

112. Given the following synthesis of ethyl 3-chloro-3-methylbutanoate, fill in the missing intermediates or reactants.



- 113.** For the chlorination of propane, the two isomers shown here are possible.



Propane has six hydrogen atoms on terminal carbon atoms—called primary (1°) hydrogen atoms—and two hydrogen atoms on the interior carbon atom—called secondary (2°) hydrogen atoms.

- a. If the two different types of hydrogen atoms were equally reactive, what ratio of 1-chloropropane to 2-chloropropane would we expect as monochlorination products?
 - b. The result of a reaction yields 55% 2-chloropropane and 45% 1-chloropropane. What can we conclude about the relative reactivity of the two different kinds of hydrogen atoms? Determine a ratio of the reactivity of one type of hydrogen atom to the other.
- 114.** There are two isomers of C_4H_{10} . Suppose that each isomer is treated with Cl_2 and the products that have the composition $\text{C}_4\text{H}_8\text{Cl}_2$ are isolated. Find the number of different products that form from each of the original C_4H_{10} compounds. Do not consider optical isomerism.

- 115.** Identify the compounds formed in the previous problem that are chiral.

- 116.** Nitromethane has the formula CH_3NO_2 , with the N bonded to the C and without O—O bonds. Draw its two most important contributing structures.

- a. What is the hybridization of the C and how many hybrid orbitals are in the molecule?
- b. What is the shortest bond?
- c. Between which two atoms is the strongest bond found?
- d. Predict whether the HCH bond angles are greater or less than 109.5° and justify your prediction.

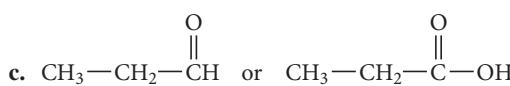
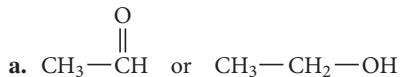
- 117.** Free radical fluorination of methane is uncontrollably violent and free radical iodination of methane is a very poor reaction. Explain these observations in light of bond energies.

- 118.** There are two compounds with the formula, C_3H_6 , one of which does not have a multiple bond. Draw its structure and explain why it is much less stable than the isomer with the double bond.

- 119.** Consider molecules that have two carbons and two chlorines. Draw the structures of three of these with no dipole moment and two with a dipole moment.

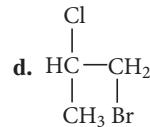
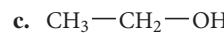
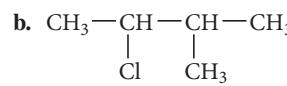
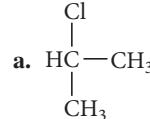
Conceptual Problems

- 120.** Pick the more oxidized structure from each pair.



- 121.** Draw the structure and name a compound with the formula C_8H_{18} that forms only one product with the formula $\text{C}_8\text{H}_{17}\text{Br}$ when it is treated with Br_2 .

- 122.** Determine whether each structure is chiral.



Answers to Conceptual Connections

Organic Structures

- 20.1 (d)** The others are simply the same structure drawn in slightly different ways.

Optical Isomers

- 20.2 (b)** This structure is the only one that contains a carbon atom (the one on the left) with four different substituent groups attached (a Br atom, a Cl atom, an H atom, and a CH_3 group).

Oxidation

- 20.3 (c, d, a, b)** Oxidation includes the gain of oxygen or the loss of hydrogen.

21

Biochemistry

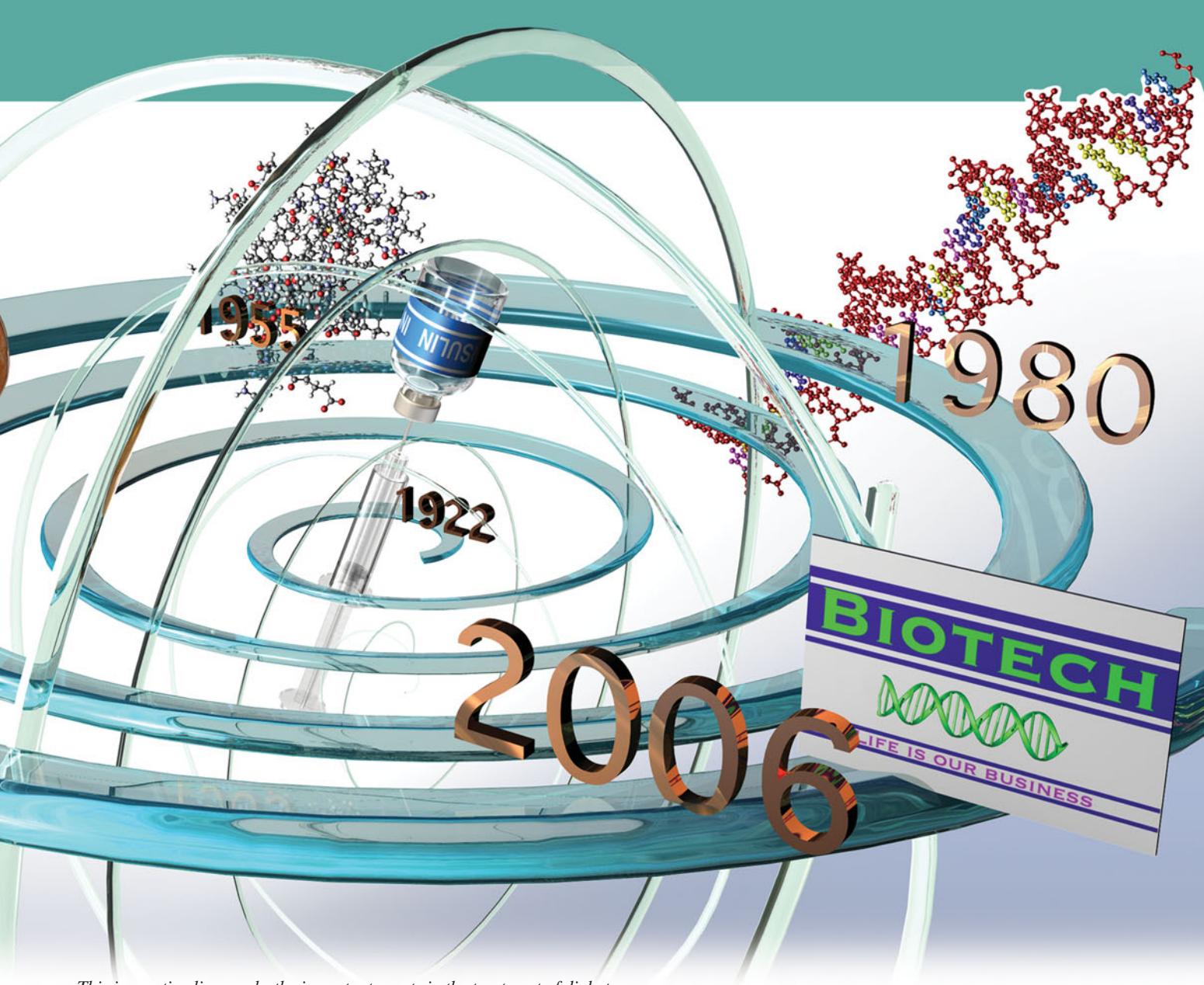
We've discovered the secret of life.

—Francis H. C. Crick (1916–2004)

21.1	Diabetes and the Synthesis of Human Insulin	1001
21.2	Lipids	1002
21.3	Carbohydrates	1006
21.4	Proteins and Amino Acids	1010
21.5	Protein Structure	1014
21.6	Nucleic Acids: Blueprints for Proteins	1018
21.7	DNA Replication, the Double Helix, and Protein Synthesis	1022
Key Learning Outcomes 1027		

In **CHAPTER 20**, we examined organic chemistry and learned about the different types of organic compounds and their structures and chemistry. In this chapter, we turn to biochemical compounds, those organic compounds important in living organisms. Biochemistry—the area of study at the interface between chemistry and biology that strives to understand living organisms at the molecular level—exploded in the second half of the twentieth century. That explosion began with the discovery of the structure of DNA in 1953 by James D. Watson and Francis H. C. Crick and continues to this day, most recently marked by the 2003 completion of the Human Genome Project, which succeeded in mapping the 3 billion base pairs within the DNA of humans. The benefits of biochemistry to humankind are numerous, ranging from a better understanding of illnesses and better drugs to cure them to a better understanding of ourselves and our origins.





This image timeline marks the important events in the treatment of diabetes.

21.1 Diabetes and the Synthesis of Human Insulin

Diabetes afflicts over 16 million people in the United States alone. Today, it is a chronic but generally manageable ailment; at the beginning of the twentieth century, however, it was often fatal. The most dangerous form, type 1 diabetes, develops when the pancreas does not make enough *insulin*, a protein that promotes the absorption of glucose from the blood into cells, where glucose is used for energy. Consequently, people with diabetes have high blood-sugar levels that can lead to a number of complications, including heart disease, blindness, and kidney failure. Before 1922, the only option diabetics had was to control their blood-sugar levels through diet, but this was often not enough to overcome the disease.

Important advances throughout the twentieth century dramatically changed the prognosis for diabetics. The initial breakthrough came in 1922, when researchers first injected insulin from animal sources into a diabetic. The insulin worked, resulting in a nearly complete recovery for the patient. Within a year, insulin harvested from the pancreases of slaughtered pigs became widely available, and, for many patients, diabetes became a long-term manageable disease. However, insulin taken from pigs and cattle is not identical to human insulin, and some patients do not tolerate the animal insulin as well as others.

In 1955, Frederick Sanger discovered the detailed chemical structure of human insulin. As we will see later in this chapter, proteins are biological molecules composed of repeating units called amino acids (of which there are 20 different types in humans). Sanger was able to determine the specific sequence of amino acids in human insulin, work for which he received the 1958 Nobel Prize in Chemistry. Knowing the amino acid sequence allowed researchers to synthesize human insulin in the laboratory by 1963. Unfortunately, they could not make sufficient amounts to meet the needs of diabetics.

The growing field of biotechnology, however, allowed a fledgling company called Genentech to synthesize human insulin on a large scale by the early 1980s. Researchers at Genentech were able to insert the human *gene* for insulin—the blueprint that determines how insulin is synthesized in humans—into the DNA of bacterial cells. When the bacteria reproduced in culture, they made copies of the inserted human insulin gene and passed it on to their offspring. Furthermore, as the growing bacterial culture synthesized the bacterial proteins that it needed to grow and survive, it also synthesized human insulin. In other words, researchers at Genentech were able to get bacteria to produce human insulin for them! The ability to synthesize human insulin in this way revolutionized the treatment of diabetes, resulting in better health and extended lives for hundreds of millions of people who suffer from this disease.

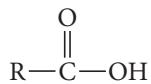
The study of the chemistry occurring in living organisms is **biochemistry**, the topic of this chapter. Many biologically important molecules are very large and complex—they are *macromolecules*. However, understanding their structures is not as difficult as you might imagine, because most of them consist of much smaller, simpler components linked together into long chains (*polymers*). In this chapter, we divide our study of biochemistry along the lines of the major chemical components of cells: lipids, carbohydrates, proteins, and nucleic acids.

21.2 Lipids

Lipids are the chemical components of the cell that are insoluble in water but soluble in non-polar solvents. Fatty acids, fats, oils, phospholipids, glycolipids, and steroids are all lipids. Their insolubility in water makes it possible for lipids to compose the structural components of cell membranes, which separate the aqueous interior of the cell from its aqueous environment in the body. Lipids also play a role in long-term energy storage and insulation.

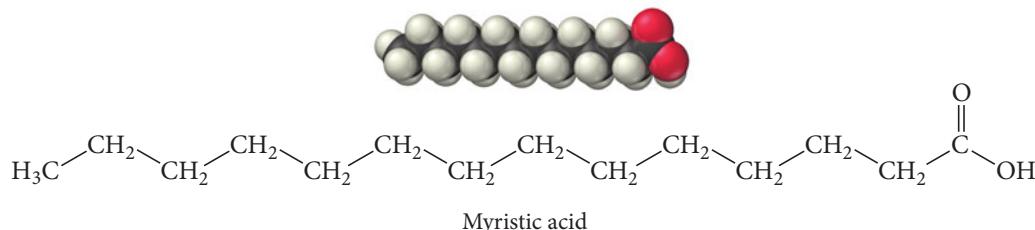
Fatty Acids

One type of lipid is the **fatty acid**, a carboxylic acid (see Section 20.11) with a long hydrocarbon tail. The general structure for a fatty acid contains the carboxylic acid group.

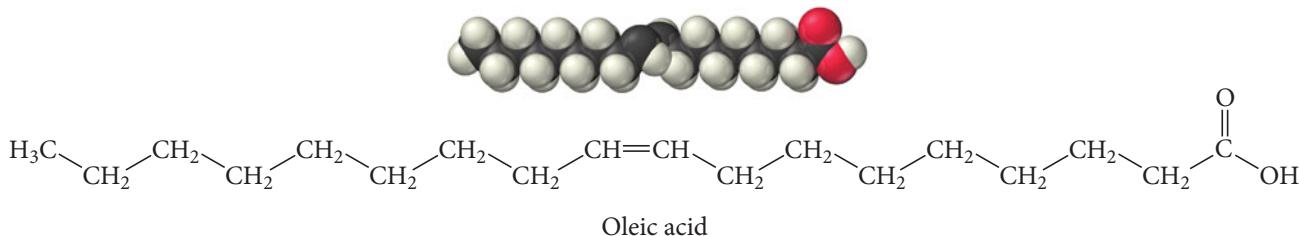


Fatty acid general structure

The R on the left side of the structure represents a hydrocarbon chain containing 3 to 19 carbon atoms. Fatty acids differ only in their R group.



Myristic acid, found in butterfat and in coconut oil, has the R group $\text{CH}_3(\text{CH}_2)_{12}$. Myristic acid is a *saturated* fatty acid: its carbon chain has no double bonds. Other fatty acids—called *monounsaturated* or *polyunsaturated* fatty acids—have one or more double bonds in their carbon chains. For example, oleic acid—found in olive oil, peanut oil, and human fat—is a monounsaturated fatty acid.



The long hydrocarbon tails of fatty acids make them insoluble in water. Table 21.1 lists several fatty acids, some common sources for each, and their melting points. Notice that the melting points of the fatty acids *increase* as their carbon chain lengths increase. The longer the chains, the greater the dispersion forces between adjacent molecules in the solid state, and the higher the melting point. Notice also that the melting points *decrease* with the presence of double bonds. For example, stearic acid and oleic acid have the same number of carbon atoms, but stearic acid melts at 70 °C and oleic acid melts at 4 °C. The double bond puts a “kink” in the carbon chain that makes it more difficult for neighboring molecules to interact over the entire length of the chain (Figure 21.1 ▶), thus lowering the melting point.

Dispersion forces are discussed in Section 11.3.

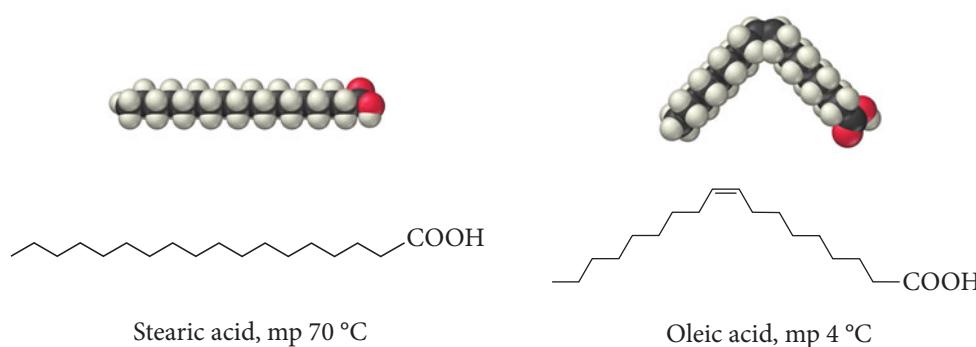
TABLE 21.1 Fatty Acids

Saturated Fatty Acids				
Name	Number of Carbons	mp (°C)	Structure	Sources
Butyric acid	4	−7.9	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	Milk fat
Caproic acid	10	31	$\text{CH}_3(\text{CH}_2)_8\text{COOH}$	Milk fat, whale oil
Myristic acid	14	59	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$	Butterfat, coconut oil
Palmitic acid	16	64	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	Beef fat, butterfat
Stearic acid	18	70	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	Beef fat, butterfat

Unsaturated Fatty Acids

Name	Number of Carbons	Number of Double Bonds	mp (°C)	Structure	Sources
Oleic acid	18	1	4	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	Olive oil, peanut oil
Linoleic acid	18	2	−5	$\text{CH}_3(\text{CH}_2)_4(\text{CH}=\text{CHCH}_2)_2(\text{CH}_2)_6\text{COOH}$	Linseed oil, corn oil
Linolenic acid	18	3	−11	$\text{CH}_3\text{CH}_2(\text{CH}=\text{CHCH}_2)_3(\text{CH}_2)_6\text{COOH}$	Linseed oil, corn oil

The Effect of Unsaturation

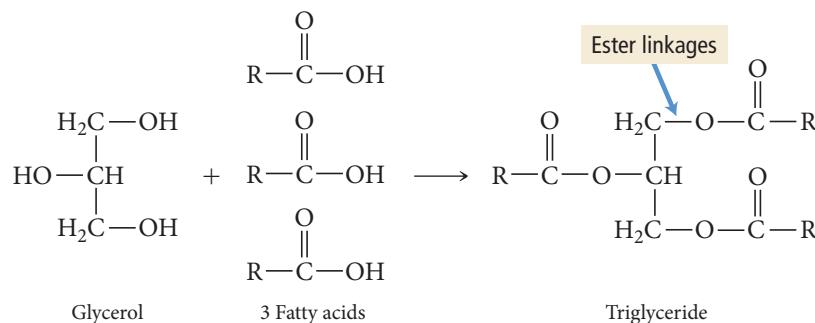


◀ **FIGURE 21.1** The Effect of Unsaturation A double bond results in a bend in the carbon chain of a fatty acid or fat that makes it more difficult for neighboring molecules to interact over the entire length of the carbon chain, thus lowering the melting point.

Fats and Oils

We discussed the general structure of esters in Section 20.11.

Fats and oils are **triglycerides**, triesters composed of glycerol with three fatty acids attached. Triglycerides form when a glycerol molecule reacts with three fatty acids.

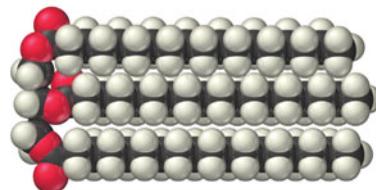
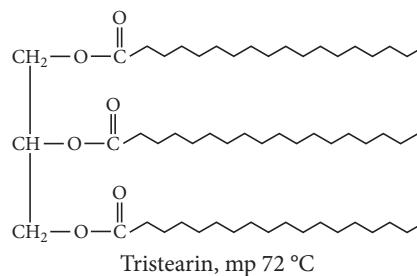


The bonds that join the glycerol to the fatty acids are called **ester linkages**. For example, tristearin—the main component of beef fat—forms from the reaction of glycerol and three stearic acid molecules (Figure 21.2 ▶). If the fatty acids in a triglyceride are saturated, the triglyceride is a **saturated fat** and tends to be solid at room temperature. Triglycerides from warm-blooded animals (for example, lard from pigs) are generally saturated.

Tristearin: A Saturated Fat



▲ Tristearin is a triglyceride found in lard; it is a saturated fat.

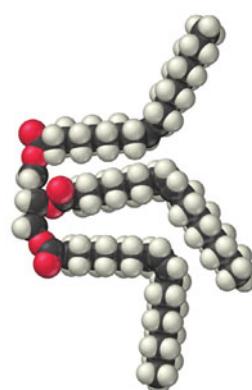
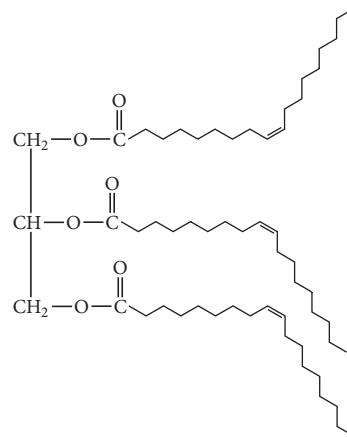


If the fatty acids in a triglyceride are unsaturated, the triglyceride is an **unsaturated fat**, or an oil, and tends to be liquid at room temperature. Triglycerides from plants (olive oil, corn oil, canola oil, etc.) or from cold-blooded animals (fish oil) are generally unsaturated.

Triolein: A Monounsaturated Fat

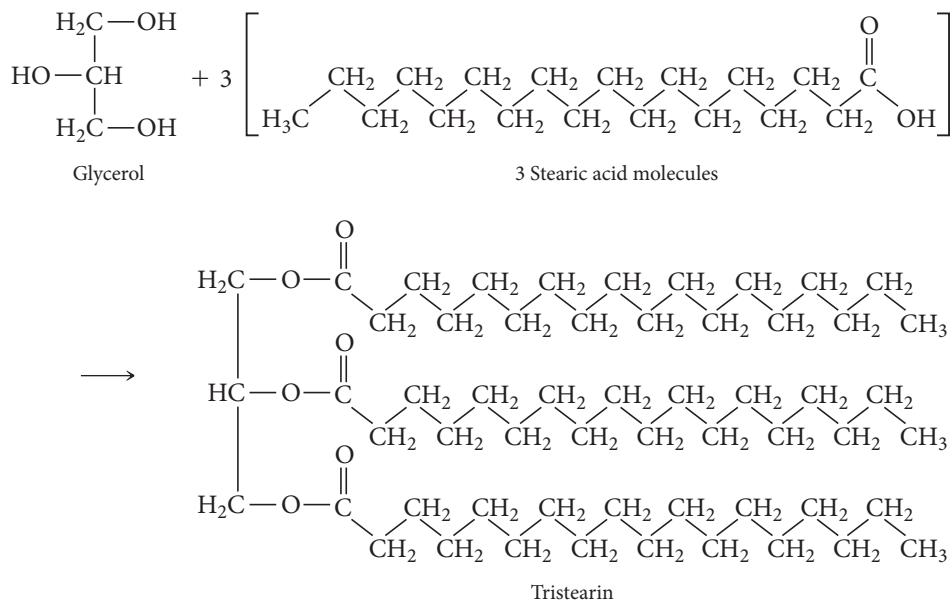


► Triolein is a triglyceride found in olive oil; it is a monounsaturated fat.



Triolein, mp -4 °C

Most of the fats and oils in our diet are triglycerides. During digestion, triglycerides are broken down into fatty acids, glycerol, monoglycerides, and diglycerides. These products pass through the intestinal wall and reassemble into triglycerides before they are absorbed into the blood. This process is slower than the digestion of other food types, and for this reason eating fats and oils gives a lasting feeling of fullness.



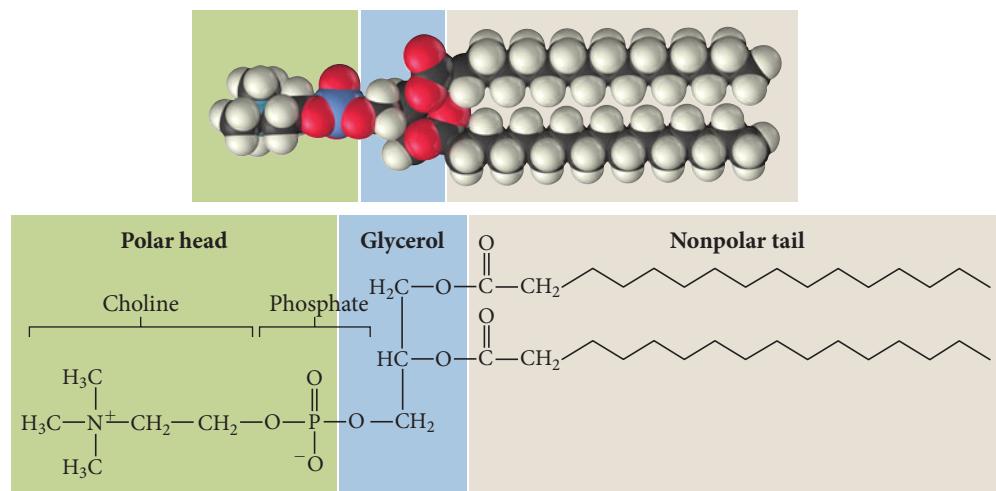
► FIGURE 21.2 The Formation of Tristearin The reaction between glycerol and stearic acid forms tristearin.

The effect of fats and oils on health has been widely debated. Some diets call for a drastic reduction of our daily intake of fats and oils, whereas others actually call for an *increase* in fats and oils. The U.S. Food and Drug Administration (FDA) recommends moderate consumption of fats and oils, less than 30% of total caloric intake.

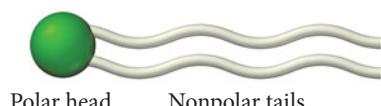
Other Lipids

Additional lipids found in cells include phospholipids, glycolipids, and steroids. **Phospholipids** have the same basic structure as triglycerides, except that one of the fatty acid groups is replaced with a phosphate group. Unlike a fatty acid, which is nonpolar, the phosphate group is polar. A phospholipid molecule therefore has a polar region and a nonpolar region. Consider the structure of phosphatidylcholine, a phospholipid found in the cell membranes of higher animals (Figure 21.3 ▶). The polar part of the molecule is *hydrophilic* (has a strong affinity for water) while the nonpolar part is *hydrophobic* (is repelled by water). **Glycolipids** have similar structures and properties. The nonpolar section of a glycolipid is composed of a fatty acid chain and a hydrocarbon chain. The polar section is a sugar molecule such as glucose. We often portray phospholipids or glycolipids schematically as a circle with

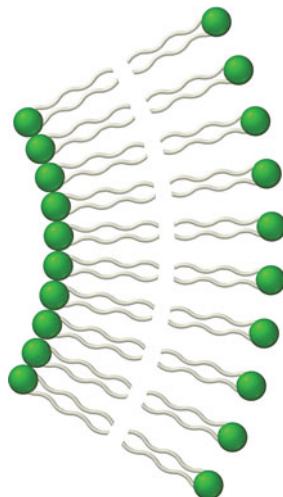
Phosphatidylcholine: A Phospholipid



► FIGURE 21.3 Phosphatidylcholine Phosphatidylcholine is a phospholipid. The structure is similar to a triglyceride except that one of the fatty acid groups is replaced with a phosphate group.



▲ FIGURE 21.4 Schematic for Phospholipid or Glycolipid We represent a phospholipid or a glycolipid as a circle (the polar part of the molecule) with two long tails (the nonpolar part of the molecule).



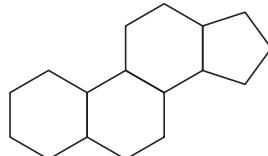
▲ FIGURE 21.5 Lipid Bilayer
Lipid bilayers are composed of phospholipids or glycolipids arranged in a structure that encapsulates cells and many cellular structures.

Hormones are chemical messengers that are released by cells in one part of the body and cause an effect in cells in another part of the body.

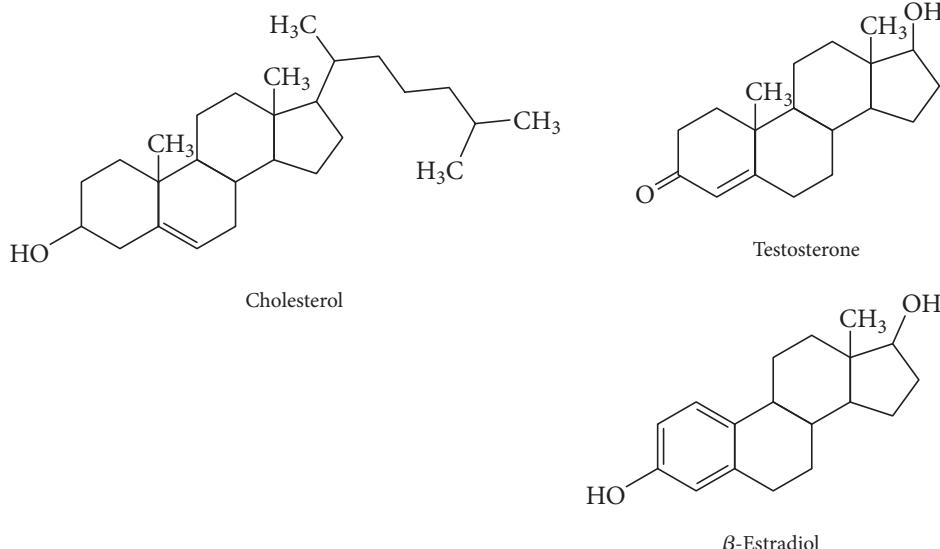
The name should not be taken literally—the hydrogen and oxygen in carbohydrates do not bond together in the same way that they bond in water.

two long tails (Figure 21.4 ▲). The circle represents the polar, hydrophilic part of the molecule and the tails represent the nonpolar, hydrophobic parts. Phospholipids and glycolipids are key components of cell membranes; the polar parts interact with the aqueous environments inside and outside the cell and the nonpolar parts interact with each other, forming a double-layered structure called a **lipid bilayer** (Figure 21.5 ▼). Lipid bilayers encapsulate cells and many cellular structures.

Steroids are lipids with a four-ring structure:



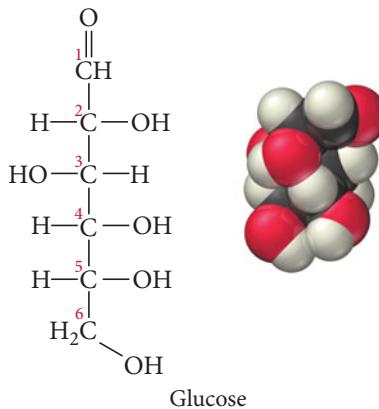
Cholesterol, testosterone, and β -estradiol are common steroids.



Although cholesterol has a bad reputation, it serves many important functions in the body. Like phospholipids and glycolipids, cholesterol is part of cell membranes. Cholesterol also serves as a starting material (or precursor) for the body's synthesis of other steroids such as testosterone, a principal male hormone, and β -estradiol, a principal female hormone.

21.3 Carbohydrates

Carbohydrates are responsible for short-term storage of energy in living organisms, and they make up the main structural components of plants. Carbohydrates—as their name, which means carbon and water, implies—often have the general formula $(CH_2O)_n$. Structurally, we identify **carbohydrates** as polyhydroxy aldehydes or ketones. For example, glucose, with the formula $C_6H_{12}O_6$, has the following structure:



Glucose is a six-carbon aldehyde (that is, it contains the —CHO group) with —OH groups on five of the six carbon atoms. The many —OH groups make glucose soluble in water (and therefore in blood), which is crucial to glucose's role as the primary fuel of cells. Glucose is easily transported in the bloodstream and is soluble within the aqueous interior of a cell. Carbohydrates can be broadly classified as simple carbohydrates (or simple sugars) and complex carbohydrates.

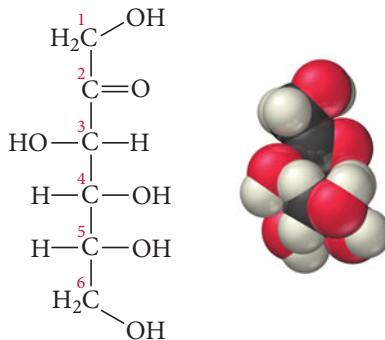
Recall from Section 20.10 that aldehydes have the general structure RCHO , and ketones have the general structure RCOR .

Simple Carbohydrates: Monosaccharides and Disaccharides

Monosaccharides—meaning “one sugar”—are the simplest carbohydrates. Monosaccharides contain between three and eight carbon atoms and have only one aldehyde or ketone functional group. The general names for monosaccharides begin with a prefix that indicates the number of carbon atoms, followed by the suffix *-ose*. The most common carbohydrates in living organisms are pentoses and hexoses.

Glucose, whose structure we saw previously, is an example of a **hexose**, a six-carbon sugar. Glucose is also an example of an **aldose**, a sugar with an aldehyde group. Often, we combine these two ways of designating sugars; glucose is an *aldohexose* (*aldo-* indicates that it is an aldehyde; *-hex-* indicates that it has six carbon atoms; and *-ose* indicates that it is a carbohydrate).

Another common carbohydrate is fructose, a polyhydroxy *ketone* with the following structure:



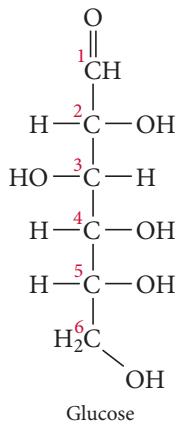
Fructose

Glucose and fructose are structural isomers—they both have the same formula ($\text{C}_6\text{H}_{12}\text{O}_6$), but they have different structures. Fructose is a **ketose**, a sugar that is a ketone. Since fructose has six carbon atoms, it is a *ketohexose*. Fructose, often called fruit sugar, is in many fruits and vegetables and is a major component of honey.

3-carbon sugar: triose
4-carbon sugar: tetrose
5-carbon sugar: pentose
6-carbon sugar: hexose
7-carbon sugar: heptose
8-carbon sugar: octose

EXAMPLE 21.1 Carbohydrates and Optical Isomerism

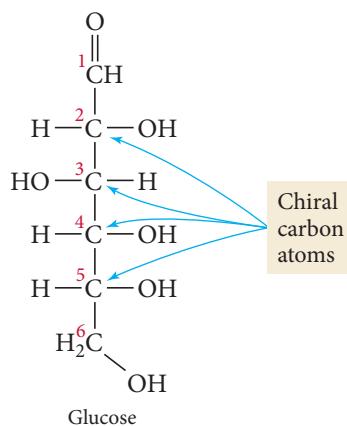
Closely examine the structure of glucose shown here. Does glucose exhibit optical isomerism (discussed in Section 20.3)? If so, which carbon atoms are chiral?



Glucose

SOLUTION

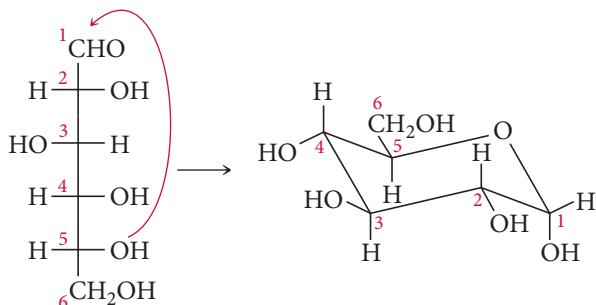
Any carbon atom with four different substituents attached to it is chiral. Glucose has four chiral carbon atoms (labeled 2, 3, 4, and 5) and therefore exhibits optical isomerism.



Variations in the positions of the —OH and —H groups on these carbon atoms result in a number of different possible isomers for glucose. For example, switching the relative positions of the —OH and —H group on the carbon atom closest to the carbonyl group results in mannose, an optical isomer of glucose.

FOR PRACTICE 21.1

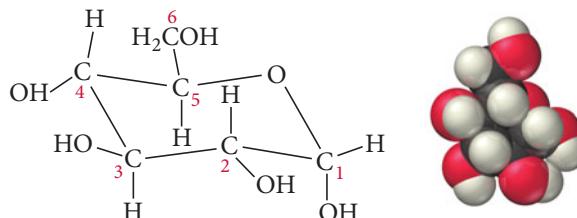
Examine the structure of fructose (p. 1007). Does fructose exhibit optical isomerism? How many of the carbon atoms in fructose are chiral?



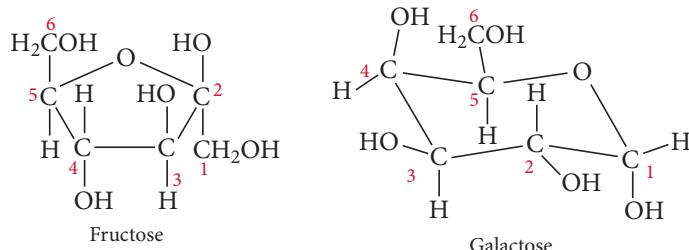
▲ FIGURE 21.6 Intramolecular Reaction of Glucose to Form a Ring

The alcohol group on C5 in glucose reacts with the carbonyl group (C1) to form a closed ring.

Most five- and six-carbon monosaccharides undergo intramolecular reactions that convert their straight carbon chain into a ring. For example, in glucose, the alcohol group on C5 reacts with the carbonyl group (C1) as shown in Figure 21.6 ▲ to form the ring structure shown here.



In a glucose solution, the vast majority of the molecules are in ring form. However, the molecules in ring form exist in equilibrium with a small fraction in the open-chain form. Other common monosaccharides, in their ring form, include fructose (discussed previously in its straight-chain form) and galactose:



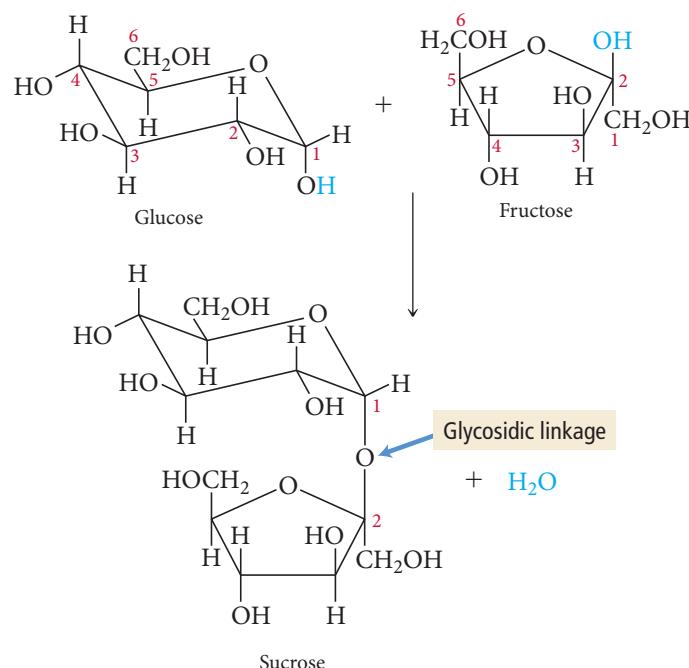
Galactose, also known as brain sugar, is a hexose usually found combined with other monosaccharides in disaccharides such as lactose (see next paragraph). Galactose also occurs within the brain and nervous system of most animals. Galactose and glucose differ only in the stereochemistry at C4. Notice that in galactose the —OH group is roughly perpendicular to the plane of the ring while in glucose it is roughly in the same plane as the ring.

Two monosaccharides can link together via a **glycosidic linkage** to form a **disaccharide**, a carbohydrate that can be decomposed into two simpler sugars. For example, glucose and fructose join to form sucrose, commonly known as table sugar (Figure 21.7 ▶). When we eat disaccharides, the link between individual monosaccharides is broken during digestion by **hydrolysis**, the splitting of a chemical bond with water that results in the addition of H and OH to the products.

The resultant monosaccharides readily pass through the intestinal wall and enter the bloodstream to become fuel for cells.

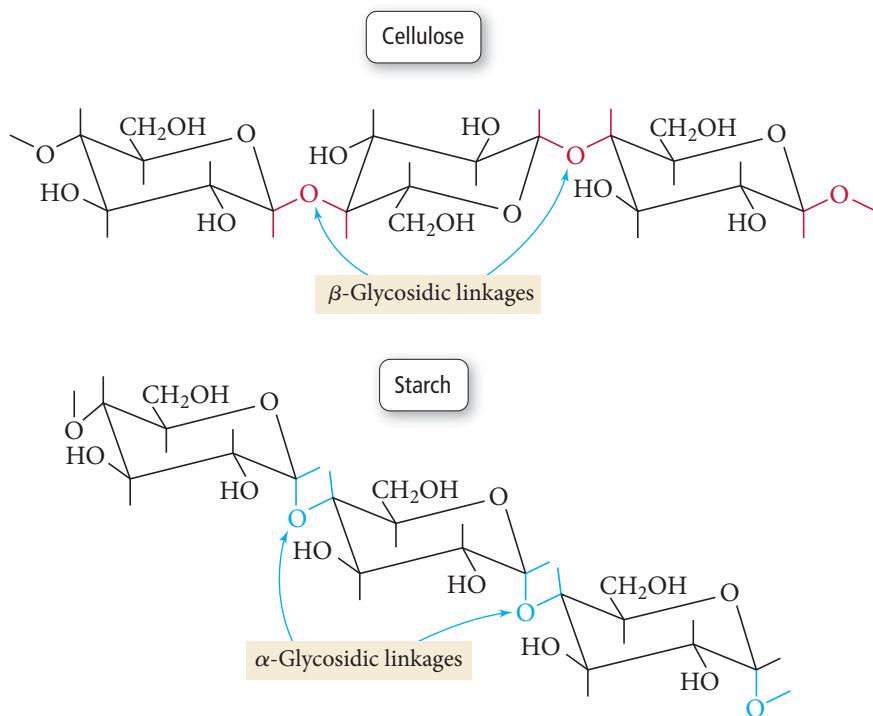
Complex Carbohydrates

Monosaccharides can also link together to form a type of natural polymer (or biopolymer) called a **polysaccharide**, a long, chain-like molecule composed of many monosaccharide units bonded together. Polysaccharides are known as **complex carbohydrates** because of their long chains of sugars. The most common polysaccharides are *cellulose*, *starch*, and *glycogen*, all three of which are composed of repeating glucose units. The main difference among them lies in the way the units are bonded together. In cellulose, the oxygen atoms are roughly parallel with the planes of the rings. This is referred to as a β -glycosidic linkage. In starch and glycogen, the oxygen atoms joining neighboring glucose units point down relative to the planes of the rings. This is an α -glycosidic linkage.



▲ FIGURE 21.7 Formation of a Glycosidic Linkage Glucose and fructose can join, eliminating water and forming a glycosidic linkage that results in the disaccharide sucrose, commonly known as table sugar.

◀ The primary difference between starch and cellulose is in the way the units are bonded together.



Cellulose The main structural component of plants, **cellulose**, is the most abundant organic substance on Earth and consists of glucose units bonded together by β -glycosidic linkages. This structure allows neighboring cellulose molecules to form multiple hydrogen bonds with one another, resulting in the rigid and structurally stable properties we associate with wood and fiber. Humans lack the enzyme required to digest cellulose. When we eat cellulose (usually called fiber when it is present in foods), it passes right

through our intestines, providing bulk to stools and preventing constipation. Some bacteria have the enzyme required to metabolize cellulose into its component glucose units. These bacteria are common in the guts of termites and ruminants such as cows, allowing them to extract caloric content from cellulose.

Starch The main energy storage medium for plants is **starch**, the soft, pliable substance abundant in potatoes and grains. Starch is composed of two slightly different polysaccharides, *amylose* and *amylopectin*. Both are made up of glucose units bonded together by α -glycosidic linkages, but amylopectin contains branches in the chains. When animals digest starch, the link between individual glucose units is broken by hydrolysis, allowing glucose molecules to pass through the intestinal wall and into the bloodstream.

Glycogen The structure of **glycogen** is similar to that of amylopectin, but the chain is even more highly branched. Animals use glycogen to store glucose in the muscles. Glycogen's highly branched structure leaves many end groups that can be quickly hydrolyzed to meet energy needs. When muscles become depleted of glycogen, muscle movement and exercise become much more difficult. Marathon runners often “hit the wall” at about mile 20 because they have depleted most of the glycogen from their muscles.

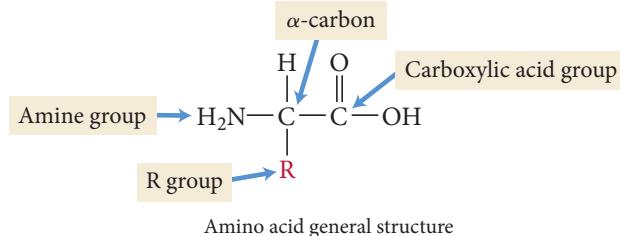
21.4 Proteins and Amino Acids

Proteins are the workhorse molecules in living organisms; they are involved in virtually every facet of cell structure and function. For example, most of the chemical reactions that occur in living organisms are enabled by **enzymes**, proteins that act as catalysts in biochemical reactions. Without enzymes, life would be impossible. Proteins are also the structural elements of muscle, skin, and cartilage. They transport oxygen in the blood, act as antibodies to fight disease, and function as hormones to regulate metabolic processes. Proteins reign supreme as the working molecules of life. Table 21.2 summarizes the functions of some of the important classes of proteins and lists examples of each.

Amino Acids: The Building Blocks of Proteins

In a protein, the presence of an R group does not necessarily indicate a pure alkyl group. See Table 21.3 for possible R groups.

Proteins are polymers of amino acids. Each **amino acid** molecule consists of a carbon atom—called the α -carbon—bonded to four different groups: an amine group, an R group (also called a side chain), a carboxylic acid group, and a hydrogen atom.



Amino acids differ from each other in their R groups. For example, the R group in alanine is a methyl group (CH_3):

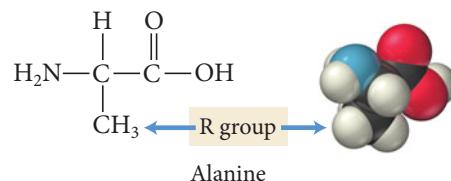
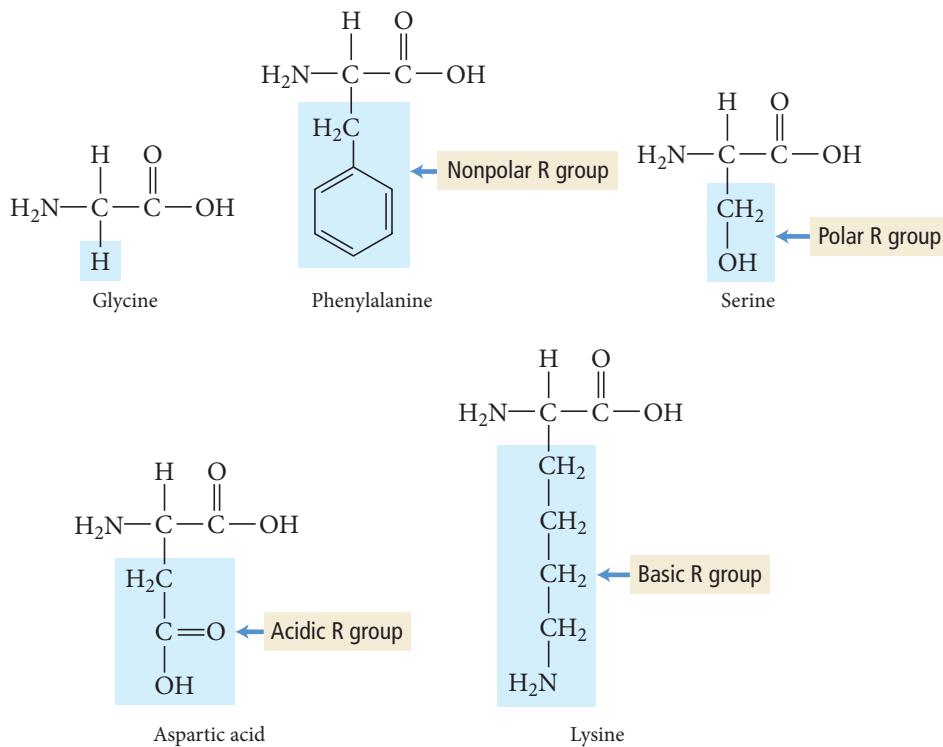


TABLE 21.2 Protein Functions

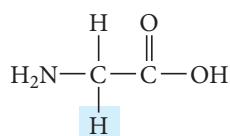
Class of Protein	Primary Function	Example
Structural proteins	Compose structures within living organisms	Collagen (skin, tendon, cartilage), keratin (hair, fingernails)
Enzymes	Catalyze and control biochemical reactions	DNA polymerase (involved in replication of DNA)
Hormones	Regulate metabolic processes	Insulin (regulates glucose metabolism)
Transport proteins	Transport substances from one place to another	Hemoglobin (transports oxygen)
Storage proteins	Provide source of essential nutrients	Casein (protein in mammalian milk)
Contractile and motile proteins	Mediate motion and muscle contraction	Actin and myosin (provide muscle contraction)
Protective proteins	Protect and defend cells	Antibodies (neutralize infectious agents)

Other amino acids are glycine ($R = H$), phenylalanine ($R = CH_2C_6H_5$), serine ($R = CH_2OH$), aspartic acid ($R = CH_2COOH$), and lysine ($R = CH_2CH_2CH_2CH_2NH_2$).

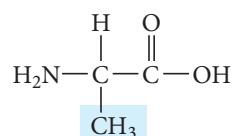


The R groups, or side chains, differ chemically. For example, phenylalanine has a large nonpolar R group, whereas serine has a polar one. Aspartic acid has an acidic R group, whereas lysine, since it contains nitrogen, has a basic one. When amino acids are strung together to make a protein, the chemical properties of the R groups determine the structure and properties of the protein. Table 21.3 (on the next page) shows the most common amino acids in proteins and their three-letter abbreviations. The diversity of amino acids creates the possibility for an even larger diversity of proteins.

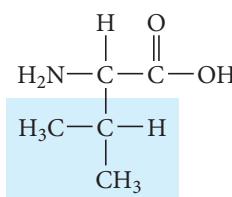
Because all amino acids (except glycine) contain four different groups attached to a tetrahedral carbon (the α -carbon), all amino acids are chiral about that carbon. The amino acids that compose naturally occurring proteins are the L-enantiomers, and they

TABLE 21.3 Common Amino Acids

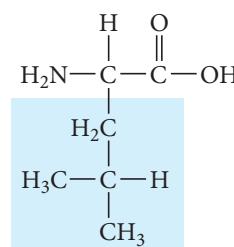
Glycine (Gly)



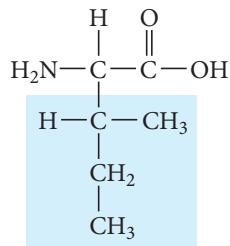
Alanine (Ala)



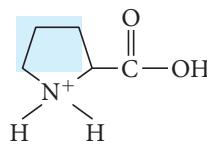
Valine (Val)



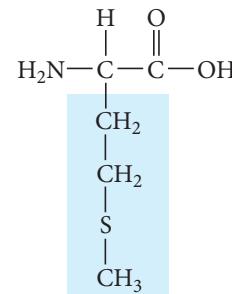
Leucine (Leu)



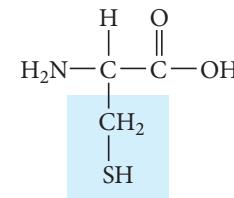
Isoleucine (Ile)



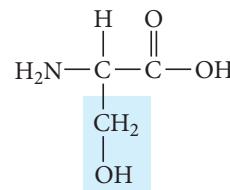
Proline (Pro)



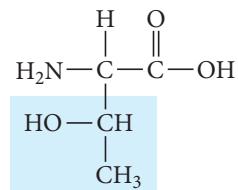
Methionine (Met)



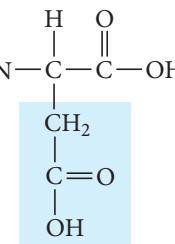
Cysteine (Cys)



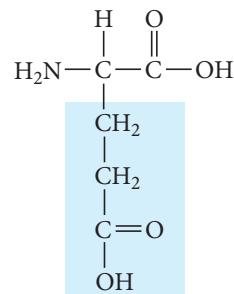
Serine (Ser)



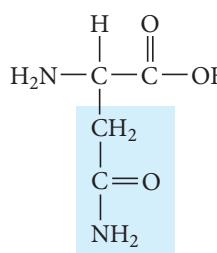
Threonine (Thr)



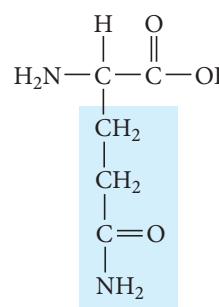
Aspartic acid (Asp)



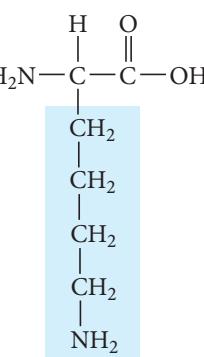
Glutamic acid (Glu)



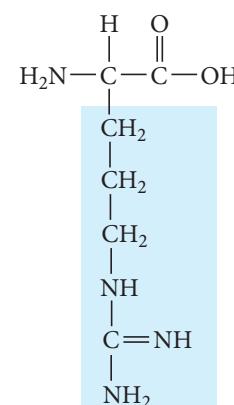
Asparagine (Asn)



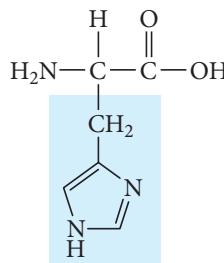
Glutamine (Gln)



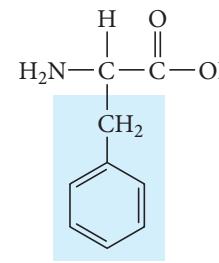
Lysine (Lys)



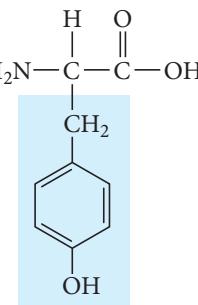
Arginine (Arg)



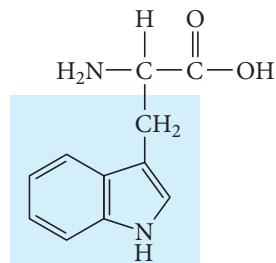
Histidine (His)



Phenylalanine (Phe)



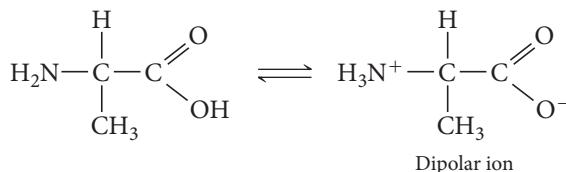
Tyrosine (Tyr)



Tryptophan (Trp)

are called L-amino acids. Why life on Earth is based on this enantiomer over the other is an interesting question that remains to be answered. (It seems just as likely that life could have used the D-enantiomer.)

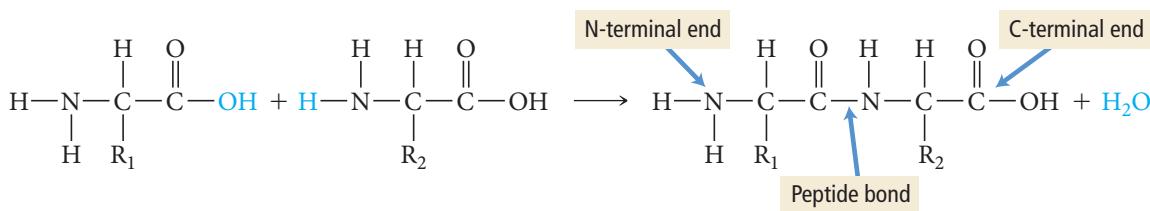
Although we usually write the structures of amino acids as neutral, their actual structure is ionic and depends on pH. In general, amino acids undergo an intramolecular acid–base reaction and form a *dipolar ion*, or *zwitterion*.



At room temperature this equilibrium lies far to the right. Since one side of the dipolar ion is positively charged and the other negatively charged, amino acids are highly polar and soluble in water. They also have fairly high melting points (usually $>200\text{ }^{\circ}\text{C}$). In addition, the intramolecular acid–base reaction makes amino acids less acidic and less basic than most carboxylic acids and amines, respectively.

Peptide Bonding between Amino Acids

Amino acids link together through the reaction of the amine end of one amino acid with the carboxylic end of another.

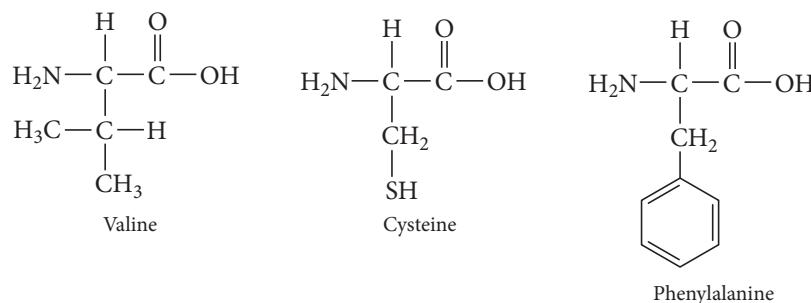


The resulting bond is a **peptide bond**, and the resulting molecule—two amino acids linked together—is a **dipeptide**. When two or more amino acids link in this way, the molecule they form has two distinct ends: an amino terminal (or N-terminal end) and a carboxyl terminal (or C-terminal end). A **tripeptide** is three amino acids joined by peptide bonds; a **tetrapeptide** is four; and so on. Short chains of amino acids are generally called **oligopeptides**, and longer chains (more than 20) are called **polypeptides**. Functional proteins usually contain one or more polypeptide chains with each chain consisting of hundreds or even thousands of amino acids joined by peptide bonds.

The formation of a peptide bond is an example of a condensation reaction (see Section 20.11).

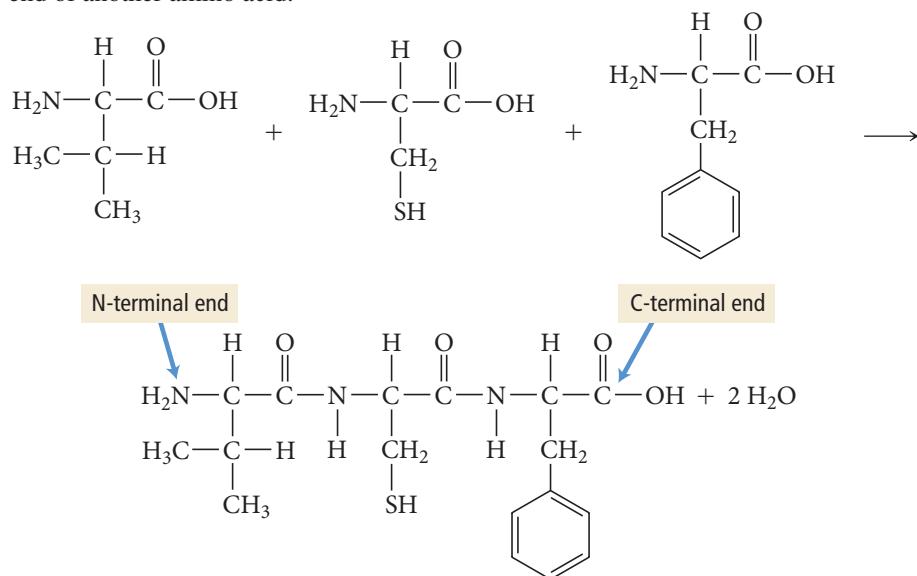
EXAMPLE 21.2 Peptide Bonds

Show the reaction by which valine, cysteine, and phenylalanine (in that order) link via peptide bonds. Designate valine as N-terminal and label the N-terminal and C-terminal ends in the resulting tripeptide.

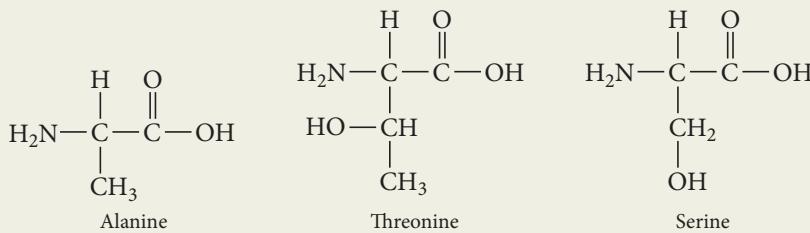


SOLUTION

Peptide bonds form when the carboxylic end of one amino acid reacts with the amine end of another amino acid.

**FOR PRACTICE 21.2**

Show the reaction by which alanine, threonine, and serine (in that order) link via peptide bonds. Designate alanine as the N-terminal and label the N-terminal and C-terminal ends in the resulting tripeptide.



Conceptual Connection 21.1 Peptides

How many different tripeptides can form from the three amino acids listed here? (The amino acids are indicated using the three-letter amino acid abbreviations from Table 21.3.)

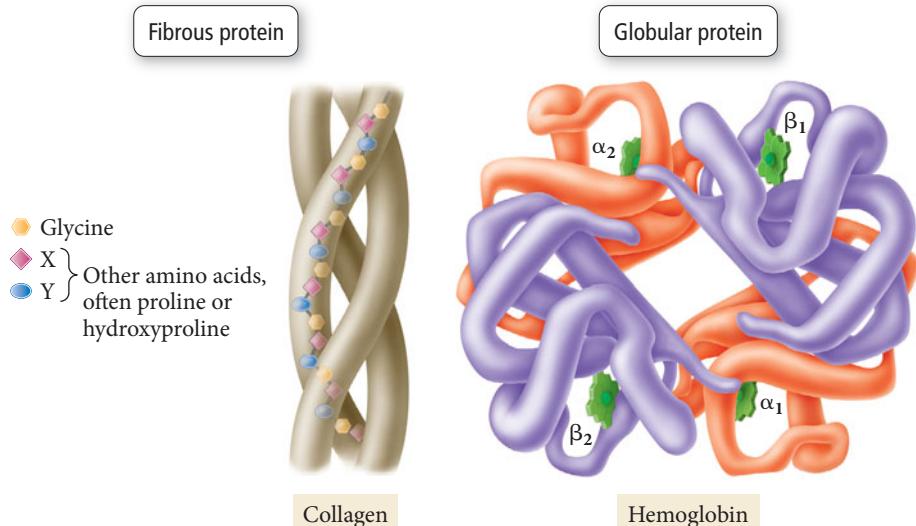
Ser, Ala, Gly

21.5 Protein Structure

A protein's structure is critical to its function. For example, recall from Section 21.1 that insulin is a protein that promotes the absorption of glucose out of the blood and into muscle cells where the glucose is needed for energy. Insulin recognizes muscle cells because muscle cell surfaces contain *insulin receptors*, molecules that fit a specific portion of the insulin protein. If insulin were a different shape, it would not latch onto insulin receptors on muscle cells and could not do its job. Thus, the shape or *conformation* of a protein is crucial to its function.

We can broadly classify proteins into two main structural categories: fibrous proteins and globular proteins (Figure 21.8 ▶). **Fibrous proteins** tend to have relatively simple linear structures and be insoluble in aqueous solutions. They serve primarily structural

Fibrous and Globular Proteins



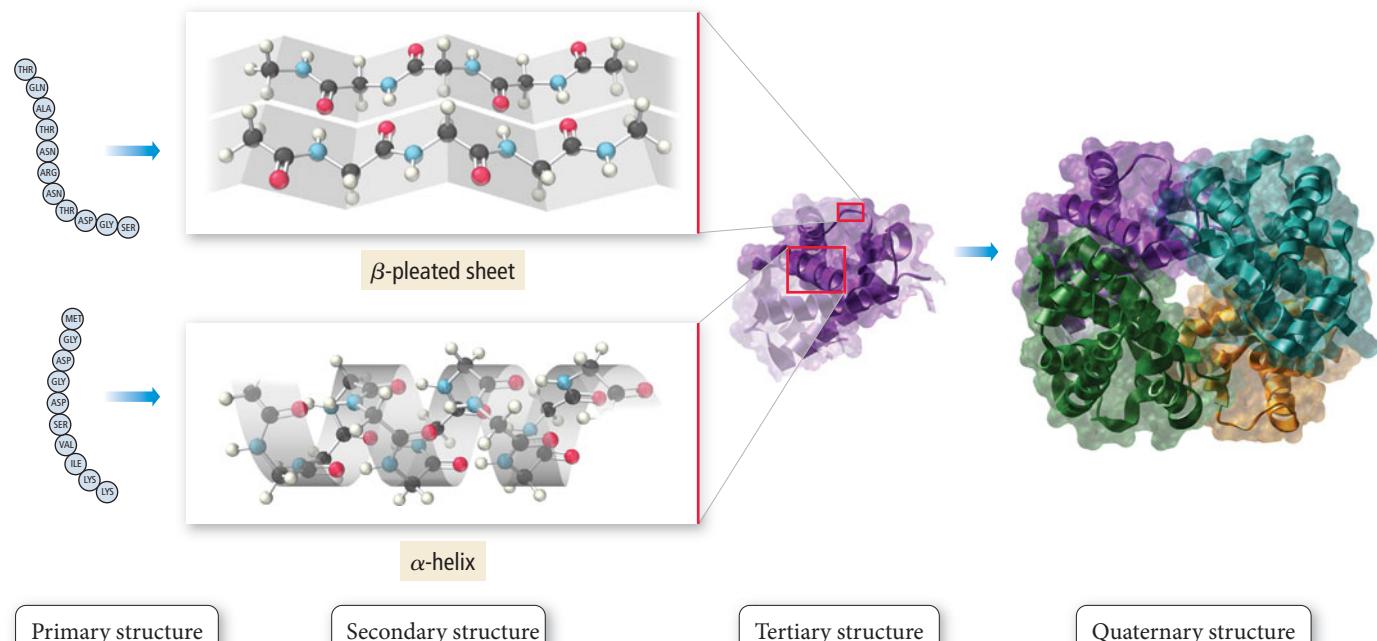
◀ FIGURE 21.8 Fibrous and Globular Proteins

Proteins Proteins are broadly divided into fibrous proteins (which have relatively simple linear structures) and globular proteins (which have more complex three-dimensional structures).

functions within living organisms. Collagen and keratin, for example, are both fibrous proteins (see Table 21.2). **Globular proteins** tend to have more complex structures but are often roughly spherical in overall shape. Globular proteins are generally structured so that polar side chains on amino acids are oriented toward the exterior of the protein, while nonpolar side chains are oriented toward the interior of the protein. Consequently, globular proteins tend to be soluble in water, but they maintain a nonpolar environment within the protein that excludes water. Hemoglobin and insulin are both globular proteins.

Protein structure is analyzed at four levels: primary structure, secondary structure, tertiary structure, and quaternary structure (Figure 21.9 ▼). We examine each of these categories separately.

Levels of Protein Structure



▲ FIGURE 21.9 Levels of Protein Structure Protein structure is analyzed at four levels: primary, secondary, tertiary, and quaternary.



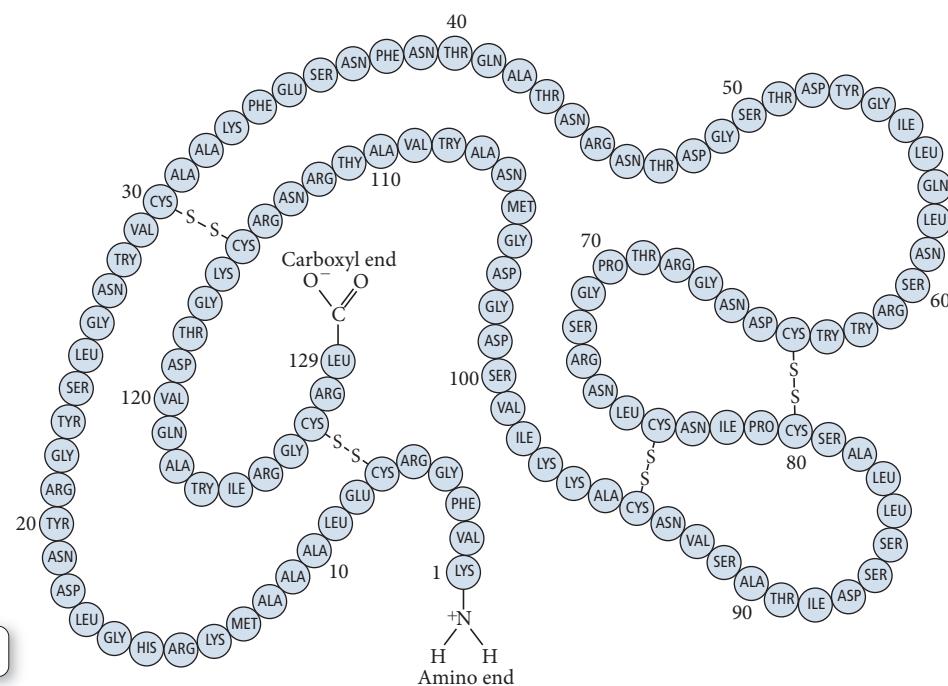
▲ The genetic disease known as sickle-cell anemia results in red blood cells with a sickle shape. These cells impede circulation of blood, causing damage to major organs.

► FIGURE 21.10 Primary Structure of Egg-White Lysozyme Primary structure refers to the sequence of amino acids in a protein.

Primary Structure

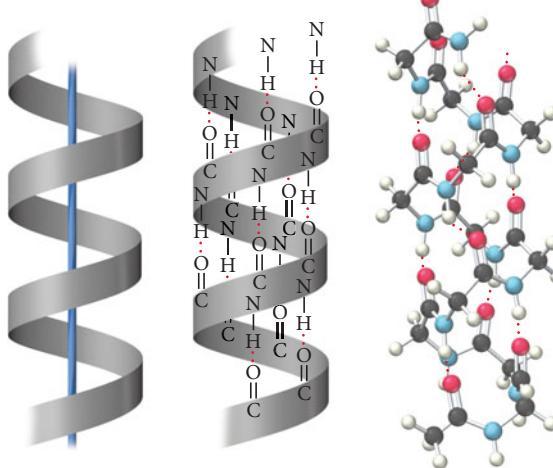
The **primary structure** of a protein is the sequence of amino acids in its chain(s). Primary structure, which determines the other three kinds of structure, is maintained by the covalent peptide bonds between individual amino acids. The primary structure of egg-white lysozyme—a protein that helps fight infection—is shown in Figure 21.10 ▼. The figure illustrates the amino acid sequence, the N-terminal and C-terminal ends, and the presence of *disulfide linkages*, covalent cross-links between cysteine amino acids in the polymer. We discuss disulfide linkages in more detail later in the section on tertiary structure. Researchers determined the first amino acid sequences for proteins in the 1950s. Today, the amino acid sequences for thousands of proteins are known.

Changes in the amino acid sequence of a protein, even minor ones, can destroy the function of a protein. Hemoglobin, as we saw in Chapter 1, is a protein that transports oxygen in the blood. It is composed of four polypeptide chains made up of a total of 574 amino acid units. If valine is replaced by glutamic acid in just one position on two of these chains the disease known as sickle-cell anemia results. The red blood cells of people with sickle-cell anemia take on a sickle shape that impedes circulation, causing damage to major organs. In the past, sickle-cell anemia was fatal, often resulting in death before age 30—all due to a change in a few atoms of 2 amino acids out of 574. Modern therapies have extended the life span of sickle-cell anemia patients so they now live into their 40s and 50s.



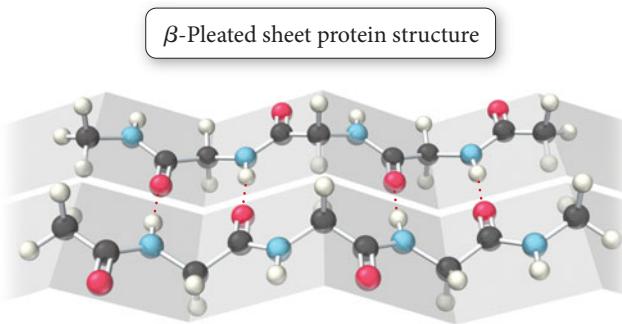
▼ FIGURE 21.11 The α -Helix Structure The α -helix is an example of secondary protein structure.

α -Helix protein structure



Secondary Structure

The **secondary structure** of a protein refers to certain regular periodic or repeating patterns in the arrangement of protein chains. Secondary structure is maintained by interactions between amino acids that are fairly close together in the linear sequence of the protein chain or that are adjacent to each other on neighboring chains or chains that fold back on themselves. The most common of these patterns is the **α -helix**, shown in Figure 21.11 ▲. In the α -helix structure, the amino acid chain wraps into a tight coil from which side chains extend. The structure is maintained by hydrogen-bonding interactions between NH and CO groups along the peptide backbone of the protein. Some proteins—such as keratin, which composes human hair—have the α -helix pattern throughout their entire chain. Other proteins have very little or no α -helix pattern in their chain.



◀ FIGURE 21.12 The β -Pleated Sheet

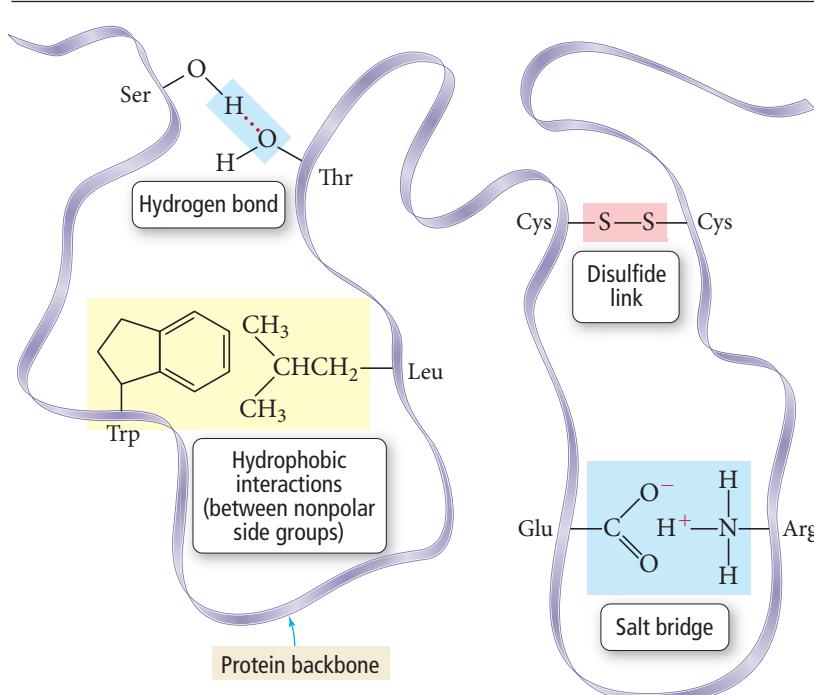
Structure The β -pleated sheet is a secondary protein structure.

A second common pattern in the secondary structure of proteins is the **β -pleated sheet** (Figure 21.12 ▲). In this structure, the chain is extended (as opposed to coiled) and forms a zigzag pattern. The peptide backbones of neighboring chains interact with one another through hydrogen bonding to form zigzag-shaped sheets. Some proteins—such as silk—have the β -pleated sheet structure throughout their entire chain. Since the protein chains in the β -pleated sheet are fully extended, silk is inelastic. Many proteins have some sections that are β -pleated sheet, other sections that are α -helical, and still other sections that have less-regular patterns referred to as **random coils**.

Tertiary Structure

The **tertiary structure** of a protein consists of the large-scale bends and folds resulting from interactions between the R groups of amino acids that are separated by large distances in the linear sequence of the protein chain. These interactions, shown in Figure 21.13 ▼, include hydrogen bonding, disulfide linkages (covalent bonds between cysteine amino acids), hydrophobic interactions (attractions between large, nonpolar side chains), and salt bridges (acid–base interactions between acidic and basic side chains). Fibrous proteins generally lack tertiary structure; they simply extend in a long continuous chain with some secondary structure. Globular proteins, by contrast, fold in on themselves, forming complex globular shapes rich in tertiary structure.

Interactions That Maintain Tertiary Structure



◀ FIGURE 21.13 Interactions within Proteins

The tertiary structure of a protein is maintained by interactions between the R groups of amino acids that are separated by large distances in the linear sequence of the protein chain.

Quaternary Structure

Some proteins—called *monomeric* proteins—are composed of only one polypeptide chain. However, *multimeric* proteins are composed of several polypeptide chains, called subunits. We just saw, for example, that hemoglobin is composed of four such subunits. The way that subunits fit together in a multimeric protein is referred to as the **quaternary structure** of the protein. Quaternary structure is maintained by the same types of interactions that maintain tertiary structure, but the interactions are between amino acids on different subunits.

Summarizing Protein Structure:

- ▶ Primary structure is the amino acid sequence. It is maintained by the peptide bonds that hold amino acids together.
- ▶ Secondary structure refers to the repeating patterns in the arrangement of protein chains. These are maintained by interactions between the peptide backbones of amino acids that are close together in the chain sequence or adjacent to each other on neighboring chains. Secondary structure is characteristic of fibrous proteins, but globular proteins also frequently feature regions of α -helix, β -pleated sheet, and random coil secondary structure.
- ▶ Tertiary structure refers to the large-scale twists and folds of globular proteins. These are maintained by interactions between the R groups of amino acids that are separated by long distances in the chain sequence.
- ▶ Quaternary structure refers to the arrangement of subunits in proteins that have more than one polypeptide chain. Quaternary structure is maintained by interactions between amino acids on different subunits.

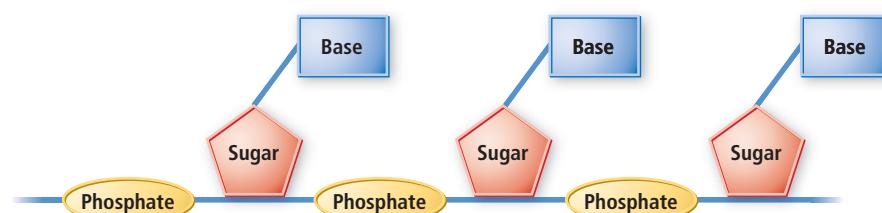
21.6 Nucleic Acids: Blueprints for Proteins

We have seen that the amino acid sequence in a protein determines that protein's structure and function. If the amino acid sequence is incorrect, the protein is unlikely to function properly. How do cells in living organisms synthesize the many thousands of different required proteins, each with the correct amino acid sequence? The answer lies in nucleic acids, molecules that serve as blueprints for protein synthesis. Nucleic acids employ a chemical code to specify the correct amino acid sequences for proteins. Nucleic acids are broadly divided into two types: deoxyribonucleic acid, or DNA, which exists primarily in the nucleus of the cell; and ribonucleic acid, or RNA, which exists throughout the cell.

The Basic Structure of Nucleic Acids

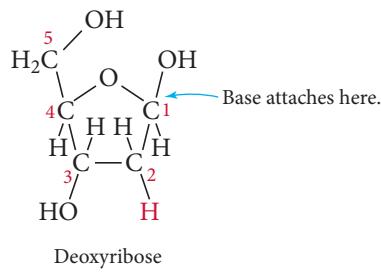
Like proteins, nucleic acids are polymers. The individual units composing nucleic acids are **nucleotides**. Each nucleotide has three parts: a sugar, a base, and a phosphate group that serves as a link between sugars (Figure 21.14 ▶).

DNA: Basic Structure

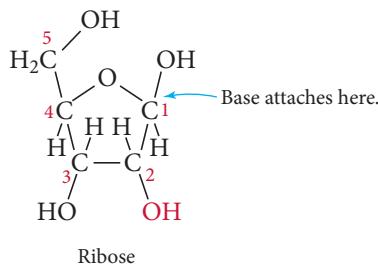


▲ FIGURE 21.14 DNA Structure DNA is composed of repeating units called nucleotides. Each nucleotide contains a sugar, a base, and a phosphate group.

Sugars In DNA, the sugar is deoxyribose, whereas in RNA the sugar is ribose.



Deoxyribose

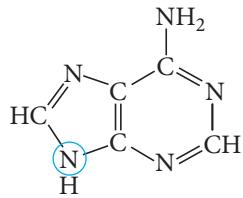


Ribose

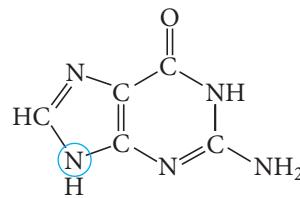
The base attaches to the sugar at C1 and the phosphate attaches to the sugar at C3 and C5. When a base is attached to the sugar, the numbers of the carbon atoms in the sugar ring are primed to distinguish them from the carbon atoms on the bases (which are not primed). For example, C5 becomes C5' and C3 becomes C3'.

Bases Every nucleotide in DNA has the same sugar, but each nucleotide has just one of four different bases. In DNA, the four bases are adenine (A), cytosine (C), guanine (G), and thymine (T). Each of these bases bonds to the sugar via the nitrogen atom circled in the illustrations shown here:

Purine Bases

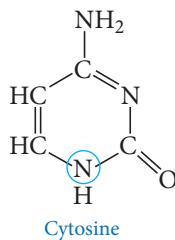


Adenine

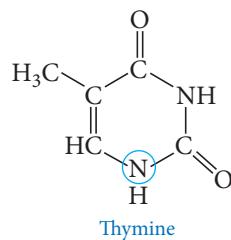


Guanine

Pyrimidine Bases

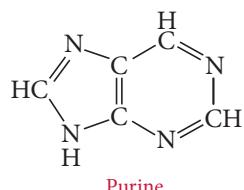


Cytosine

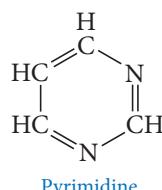


Thymine

Adenine and guanine are called *purine* bases because they resemble the bicyclic compound purine. Cytosine and thymine are called *pyrimidine* bases because they resemble the monocyclic compound pyrimidine.

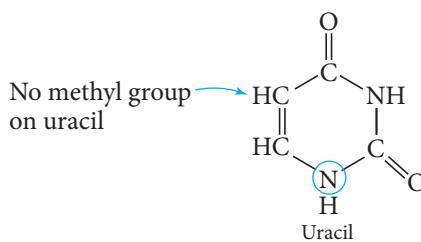


Purine

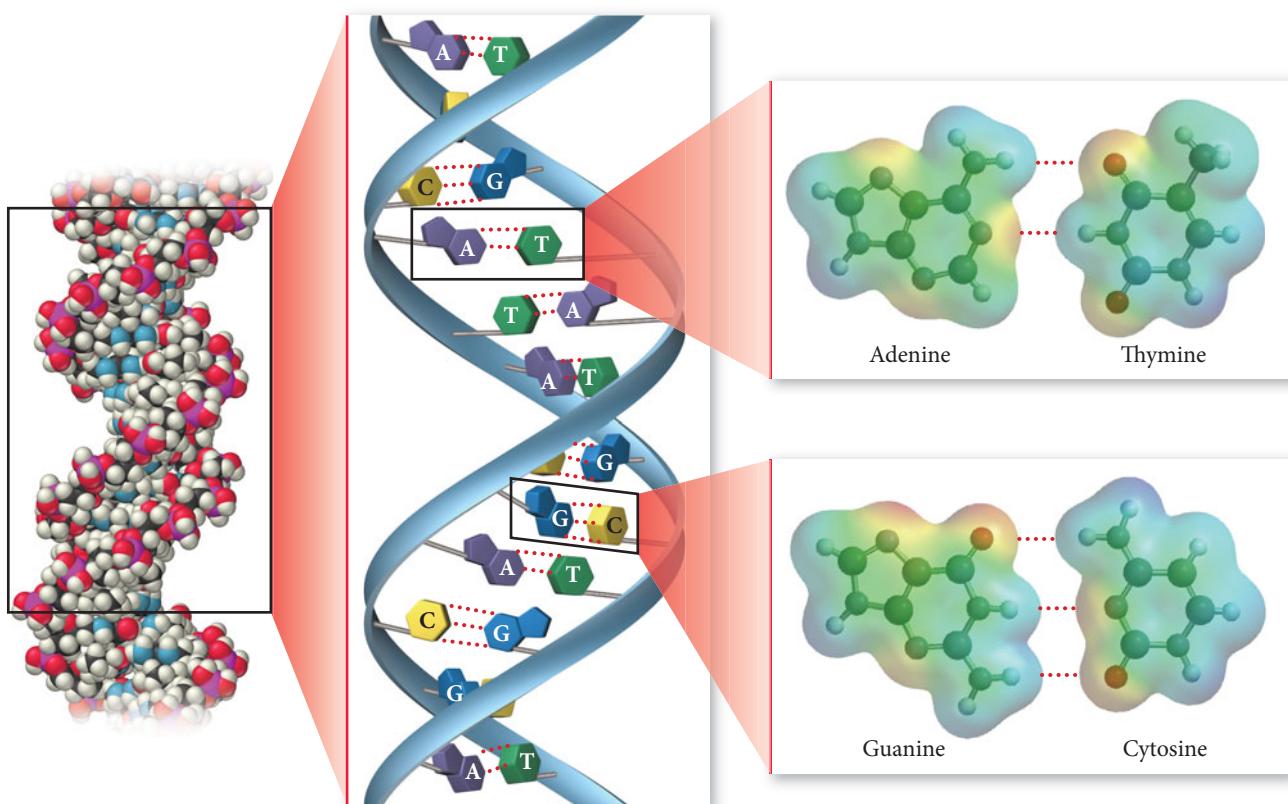


Pyrimidine

In RNA, the base uracil (U), also a pyrimidine base, replaces thymine. Uracil and thymine differ only in a methyl (—CH₃) group.



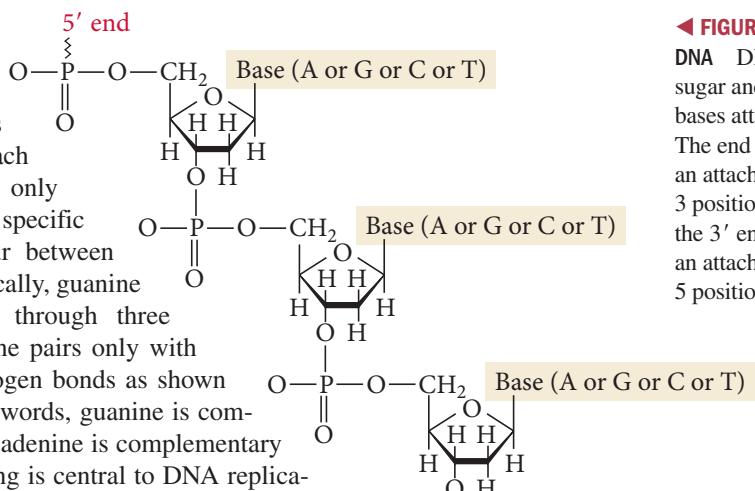
Base Pairing in DNA



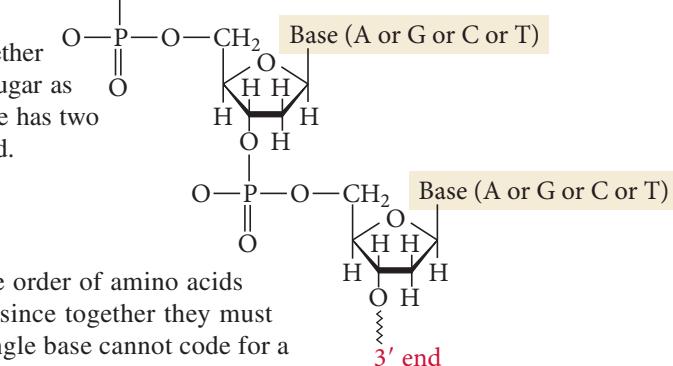
▲ FIGURE 21.15 Base Pairing in DNA The bases in nucleic acids are complementary. Each pyrimidine base pairs with only one purine base (G with C, A with T) via specific hydrogen bonds that occur between the two bases.

The bases in nucleic acids are complementary—that is, each one precisely pairs with another base. Each pyrimidine base pairs with only one purine base via specific hydrogen bonds that occur between the two bases. More specifically, guanine pairs only with cytosine through three hydrogen bonds and adenine pairs only with thymine through two hydrogen bonds as shown in Figure 21.15 ▲. In other words, guanine is complementary to cytosine and adenine is complementary to thymine. This base pairing is central to DNA replication, as we discuss in Section 21.7.

Phosphate Links The sugar units in nucleic acids link together by phosphate groups, which bind to C5' and C3' of the sugar as shown in Figure 21.16 ▷. Note that a nucleic acid molecule has two distinct ends, which we refer to as the 5' end and the 3' end.

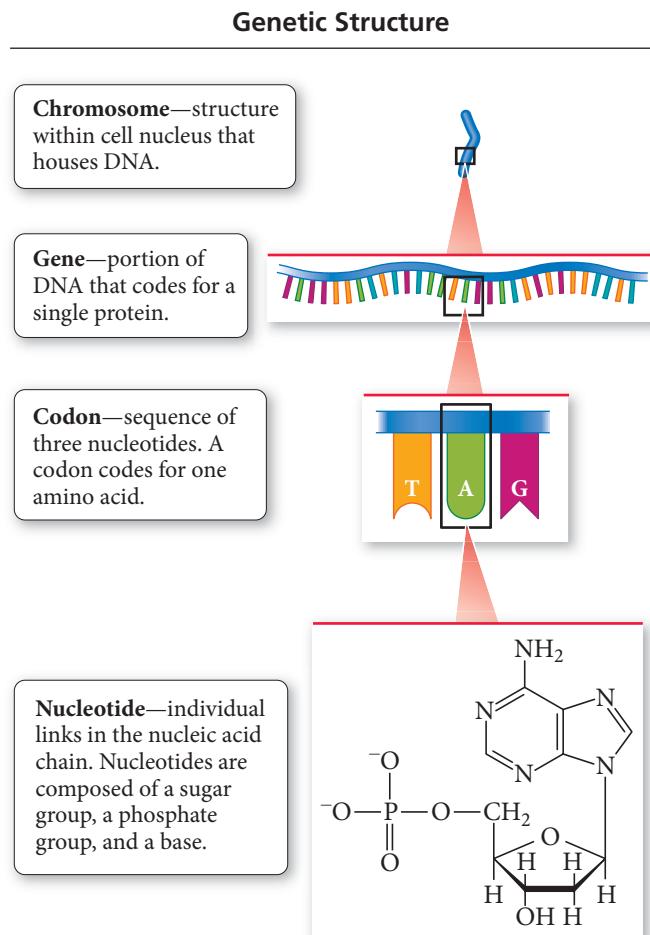


◀ FIGURE 21.16 Short Strand of DNA DNA contains alternating sugar and phosphate groups with bases attached to each sugar. The end of the molecule missing an attachment at the number 3 position in the sugar ring is called the 3' end, and the end missing an attachment at the number 5 position is called the 5' end.



The Genetic Code

The order of bases in a nucleic acid chain determines the order of amino acids in a protein. However, since there are only 4 bases, and since together they must have the ability to code for 20 different amino acids, a single base cannot code for a



▲ **FIGURE 21.17 Genetic Structure** The hierarchical structure of genetic information is chromosome, gene, codon, and nucleotide.

a single amino acid. A sequence of three nucleotides—called a **codon**—codes for one amino acid (Figure 21.17 ▲). The genetic code—the code that identifies the amino acid specified by a particular codon—was worked out in 1961. It is nearly universal—the same codons specify the same amino acids in nearly all organisms. For example, in DNA the sequence AGT codes for the amino acid serine and the sequence ACC codes for the amino acid threonine. It does not matter if the DNA is in a rat, a bacterium, or a human—the code is the same.

A **gene** is a sequence of codons within a DNA molecule that codes for a single protein. Since proteins vary in size from a few dozen to thousands of amino acids, genes vary in length from dozens to thousands of codons. For example, egg-white lysozyme (Figure 21.10, p. 1016) is composed of 129 amino acids. So the lysozyme gene contains 129 codons—one for each amino acid in the lysozyme protein. Each codon is like a three-letter word that specifies one amino acid. String the correct number of codons together in the correct sequence, and you have a gene, the instructions for the amino acid sequence in a protein. Genes are contained in structures called **chromosomes** (Figure 21.18 ▶). A human cell generally contains 46 chromosomes in its nucleus.



▲ **FIGURE 21.18 Chromosomes**
Genes are contained in structures called chromosomes. Most human cells contain 46 chromosomes.

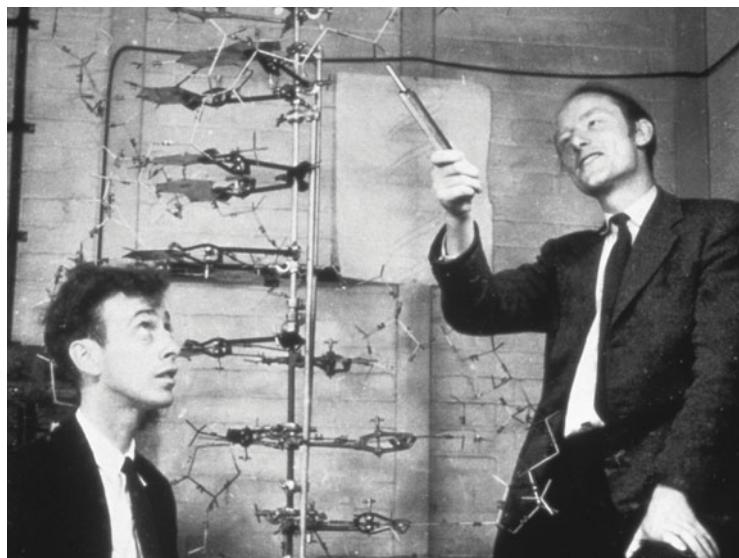
In addition to having a codon for each amino acid, genes also contain additional coding that signals, for example, where the gene begins and where it ends.

Conceptual Connection 21.2 The Genetic Code

Assuming you have four different bases, how many amino acids can you code for with two-base sequences? Three-base sequences?

21.7 DNA Replication, the Double Helix, and Protein Synthesis

Most of the cells in our bodies contain all of the genes required to make all of the proteins that we need—the DNA within any one cell is *complete*. However, any particular cell does not express all those genes; it does not synthesize all those proteins. Cells synthesize only the proteins that are important to their function. For example, a pancreatic cell expresses the insulin gene within its nucleus to synthesize insulin. Pancreatic cells do not express the gene for keratin (the protein in hair), even though the keratin gene is also contained in their nuclei. The cells in our scalp, in contrast, which also have both insulin and keratin genes in their nuclei, synthesize keratin but not insulin.



▲ FIGURE 21.19 Watson and Crick

James Watson and Francis Crick discovered the structure of DNA, including the double helix and the pairing of complementary bases.

DNA Replication and the Double Helix

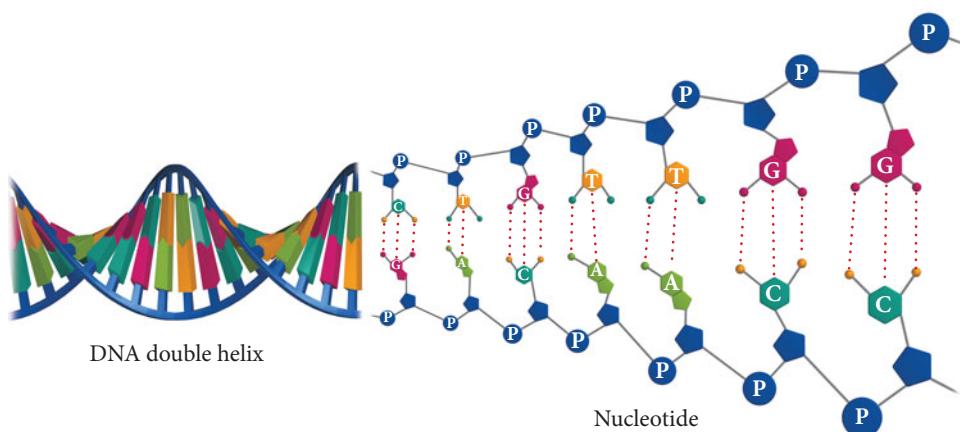
The human body contains on the order of 10^{13} cells, most of which have complete copies of the DNA that originally was present in a single cell (the fertilized egg). When a cell divides, it makes complete copies of its DNA for each daughter cell. The ability of DNA to copy itself is related to its structure, discovered in 1953 by James D. Watson and Francis H. C. Crick. Watson and Crick, aided by evidence from X-ray diffraction photos (see Section 11.10), determined that DNA exists as two complementary strands wound around each other in a double helix (Figure 21.19 ▲). The strands are anti-parallel, so one runs $3' \longrightarrow 5'$ while the other runs $5' \longrightarrow 3'$. The bases on each DNA strand are directed toward the interior of the helix, where they hydrogen bond to their complementary bases on the other strand. For example, if a section of DNA contains the bases:



the complementary strand would have the sequence:

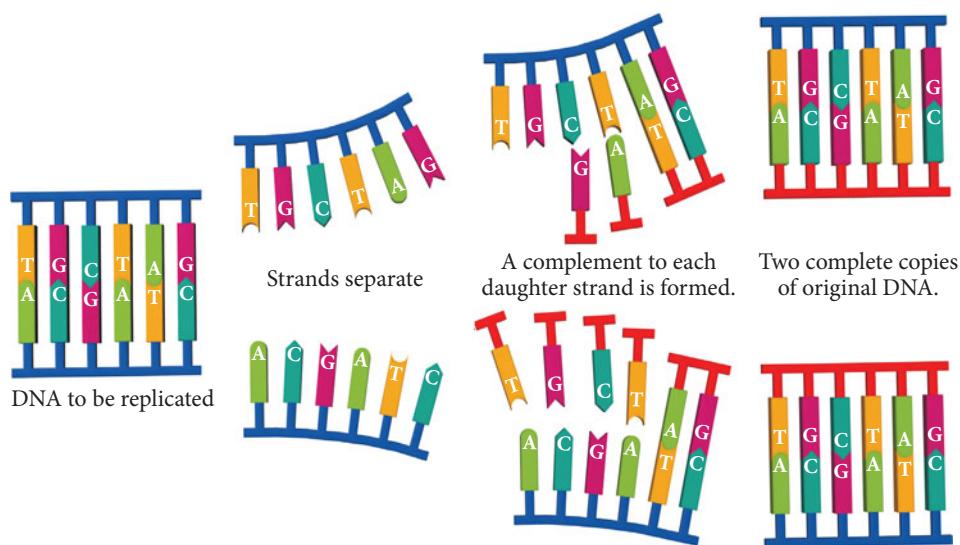


As we saw earlier, A pairs only with T, and C pairs only with G. The two complementary strands are tightly wrapped into a helical coil, the famous DNA double helix structure (Figure 21.20 ▼).



► FIGURE 21.20 DNA Double Helix

Two complementary strands of DNA wrap around one another to form a double helix.



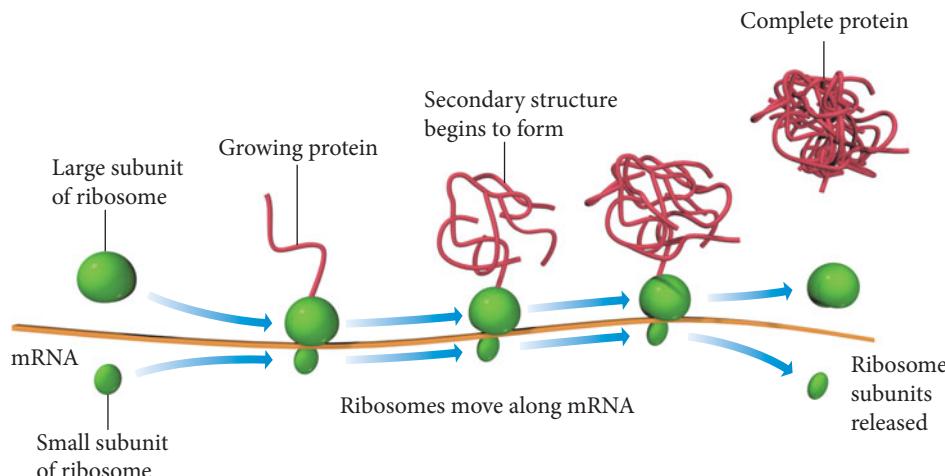
◀ FIGURE 21.21 DNA Replication

When a cell is about to divide, its DNA unwinds. With the help of the enzyme DNA polymerase, a complement to each daughter strand is formed, resulting in two complete copies of the original DNA.

When a cell is about to divide, the DNA unwinds, and the hydrogen bonds joining the complementary bases break (Figure 21.21 ▲), forming two daughter strands. With the help of the enzyme DNA polymerase, a complement to each daughter strand—with the correct complementary bases in the correct sequence—forms. The hydrogen bonds between the old strands and the newly complementary strands then re-form, resulting in two complete copies of the original DNA, one for each daughter cell.

Protein Synthesis

Living organisms must continually synthesize thousands of proteins to survive, each when it is needed and in the quantities required. When a cell needs to make a particular protein, the gene—the section of the DNA that codes for that particular protein—unravels. Complementary copies of that gene are then synthesized (or transcribed) as single strands of *messenger RNA* (or mRNA). The mRNA moves out of the cell's nucleus to structures in the cytoplasm called *ribosomes*. At the ribosome, protein synthesis occurs. The ribosome (which has a large subunit and a small subunit) moves along the mRNA chain that codes for the protein, “reading” the sequence of codons. At each codon, the specified amino acid is brought into place and a peptide bond forms with the previous amino acid (Figure 21.22 ▼). As the ribosome moves along the mRNA, the protein is formed. All of this is orchestrated by enzymes that catalyze the necessary reactions.



▲ FIGURE 21.22 Protein Synthesis A ribosome moves along a strand of mRNA, joining amino acids to form a protein.



Chemistry and Medicine

The Human Genome Project

In 1990, the U.S. Department of Energy (DOE) and the National Institutes of Health (NIH) embarked on a 15-year project to map the human genome, all of the genetic material of a human being. Over 2500 researchers from 18 countries contributed to this research, which has been referred to as the Mt. Everest of biology. An initial draft of the map was completed in 2001 and the final draft was completed in 2003. Here, we highlight some of what has been learned through this massive undertaking.

- The human genome contains 3165 million nucleotide base pairs.
- The average gene contains about 3000 base pairs. The largest gene is for the protein dystrophin (dystrophin deficiency is the root cause of muscular dystrophy); it contains 2.4 million base pairs.
- The human genome contains about 30,000 genes. The function of over half of these is still unknown. Before the Human Genome Project, researchers had estimated that humans had about 100,000 genes. The number of genes in humans is not much larger than the number found in many simpler organisms. For example, the number of genes in a roundworm is nearly 20,000. Whatever makes humans unique, it is not the number of genes in our genome.
- Less than 2% of human DNA actually consists of genes. These genes are aggregated in seemingly random areas within the genome, with vast expanses of noncoding DNA between the coding regions. This stands in contrast to other organisms, which tend to have more uniform distribution of genes throughout their genome.

- The order of DNA base pairs is 99.9% identical in all humans.
- About 1.4 million single base-pair differences (called SNPs for single-nucleotide polymorphisms) have been identified in the human genome. Understanding SNPs can help in identifying individuals who are susceptible to certain diseases. Knowledge of SNPs may also allow physicians to tailor drugs to match individuals.

Knowledge of the human genome is expected to lead to the development of new therapies in several ways. First, knowledge of genes can lead to smart drug design. Instead of developing drugs by trial and error (the current procedure for many drugs), knowledge of a specific gene will allow scientists to design drugs to carry out a specific function related to that gene or its protein product. Second, human genes themselves can provide the blueprint for the production of certain types of drugs, either in the laboratory or by other organisms. For example, we have seen that insulin can be made by inserting the insulin gene into bacteria, which then synthesize the needed drug. Intriguingly, it may even be possible to replace abnormal or missing genes in the cells of diseased patients. Such gene therapies are still in the early stages of development, but they may eventually give us a powerful new tool for combating inherited diseases.

Although the completion of the Human Genome Project may seem like the end, it is really just the beginning. Thousands of studies in the coming years will rely on the data obtained through this endeavor.

Summarizing DNA Coding:

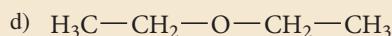
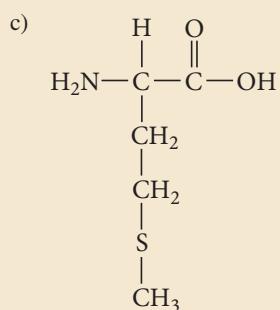
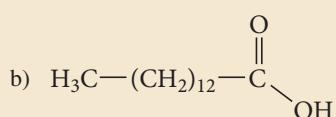
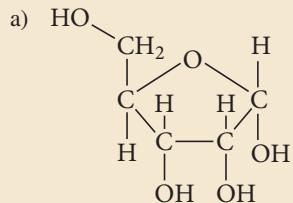
- ▶ DNA contains the code for the sequence of amino acids in proteins.
- ▶ A codon—three nucleotides with their bases—codes for one amino acid.
- ▶ A gene—a sequence of codons—codes for one protein.
- ▶ Genes are contained in structures called chromosomes that occur within cells. Humans have 46 chromosomes in the nuclei of their cells.
- ▶ When a human cell divides, each daughter cell receives a complete copy of the DNA—all 46 chromosomes.
- ▶ When a cell synthesizes a protein, the base sequence of the gene that codes for that protein is transferred to mRNA. mRNA then moves to a ribosome, where the amino acids are linked in the correct sequence to synthesize the protein. The general sequence of information flow is:

DNA → RNA → PROTEIN

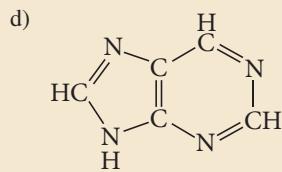
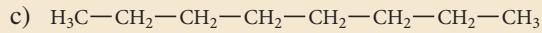
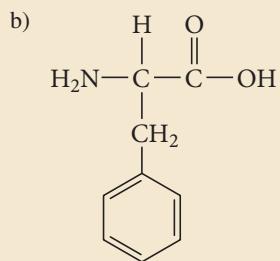
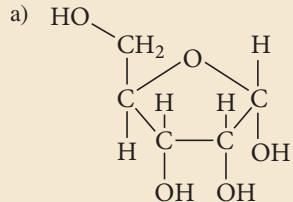
CHAPTER IN REVIEW

Self Assessment Quiz

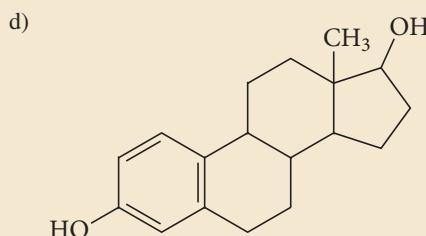
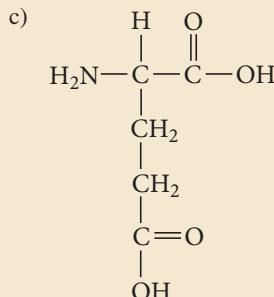
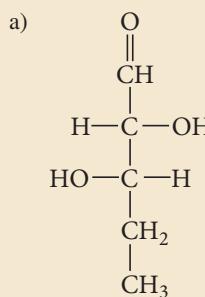
Q1. Which compound is a lipid?



Q2. Which compound is a carbohydrate?



Q3. Which compound is an amino acid?



Q4. The sequence of amino acids in a protein chain is an example of which kind of protein structure?

- a) primary
- b) secondary
- c) tertiary
- d) quaternary

Q5. A section of DNA contains the bases ATTCGGAA. What is the correct sequence of bases in the complementary strand?

- a) CGGATTC
- b) ATTCGGAA
- c) AAGGCTTA
- d) TAAGCCTT

Q6. A codon is a sequence within DNA that codes for what?

- a) an amino acid
- b) a protein
- c) a carbohydrate
- d) a fat

- Q7.** Which of the functions listed is *not* attributed to proteins?
- catalyze biochemical reactions
 - transport substances from one place to another
 - mediate muscle contraction
 - none of the above (all of these functions are attributed to proteins)
- Q8.** Which is a primary function of nucleic acids?
- energy storage
 - coding the amino acid sequence for proteins
 - oxygen transport
 - regulation of metabolic processes

- Q9.** Peptide bonds occur in which type of biochemical compounds?

- lipids
- carbohydrates
- proteins
- nucleic acids

- Q10.** How many nucleotides are required to code for all of the amino acids in a protein that contains 186 amino acids?

- 186
- 372
- 558
- 1

Answers: 1. (b) 2. (a) 3. (c) 4. (a) 5. (d) 6. (a) 7. (d) 8. (b) 9. (c) 10. (c)

Key Terms

Section 21.1

biochemistry (1002)

Section 21.2

lipid (1002)
fatty acid (1002)
triglyceride (1004)
ester linkage (1004)
saturated fat (1004)
unsaturated fat (1004)
phospholipid (1005)
glycolipid (1005)
lipid bilayer (1006)
steroid (1006)

Section 21.3

carbohydrate (1006)
monosaccharide (1007)
hexose (1007)
aldose (1007)
ketose (1007)
glycosidic linkage (1009)
disaccharide (1009)
hydrolysis (1009)
polysaccharide (1009)
complex carbohydrate (1009)
cellulose (1009)
starch (1010)
glycogen (1010)

Section 21.4

enzyme (1010)
amino acid (1010)
peptide bond (1013)
dipeptide (1013)
polypeptide (1013)

Section 21.5

fibrous protein (1014)
globular protein (1015)
primary structure (1016)
secondary structure (1016)
 α -helix (1016)
 β -pleated sheet (1017)

random coil (1017)
tertiary structure (1017)
quaternary structure (1018)

Section 21.6

nucleotide (1018)
complementary (1020)
codon (1021)
gene (1021)
chromosome (1021)

Key Concepts

Diabetes and the Synthesis of Human Insulin (21.1)

- Diabetes is a chronic illness that occurs when the pancreas cannot make enough insulin, a protein that promotes the absorption of glucose into cells.
- The chemical structure of insulin was discovered in 1955 by Frederick Sanger, who made it possible for insulin to be synthesized in the laboratory.
- Eventually, scientists inserted the human gene that codes for the production of insulin into bacteria, which were then able to produce enough insulin to supply diabetics. This example demonstrates the usefulness of biochemistry, the study of the chemicals that compose living organisms.

Lipids (21.2)

- Lipids are biological chemicals that are nonpolar and, therefore, insoluble in water. In our bodies, they compose cell membranes, store energy, and provide insulation.
- A type of lipid called a fatty acid is a carboxylic acid with a long hydrocarbon chain. Fatty acids can be saturated, meaning they contain the maximum number of hydrogen atoms, or unsaturated, meaning they contain one or more carbon–carbon double bonds. Saturated fatty acids experience greater intermolecular forces, making them solid at room temperature, while unsaturated fatty acids are liquids.
- Fats and oils are triglycerides, triesters composed of glycerol bonded by ester linkages to three fatty acids. Like fatty acids, triglycerides can be saturated (fats) or unsaturated (oils).

- Other lipids include phospholipids, made up of a glycerol bonded to two nonpolar fatty acids and a polar phosphate group, used in animal cell membranes; glycolipids, similar to phospholipids but with a sugar molecule as their polar head; and steroids, four-ringed lipids that include cholesterol and sex hormones.

Carbohydrates (21.3)

- Carbohydrates are polyhydroxy aldehydes or ketones and generally have the formula $(CH_2O)_n$. They are important to short-term energy storage and plant structure composition.
- Monosaccharides, the simplest carbohydrates, contain three to eight carbons with one aldehyde or ketone functional group. Glucose, an example of a hexose, can exist both in a linear form and a ring form.
- Two monosaccharides can combine to form a disaccharide. For example, glucose and fructose can combine to form sucrose. The glycosidic linkages that connect the two monosaccharides are broken during digestion by hydrolysis.
- Polysaccharides are polymers of monosaccharides known as complex carbohydrates. They include cellulose, also called fiber, the main structural component of plants; starch, an energy storage compound found in potatoes and grains; and glycogen, used by animals to store glucose in the muscles.

Proteins and Amino Acids (21.4)

- Proteins are polymers of amino acids and serve a variety of biological functions including structure composition, metabolic regulation, and muscle contraction. Enzymes are particularly important proteins that catalyze biochemical reactions in cells.

- An amino acid contains a carbon atom bonded to an amine group, a carboxylic acid group, a hydrogen atom, and an R group. There are 20 amino acids in humans and they differ only in their R group.
- Amino acids form peptide bonds between the amine end of one amino acid with the carboxylic end of another, creating dipeptides, tripeptides, etc., or polypeptides, large examples of which are called proteins.

Protein Structure (21.5)

- Protein structure and shape are critical to protein function.
- Proteins can be broadly divided into two structural categories. Fibrous proteins are generally linear, insoluble structures that serve structural functions. Globular proteins fold into roughly spherical conformations with nonpolar side chains oriented to the interior and polar side chains oriented to the exterior; this structure makes globular proteins soluble in water.
- Protein structure can be analyzed at four levels. The primary structure is the sequence of the amino acid chain. The secondary structure refers to certain regular repeating patterns in the arrangement of protein chains, such as α -helix and β -pleated sheet patterns. The tertiary structure refers to large-scale bends and folds due to interactions between the R groups of amino acids such as hydrogen bonding, disulfide linkages, hydrophobic interactions, and salt bridges. Quaternary structure shows the way that monomeric subunits fit together in multimeric proteins that have more than one polypeptide chain.

Nucleic Acids (21.6)

- Nucleic acids, such as DNA and RNA, are the chemical blueprints used to synthesize proteins. Nucleic acids are polymers of nucleotides, which are each composed of a sugar, a base, and a phosphate group.

- The bases of DNA are adenine (A), cytosine (C), guanine (G), and thymine (T), which are subject to complementary pairing: each pyrimidine base combines with only one purine base.
- Phosphate links bind the C5' carbon of one sugar with the C3' carbon of another sugar to make the polymeric chain.
- The order of the bases in a nucleic acid chain specifies the order of amino acids in a protein.
- Each amino acid is coded by a codon, a sequence of three bases. A gene is a sequence of codons that codes for a specific protein. Genes, in turn, are contained in structures called chromosomes.

DNA Replication, the Double Helix, and Protein Synthesis (21.7)

- Though the DNA code is complete in any cell in the body, every cell does not express every gene. Cells only express the genes relevant to their function.
- DNA is composed of two complementary strands wound around each other in a double helix. The strands are antiparallel; the bases of each strand face the interior and hydrogen bond to their complements on the other strand.
- In order to replicate, a DNA strand divides and an enzyme called DNA polymerase creates the complement of each of the divided strands, thereby making two copies of the original DNA molecule.
- To synthesize proteins, the section of DNA that codes for that gene unravels. Messenger RNA (mRNA) is synthesized as a copy of the gene. The mRNA then combines with ribosomes, structures that “read” the mRNA code and synthesize the correct sequence of amino acids.

Key Learning Outcomes

Chapter Objectives	Assessment
Recognizing and Working with the Basic Structures of Lipids (21.2)  <p>Polar head Nonpolar tails</p>	Exercises 31–34
Recognizing and Working with the Basic Structures of Carbohydrates (21.3)	Exercises 37–40
Identifying Chiral Carbon Atoms in Carbohydrates (21.3)	Example 21.1 For Practice 21.1 Exercises 41, 42, 86
Drawing Structures for Amino Acids and Peptide Bonds (21.4)	Example 21.2 For Practice 21.2 Exercises 49–58
Recognizing Levels of Protein Structure (21.5) 	Exercises 59–62
Recognizing Nucleic Acids and Nucleotides (21.6)	Exercises 63, 64

EXERCISES

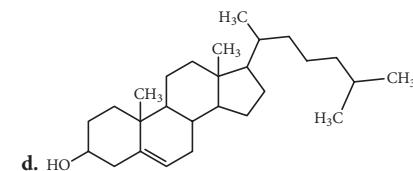
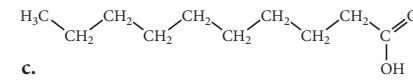
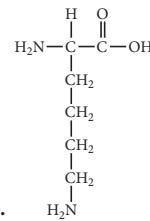
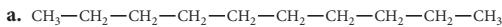
Review Questions

1. What is biochemistry? What significant advances in biochemistry have helped diabetics?
2. What is a lipid? What roles do lipids play in living organisms?
3. What is a fatty acid? Draw the general structure of a fatty acid.
4. What effect do double bonds have within the hydrocarbon chain of a fatty acid?
5. What are triglycerides? Draw a general structure of a triglyceride.
6. Explain the difference, both in terms of structure and in terms of properties, between a saturated fat and an unsaturated fat.
7. Describe the basic structure of phospholipids and glycolipids. What functions do these lipids have in living organisms?
8. What is a steroid? List some functions of steroids.
9. What are carbohydrates? What role do they play in living organisms?
10. How do monosaccharides and disaccharides differ? Aldoses and ketoses?
11. How do simple and complex carbohydrates differ?
12. How do cellulose, starch, and glycogen differ? Describe the function of each.
13. What roles do proteins play in living organisms? List specific examples.
14. Describe the basic structure of an amino acid. How are amino acids linked together to form proteins?
15. How do the properties of the R groups in amino acids relate to the properties of proteins?
16. Why are amino acids chiral?
17. Draw the structure of a neutral amino acid and its dipolar ion.
18. Draw the structure of any two amino acids, showing how they link together to form a dipeptide.
19. Why is protein structure important?
20. How do fibrous proteins and globular proteins differ?
21. Describe the various levels of protein structure (primary, secondary, tertiary, and quaternary).
22. What types of interactions or bonds maintain each of the structures listed in the previous problem?
23. Describe the secondary structures known as α -helix and β -pleated sheet.
24. What is the function of nucleic acids in living organisms?
25. What is the general structure of a nucleic acid?
26. The bases in nucleic acids are *complementary*. What does this mean?
27. What is a codon? A gene? A chromosome?
28. Do most cells contain complete copies of an organism's DNA?
Do most cells express all of the genes contained in their DNA?
29. Explain the mechanism by which DNA is replicated.
30. Explain the mechanism by which proteins are synthesized from the information contained within DNA.

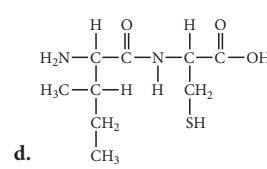
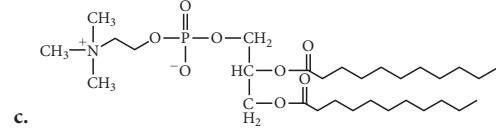
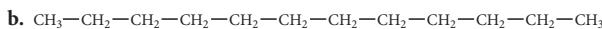
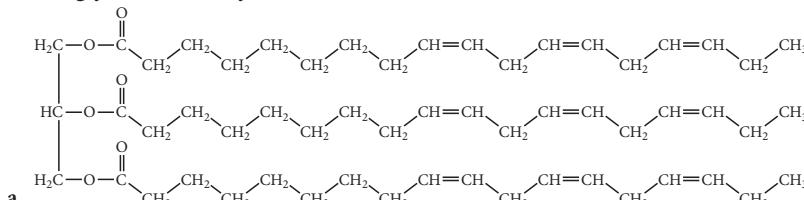
Problems by Topic

Lipids

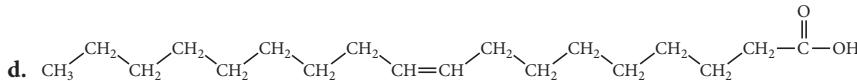
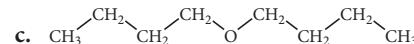
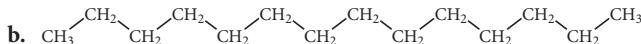
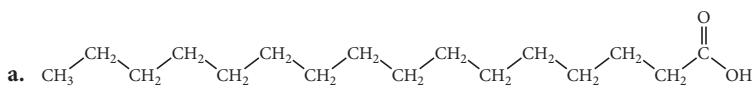
31. Determine whether or not each molecule is a lipid. If the molecule is a lipid, indicate the kind of lipid. If it is a fatty acid or a triglyceride, classify it as saturated or unsaturated.



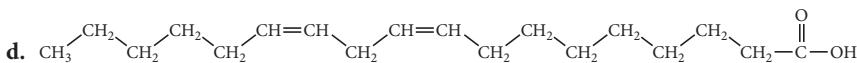
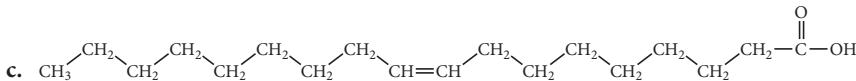
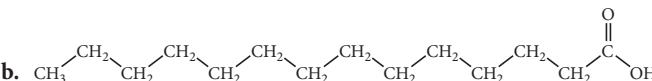
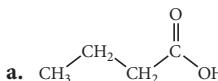
32. Determine whether or not each molecule is a lipid. If the molecule is a lipid, state the kind of lipid. If it is a fatty acid or a triglyceride, classify it as saturated or unsaturated.



- 33.** Determine whether or not each molecule is a fatty acid. If it is a fatty acid, classify it as saturated, monounsaturated, or polyunsaturated.



- 34.** Which fatty acid is most likely to be a solid at room temperature?

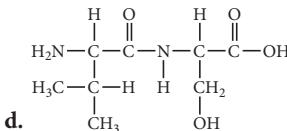
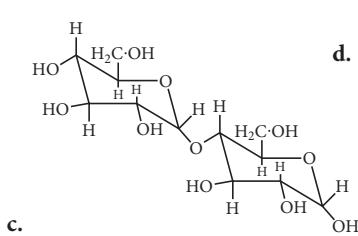
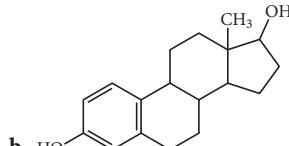
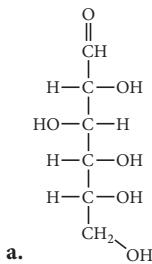


- 35.** Draw structures showing the reaction of glycerol with linoleic acid to form the triglyceride trilinolein. Would you expect this triglyceride to be a fat or an oil?

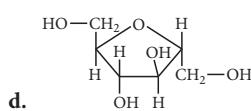
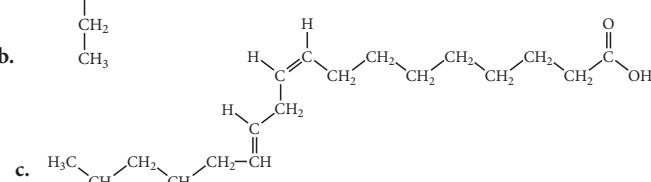
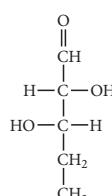
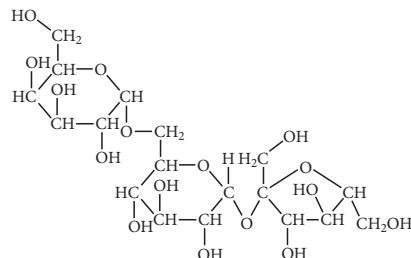
- 36.** Draw structures showing the reaction of glycerol with myristic acid to form the triglyceride trimyristin. Would you expect this triglyceride to be a fat or an oil?

Carbohydrates

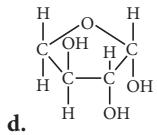
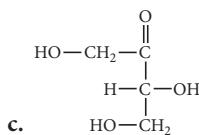
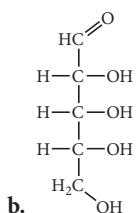
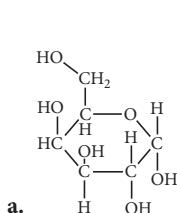
- 37.** Determine whether or not each structure is a carbohydrate. If the molecule is a carbohydrate, classify it as a monosaccharide, disaccharide, or trisaccharide.



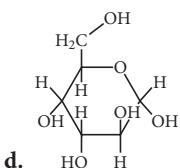
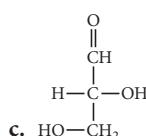
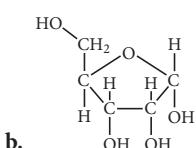
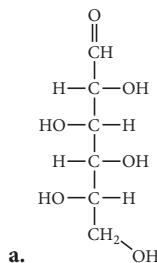
- 38.** Determine whether or not each structure is a carbohydrate. If the molecule is a carbohydrate, classify it as a monosaccharide, disaccharide, or trisaccharide.



39. Classify each saccharide as an aldose or a ketose. Also classify each as a triose, tetrose, pentose, etc.



40. Classify each saccharide as an aldose or a ketose. Also classify each as a triose, tetrose, pentose, etc.



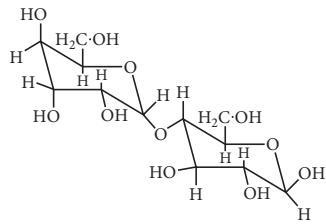
41. How many chiral carbon atoms are in each of the structures in Problem 39?

42. How many chiral carbon atoms are in each of the structures in Problem 40?

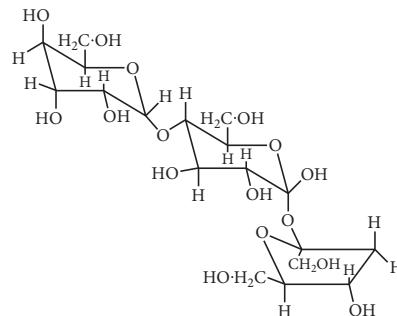
43. Draw structures for the straight-chain and ring forms of glucose.

44. Draw structures for the straight-chain and ring forms of fructose.

45. Draw the products that result from the hydrolysis of the carbohydrate.



46. Draw the products that result from the hydrolysis of the carbohydrate.



47. Draw the structure of sucrose. Label the glucose and fructose rings in this disaccharide.

48. Lactose is a disaccharide of glucose and galactose. Draw the structure of lactose.

Amino Acids and Proteins

49. Draw each amino acid in its dipolar ion form.

a. Thr b. Ala c. Leu d. Lys

50. Draw each amino acid in its dipolar ion form.

a. Val b. Phe c. Tyr d. Cys

51. Draw the structures of the two enantiomers of alanine.

52. Draw the structures of the two enantiomers of cysteine.

53. How many different tripeptides can form from serine, glycine, and cysteine? List the amino acid sequence of each one.

54. How many dipeptides can form from leucine and serine? List the amino acid sequence for each one.

55. Draw the reaction by which serine and tyrosine form a peptide bond.

56. Draw the reaction by which valine and asparagine form a peptide bond.

57. Draw a structure for each tripeptide.

a. Gln-Met-Cys b. Ser-Leu-Cys
c. Cys-Leu-Ser

58. Draw a structure for each tetrapeptide.

a. Ser-Ala-Leu-Cys b. Gln-Met-Cys-Gly
c. Gly-Cys-Met-Gln

59. A phenylalanine amino acid on a protein strand undergoes hydrophobic interactions with another phenylalanine amino acid that is 26 amino acid units away. The resulting fold in the protein is an example of which kind of structure? (primary, secondary, tertiary, or quaternary)

60. An amino acid on a protein strand forms a hydrogen bond to another amino acid that is four amino acid units away. The next amino acid on the chain does the same, hydrogen bonding to an amino acid that is four amino acids away from it. This pattern repeats itself over a significant part of the protein chain. The resulting pattern in the protein is an example of which kind of structure? (primary, secondary, tertiary, or quaternary)

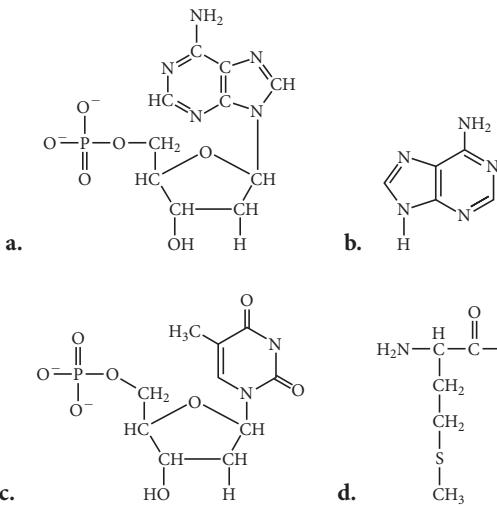
61. The amino acid sequence in one section of a protein is shown here. It represents which kind of structure? (primary, secondary, tertiary, or quaternary)

-Lys-Glu-Thr-Ala-Ala-Lys-Phe-Glu-

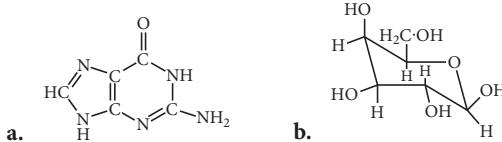
62. A dimeric protein is composed of two individual chains of amino acids. The way these two chains fit together is an example of which kind of structure? (primary, secondary, tertiary, or quaternary)

Nucleic Acids

63. Determine whether or not each structure is a nucleotide. For each nucleotide, identify the base as A, T, C, or G.



64. Determine whether or not each structure is a nucleotide. For each nucleotide, identify the base as A, T, C, or G.



Cumulative Problems

71. Determine the class of biochemical compound that contains each type of linkage.
a. peptide bonds b. glycosidic linkage
c. ester linkage

72. Name the type of polymer associated with each monomer.

a. nucleotide b. amino acid c. saccharide

73. What is the difference between a codon and a nucleotide?
A codon and a gene?

74. What is the difference between a fatty acid and a triglyceride?
A triglyceride and a phospholipid?

75. The amino acid alanine has the condensed structural formula shown here:

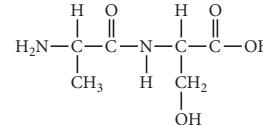
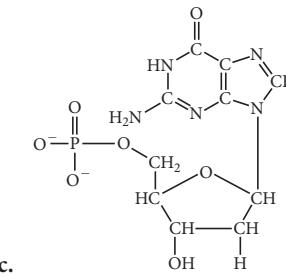


Determine the VSEPR geometry about each internal atom and make a three-dimensional sketch of the molecule.

76. The amino acid serine has the condensed structural formula shown here:



Determine the VSEPR geometry about each internal atom and make a three-dimensional sketch of the molecule.



65. Draw the structures of the two purine bases in nucleic acids.
66. Draw the structures of the three pyrimidine bases in nucleic acids.
67. Draw the DNA strand that is complementary to the DNA strand shown here.



68. Draw the DNA strand that is complementary to the DNA strand shown here.



69. A monomeric protein contains 154 amino acids. How many codons code for these amino acids? How many nucleotides?
70. A dimeric protein contains 142 amino acids in one strand and 148 in the other. How many codons code for these amino acids? How many nucleotides?

77. Which amino acids in Table 21.3 are most likely to be involved in hydrophobic interactions?

78. Sickle-cell anemia is caused by a genetic defect that substitutes valine for glutamic acid at one position in two of the four chains of the hemoglobin protein. The result is a decrease in the water solubility of hemoglobin. Examine the structures of valine and glutamic acid and explain why this occurs.

79. Determining the amino acid sequence in a protein usually involves treating the protein with various reagents that break up the protein into smaller fragments that can be individually sequenced. Treating a particular 11-amino acid polypeptide with 1 reagent produced the fragments:



Treating the same polypeptide with a different reagent produced the fragments:



What is the amino acid sequence of the polypeptide?

80. Treating a particular polypeptide with one reagent (as described in the previous problem) produced the fragments:



Treating the same polypeptide with a different reagent produced the fragments:



What is the amino acid sequence of the polypeptide?

81. Naturally occurring D-glucose is one of a pair of enantiomers. Its mirror image is L-glucose. Draw the two cyclic six-membered

isomers of L-glucose that differ in the configuration around C1 and indicate which is α and which is β .

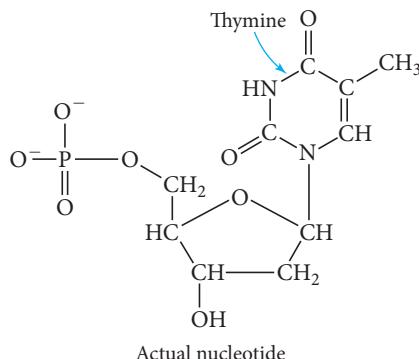
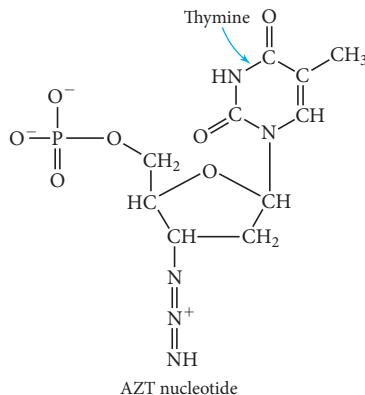
82. Calculate the mass percent of phosphorus in a strand of DNA that consists of equal amounts of each of the four N-bases.

83. The double helical structure of DNA disrupts on heating but re-forms on cooling. Use thermodynamic reasoning to account for these observations.

84. From the structural formula of cholesterol shown on page 1006, determine (a) the composition, and (b) the number of chiral centers.

Challenge Problems

85. One way to fight viral infections is to prevent a virus from replicating its DNA. Without DNA replication, the virus cannot multiply. Some viral drug therapies cause the introduction of *fake* nucleotides into cells. When the virus uses one of these fake nucleotides in an attempt to replicate its DNA, the fake nucleotide doesn't work and viral DNA replication is halted. For example, azidothymidine (AZT), a drug used to fight the human immunodeficiency virus (HIV) that causes AIDS, results in the introduction of the following fake thymine-containing nucleotide into cells. Examine the structures of the real nucleotide and the AZT fake nucleotide. Propose a mechanism for how this fake nucleotide might halt DNA replication.



86. Draw each molecule and identify the chiral centers within them.
- ribose
 - galactose
 - 5-deoxyribose (*Hint*: The 5 indicates that the oxygen is removed from the 5th carbon.)

87. Glucose transport across the red blood cell membranes (erythrocyte membrane) is a well-studied system. One laboratory project obtained the data shown here for glucose transport.

[Glucose] _{outside} (mM)	Rate of Glucose Entry ($\mu\text{M}/\text{min}$)
0.5	12
1.0	19
2.0	27
3.0	32
4.0	35

The kinetics of glucose transport through the membrane follows the Michaelis–Menten equation:

$$V_0 = \frac{V_{\max}[\text{glucose}]}{K_t + [\text{glucose}]}$$

V_0 = rate of glucose entry

V_{\max} = maximum rate (the point at which addition of glucose has no effect on the rate)

K_t = transport constant

The Michaelis–Menten equation can be rearranged so that a plot $1/V_0$ versus $1/[\text{glucose}]$ produces a straight line. Rearrange the equation and plot the data in order to determine K_t and V_{\max} for glucose transport across the erythrocyte membrane.

88. Eukaryotic DNA is equipped with special ends called telomeres. Telomeres are made up of hexanucleotide sequences that repeat at the ends of the DNA. For example, human DNA features repeating AGGGTT sequences. Functionally, telomeres protect the ends of chromosomes from being treated as a broken piece of DNA in need of repair. Interestingly, telomeres are cut off each time the DNA is replicated, indicating a possible cellular clock that allows only a certain number of cellular replications. Telomerase is the enzyme that catalyzes the synthesis of telomeres. Telomerase is present in limited quantities within certain cells such as fetal tissue, adult male germ cells, and stem cells. It is also found in over 85% of tumor cells. Researchers speculate that the telomerase activity may be linked to cancer. Propose an explanation for why telomerase activity could be associated with cancer and speculate on ways in which cancer treatments in the future may capitalize on research on this enzyme.

89. Write the major equilibrium that is established in a solution of glycine at pH = 2 and at pH = 10. The pK_a of the COOH group is 2.3 and the pK_a of the NH_3^+ group is 9.6. Determine the relative concentrations of each member of the relevant conjugate acid–base pair at pH = 2 and pH = 10. Calculate the pH at which glycine is neutral.

Conceptual Problems

90. How many different tetrapeptides can form from four different amino acids?
91. Could the genetic code have been based on just three bases and three-base codons? Explain why or why not. (Assume that the code must accommodate 20 different amino acids.)
92. The genetic code is random, which means that a particular codon could have coded for a different amino acid. The genetic code is also nearly universal, meaning that it is the

same code in nearly all organisms (and in the few where it differs, it does so only slightly). If scientists ever find life on another planet, they will be curious to know its genetic code. What would a completely different genetic code indicate about the origin of the life-form? What would a genetic code identical to terrestrial life indicate?

Answers to Conceptual Connections

Peptides

- 21.1** Six possible tripeptides can form from these three amino acids. They are (1) Ser-Gly-Ala; (2) Gly-Ala-Ser; (3) Ala-Ser-Gly; (4) Ala-Gly-Ser; (5) Ser-Ala-Gly; (6) Gly-Ser-Ala. Notice that bonding the amino acids in reverse order results in a different molecule because the N-terminal and the C-terminal ends reside on different amino acids. For example, in Ser-Gly-Ala, the N-terminal amino acid is Ser (conventionally drawn on the left) and the C-terminal side is Ala. In Ala-Gly-Ser, in contrast, the N-terminal amino acid is Ala and the C-terminal one is Ser.

The Genetic Code

- 21.2** The number of unique two-base sequences of four bases is $4^2 = 16$. The number of unique three-base sequences of four bases is $4^3 = 64$. A two-base system could code for 16 amino acids, and a three-base system could code for 64 amino acids.

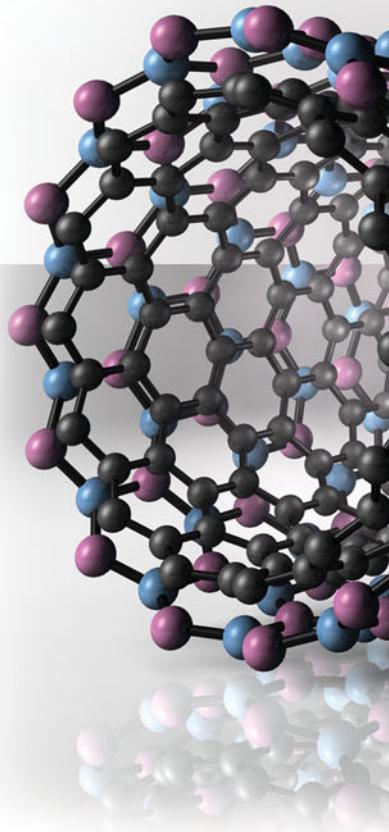
22

Chemistry of the Nonmetals

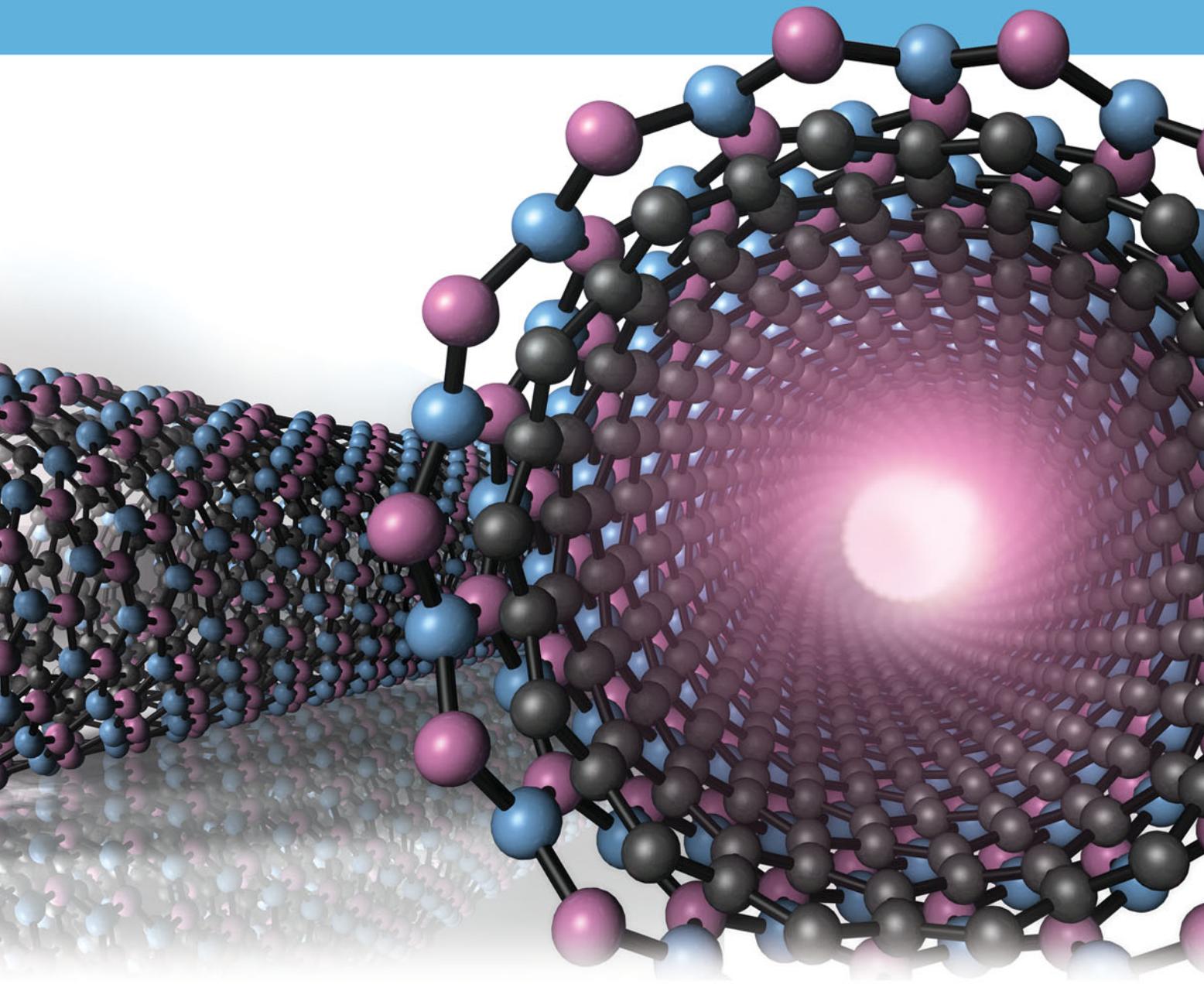
What one learns in chemistry is that Nature wrote all the rules of structuring; man does not invent chemical structuring rules; he only discovers the rules. All the chemist can do is find out what Nature permits, and any substances that are thus developed or discovered are inherently natural.

—R. Buckminster Fuller (1895–1983)

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 - 22.2** The Main-Group Elements: Bonding and Properties 1036
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THROUGHOUT THIS BOOK, YOU HAVE been introduced to many chemical topics, but you still may not know the composition of some everyday objects such as a drinking glass, a computer chip, or even rocks and soil. In these last few chapters, we explore the descriptive chemistry of the nonmetals and metals. These descriptions are part of a branch of chemistry called inorganic chemistry. We begin our exploration of descriptive inorganic chemistry by looking at the chemistry of some of the main-group elements. The main-group elements are grouped together because their valence electrons occupy only *s* or *p* orbitals; however, their properties vary greatly. The main-group elements include metals, nonmetals, and semimetals, and they may be solids, liquids, or gases at room temperature. This great diversity of properties, bonding, and structures of all the main-group elements cannot be adequately described in a single chapter. Therefore, this chapter focuses on only a few main-group elements (silicon, boron, carbon, nitrogen, phosphorus, oxygen, sulfur, and the halogens) and their compounds in an effort to illustrate the diversity within the group.



Scientists have recently been able to synthesize carbon nanotubes that have an insulating boron nitride sheath. These structures are like electrical wires 100,000 times thinner than a human hair.

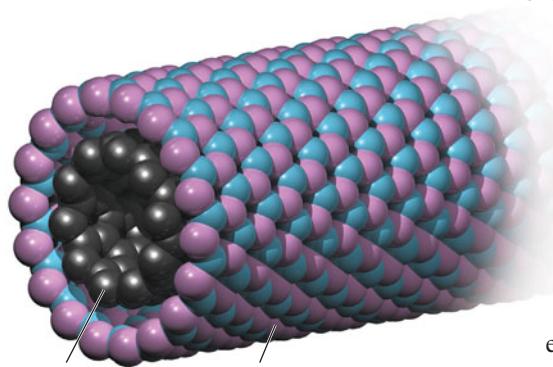
22.1 Insulated Nanowires

In 1991, scientists discovered carbon nanotubes, the long, thin, hollow cylinders of carbon atoms (see the cover of this book) that we discuss in some detail in Section 22.5. In the late 1990s, scientists discovered that they could make similar tubes from boron nitride. Boron nitride contains BN units that are isoelectronic (having the same number of electrons) with carbon in the sense that each BN unit contains eight valence electrons, or four per atom (just like carbon). The size and electronegativity of a carbon atom are also almost equal to the average of those properties for a boron atom and a nitrogen atom (Table 22.1). Because of this, BN forms a number of structures that are similar to those formed by carbon, including nanotubes.

An important difference between boron nitride nanotubes and carbon nanotubes is their conductivity. Carbon nanotubes conduct electrical current but boron nitride tubes act as insulators. In 2003, scientists were able to combine these two sorts of nanotubes into one structure: a conducting carbon nanotube with an insulating boron nitride sheath,

TABLE 22.1 Properties of BN and C

Element	Atomic Radius (pm)	Ionization Energy (kJ/mol)	Electronegativity
B N BN	85 70 77.5 average	800 1402 1101 average	2 3 2.5 average
C	77	1086	2.5



▲ FIGURE 22.1 Boron Nitride Nanotube

The model represents an insulating BN nanotube filled with a conducting carbon nanotube.

shown in Figure 22.1 ▲. The result is an insulated conducting wire that is 100,000 times thinner than a human hair. Such thin wires may someday be used in computers and other electronic devices, allowing these devices to continue to become smaller and more efficient.

The more we learn about the structures and reactivities of known materials, the better equipped we are to discover new materials and applications. Even though it may seem that most inorganic compounds have already been discovered and analyzed, new materials, with immense impacts on our society, are constantly being discovered. As Buckminster Fuller states in this chapter's opening quote, we continue to find "what Nature permits." In some cases, what nature permits turns out to be extremely useful to society.

22.2 The Main-Group Elements: Bonding and Properties

We identify the **main-group elements** by their electron configurations. In this chapter, we focus on groups 3A–7A, the major part of the *p* block in the periodic table. The *p* orbitals fill incrementally across any row of this section of the periodic table; they contain from one electron in group 3A to five electrons in group 7A (the halogens). The physical properties of the elements, such as atomic size and electronegativity, also change across each period, and this affects their reactivity and the types of compounds they form.

1A																8A				
1	H	2A															2	He		
3	Li	4	Be															5	B	
11	Na	12	Mg	3B	4B	5B	6B	7B	8B		1B	2B	13	14	15	16	17	18	Ar	
19	K	20	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	31	32	33	34	35	36	Kr
37	Rb	38	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	49	50	51	52	53	54	Xe
55	Cs	56	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	81	82	83	84	85	86	Rn
87	Fr	88	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	113	114	115	116	117*	118		

Atomic Size and Types of Bonds

Recall from Section 8.6 that the effective nuclear charge of the main-group elements becomes greater as we move to the right across any row in the periodic table. This increasing effective charge results in smaller radii, increasing electronegativity, and increasing ionization energy as we move to the right across the periods. Consequently, as we have seen since the early chapters of this book, the nonmetals on the right side of the periodic table (those toward the right of the *p* block) tend to form anions in ionic compounds.

See Section 8.6 for a more thorough discussion of the periodic trends and exceptions in these properties of the elements.

They are easily reduced, gaining electrons to completely fill their *p* orbitals and attain noble gas electron configurations. These elements act in reactions as *oxidizing agents*—they oxidize other substances while they are themselves reduced. The smallest halogens and the elements in the oxygen group are the strongest oxidizing agents in the *p* block.

Elements near the center of the *p* block have fewer *p* electrons and do not usually fill the *p* orbitals by forming anions; instead they share electrons, forming covalent bonds. We see this type of reactivity in the vast array of molecular compounds formed by the smaller elements in the carbon and nitrogen groups. The main-group elements on the far left of the *p* block have only one *p* electron and form cations in ionic compounds and electron-deficient species (species with an incomplete octet) in covalent compounds.

Notice that as we move to the right across any row in the *p* block, the type of bonding changes as the elements become less metallic. Recall from Section 8.8 that metallic character increases as we go down each column. The diagonal group of metalloid elements stretching from boron to astatine divides the main-group elements: to the left of this diagonal, the elements are metals that form cations and metallic compounds; to the right, the elements are nonmetals that form anions and covalent compounds.

The vast range in elemental properties, from those of metallic elements such as thallium and lead that have very low electronegativities of 1.8 and 1.9 (respectively) to those of the nonmetallic elements such as oxygen and fluorine that have the highest electronegativities of 3.5 and 4.0 (respectively), results in the great chemical diversity of the elements in the *p* block. These elements include metals, alloys, simple covalent compounds, enormous covalent network compounds, simple binary ionic compounds, and complex chain and layered ionic compounds.

Major Divisions of the Periodic Table

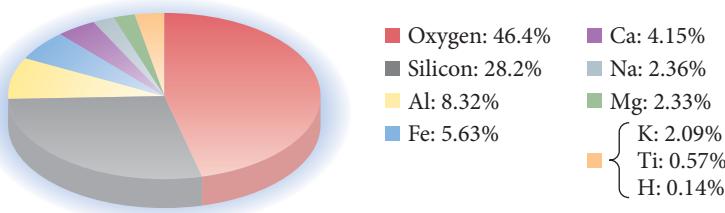
		Major Divisions of the Periodic Table																			
		Metals		Metalloids		Nonmetals		3A		4A		5A		6A		7A		8A			
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	He	
1	H	Li	Be	Na	Mg	3B 3	4B 4	5B 5	6B 6	7B 7	8B 8	9	10	1B 11	2B 12	5 B	6 C	7 N	8 O	9 F	Ne
2	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	31	32 Ge	33 As	34 Se	35 Br	36 Kr		
3	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	49	50	51 Sn	52 Sb	53 Te	54 I	Xe	
4	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	81	82	83 Bi	84 Po	85 At	86 Rn		
5	Fr	Ra	Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112	113	114	115	116	117*	118			
Lanthanides		58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu						
Actinides		90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr						

22.3 Silicates: The Most Abundant Matter in Earth's Crust

The most abundant elements in Earth's crust are oxygen (45–50% by mass) and silicon (about 28% by mass). The few other elements that individually comprise more than 1% of the crust's mass are aluminum, iron, calcium, magnesium, sodium, and potassium

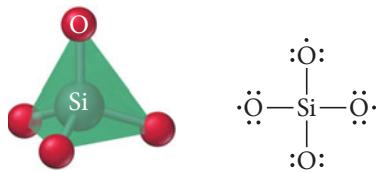
► FIGURE 22.2 Major Elements in Earth's Crust

The major components of Earth's crust are oxygen and silicon. Only a few other elements compose more than 1% of the crust each.



(Figure 22.2 ▲), and most of these are found in silicon and oxygen compounds. In order to understand the matter on Earth's surface, we must understand silicon and oxygen compounds.

Silicates are covalent atomic solids (see Section 11.12) that contain silicon, oxygen, and various metal atoms. Rocks, clays, and soils contain silicates. Their great diversity illustrates a theme that we have encountered since Chapter 1 of this book: the properties of substances are determined by their atomic and molecular structures. The structures of silicates determine their properties—and since these structures are varied, their properties are also varied. Some silicates form strong three-dimensional materials, while others break into sheets, and still others are highly fibrous. Let's examine more closely several of these structures.



▲ FIGURE 22.3 SiO_4 Tetrahedron In a SiO_4 tetrahedron, silicon occupies the center of the tetrahedron and one oxygen atom occupies each corner.

Quartz and Glass

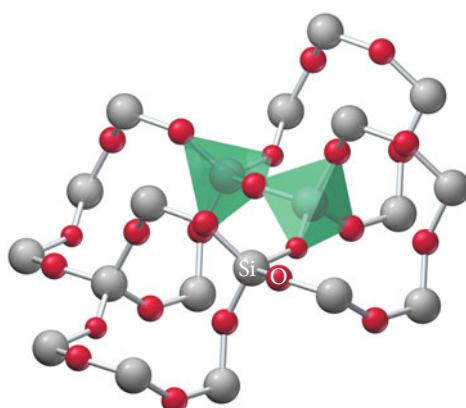
Silicon and oxygen form a network covalent structure in which a silicon atom bonds to four oxygen atoms, forming a tetrahedral shape with the silicon atom in the middle and the four oxygen atoms at the corners of the tetrahedron (Figure 22.3 ▲). In this structure, the silicon atom bonds to each oxygen atom with a single covalent sigma bond. In contrast to carbon, which often bonds to oxygen with a double bond (one sigma and one pi bond), silicon forms only a single bond with oxygen, because the silicon atom is too large to allow substantial overlap between the p orbitals on the two atoms. The silicon atom in this structure, by bonding to four oxygen atoms, obtains a complete octet. However, each oxygen atom is one electron short of an octet. Therefore, each O atom forms a second covalent bond to a different Si atom, forming the three-dimensional structure of **quartz**. Quartz has a formula unit of SiO_2 and is generally called **silica**. Each Si atom is in a tetrahedron surrounded by four O atoms, and each O atom acts as a bridge connecting the corners of two tetrahedrons (Figure 22.4 ▼). Silica melts when heated above 1500 °C. After melting, if cooled quickly, silica does not crystallize back into the quartz structure. Instead, the Si atoms and O atoms form a randomly ordered amorphous structure called a glass. Common glass is amorphous SiO_2 .

Aluminosilicates

Aluminosilicates are a family of compounds in which aluminum atoms substitute for silicon atoms in some of the lattice sites of the silica structure. Since the aluminum ion has only three valence electrons (in contrast to the four valence electrons of silicon),

a SiO_2 unit becomes AlO_2^- upon substitution of aluminum. The negative charge is balanced by a positive counterion. A common group of aluminosilicates is the feldspars. The mineral albite is a feldspar. A **mineral** is a homogenous, crystalline substance that naturally occurs in the earth's crust. In albite, one-fourth of the Si atoms are replaced by Al atoms. Na^+ ions provide the necessary balancing positive charge. The formula for albite is $\text{Na}(\text{AlSi}_3\text{O}_8)$, but it may be written as $\text{Na}(\text{AlO}_2)(\text{SiO}_2)_3$ to illustrate the substitution of Al for Si.

A rock is a heterogeneous mixture that may contain one or more minerals.



▲ FIGURE 22.4 Structure of Quartz In the quartz structure, each Si atom is in a tetrahedron surrounded by four O atoms, and each O atom is a bridge connecting the corners of two tetrahedrons.

EXAMPLE 22.1 Determining the Composition of an Aluminosilicate

Write the formula for anorthite, a crystal in which Al atoms substitute for one-half of the Si atoms and the charge is balanced by Ca^{2+} ions.

SOLUTION

The AlO_2^- unit substitutes for one-half of the SiO_2 units; therefore, the formula has equal numbers of AlO_2^- and SiO_2 units. You must balance every AlO_2^- ion in the formula by a corresponding positive charge. Since Ca^{2+} has a $2+$ charge, it can balance two AlO_2^- units. Thus, the formula for anorthite is $\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)$ or $\text{Ca}(\text{AlO}_2)_2(\text{SiO}_2)_2$.

FOR PRACTICE 22.1

Orthoclase is a crystal in which Al^{3+} substitutes for one-fourth of the Si^{4+} ions. K^+ ions balance the charge. Write the formula for orthoclase.

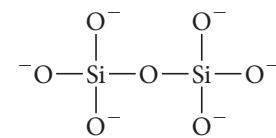
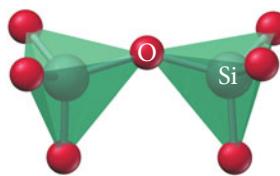
Individual Silicate Units, Silicate Chains, and Silicate Sheets

In many silicate compounds, the oxygen atoms are not connected to two silicon atoms to form the neutral compound that is found in quartz. Instead, the oxygen atoms gain electrons from metal atoms and form polyatomic anions, such as SiO_4^{4-} . The positively charged metal ions then bond to the negatively charged silicon oxide. In these minerals, the SiO_4 tetrahedrons occur singly, in chains, or in sheets.

When a tetrahedron occurs singly (not bonded to other tetrahedrons), it forms the SiO_4^{4-} polyatomic anion (which has four extra electrons that satisfy the octet rule for the four oxygen atoms). These types of silicates are **orthosilicates** (or nesosilicates) and require cations that have a total charge of $4+$ to neutralize the negative charge. The cations can be of a single metal, such as Zn^{2+} in Zn_2SiO_4 (the mineral willemite), or they can be a mixture of different metals, such as the family of crystals called olivines $[(\text{Mg}, \text{Fe})_2\text{SiO}_4]$ where the Mg^{2+} and Fe^{2+} ions can exist in variable proportions, providing a total charge of $4+$. All of these compounds are held together by the ionic bonding between the metal cations and SiO_4^{4-} polyatomic anions.

The silicate tetrahedrons can also form structures called **pyrosilicates** (or sorosilicates) in which two tetrahedrons share one corner (Figure 22.5 ▶), forming the disilicate ion, which has the formula $\text{Si}_2\text{O}_7^{6-}$. This group requires cations that balance the $6-$ charge on $\text{Si}_2\text{O}_7^{6-}$. Again, these cations can be the same metal ions or a mixture of different metal ions. For example, in the mineral hardystonite ($\text{Ca}_2\text{ZnSi}_2\text{O}_7$), two Ca^{2+} ions and one Zn^{2+} ion together provide the $6+$ charge.

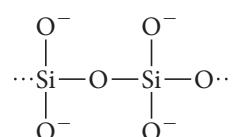
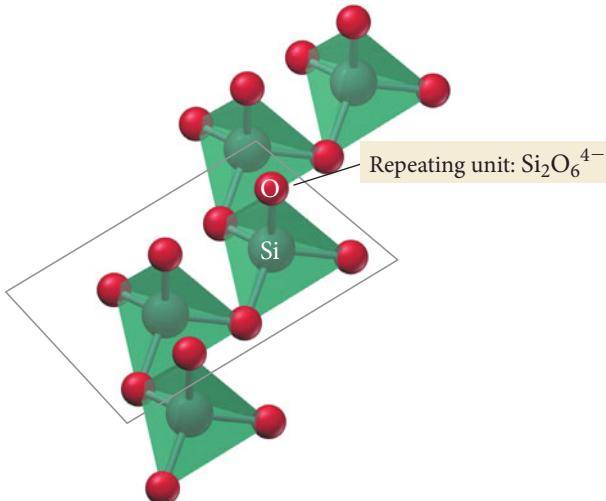
The silicon tetrahedron also forms structures called **pyroxenes** (or inosilicates) in which many of the tetrahedrons bond together creating chains (Figure 22.6 ▼). The formula unit for these chains is the SiO_3^{2-} unit, and the repeating unit in the structure is



Formula unit: $\text{Si}_2\text{O}_7^{6-}$

▲ FIGURE 22.5 Pyrosilicate Structure

In pyrosilicates, the silicate tetrahedrons share one corner, forming $\text{Si}_2\text{O}_7^{6-}$ units. Pyrosilicates are also called sorosilicates.



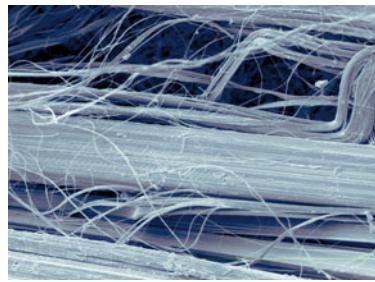
Formula unit: SiO_3^{2-}

◀ FIGURE 22.6 Pyroxene Structure

In pyroxenes, chains of silicate tetrahedrons are formed. Pyroxenes are also called inosilicates.

► FIGURE 22.7 Amphibole Structure

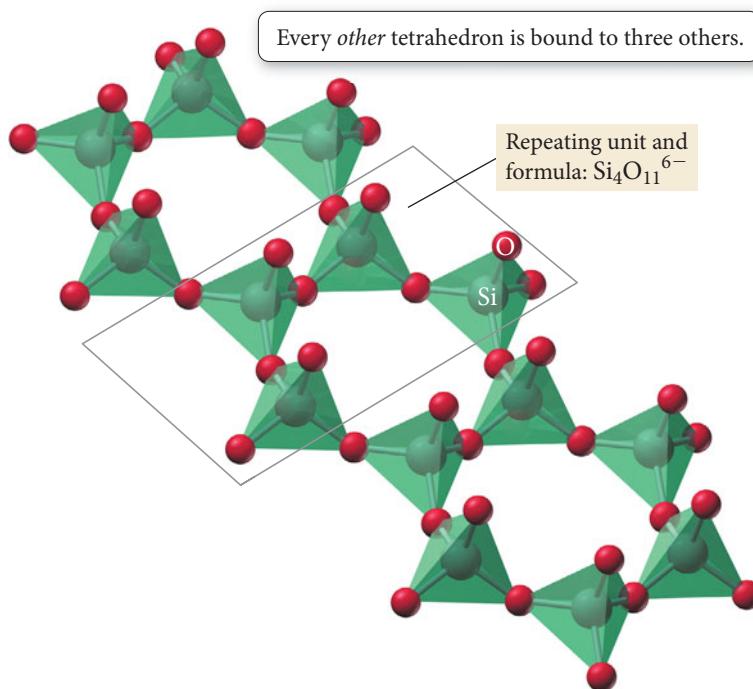
Amphiboles contain double chains of silica tetrahedrons.



▲ The fibrous texture of asbestos results from the silicate double chains of the amphibole structure.

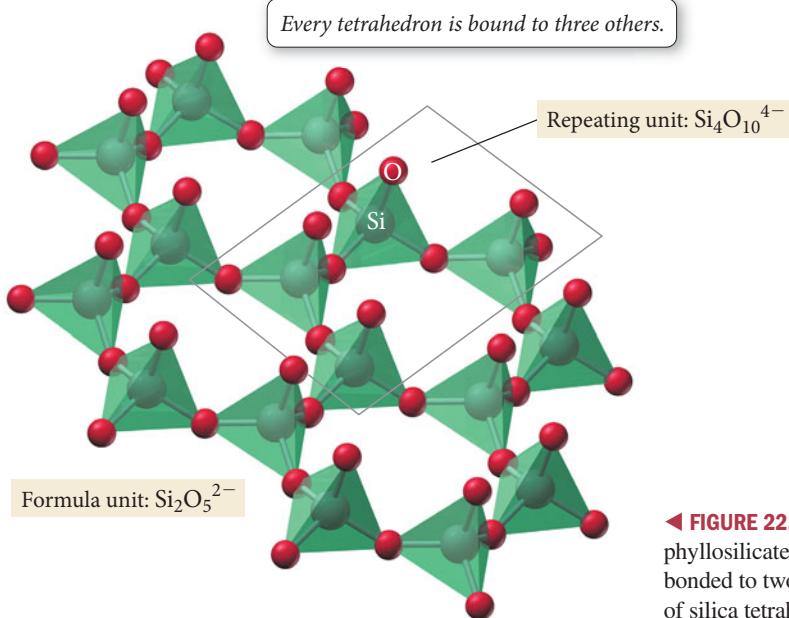


▲ The flaky texture of mica is due to silicate sheets of the phyllosilicate structure.



two formula units ($\text{Si}_2\text{O}_6^{4-}$). Two of the oxygen atoms are bonded to two silicon atoms (and thus to two other tetrahedrons) at two of the four corners of each tetrahedron. The silicate chains are held together by ionic bonding to metal cations that lie between the chains. For example, in the crystal diopside, $\text{CaMg}(\text{SiO}_3)_2$, Ca^{2+} and Mg^{2+} ions bond with the silicate chains.

Some silicate structures have *double chains* in which half of the tetrahedrons of one chain are bonded to tetrahedrons in another chain through oxygen atoms. The minerals with double silicate chains are called amphiboles, and the repeating unit in the crystal is $\text{Si}_4\text{O}_{11}^{6-}$ (Figure 22.7 ▲). Half of the tetrahedrons are bonded by two of the four corner O atoms, and half of the tetrahedrons are bonded by three of the four corners, joining the two chains together. The bonding within the double chains is very strong, but the bonding between the double chains is not so strong. This structure often results in fibrous minerals such as asbestos. An example of an asbestos-type mineral is tremolite, $\text{Ca}_2(\text{OH})_2\text{Mg}_5(\text{Si}_4\text{O}_{11})_2$. In this crystal, hydroxide ions bonded to some of the metal cations help balance the charge between the cations and the anionic silicate chains.



◀ FIGURE 22.8 Phyllosilicate Structure In phyllosilicates, three of the four oxygens are bonded to two silicon atoms, forming sheets of silica tetrahedrons.

When three of the four oxygen atoms are bonded between the silicate tetrahedrons, the sheet structure shown in Figure 22.8 ▲ results. These compounds are called phyllosilicates and have a formula unit of $\text{Si}_2\text{O}_5^{2-}$. Sheets of tetrahedral silicates are bonded together by metal cations that lie between the sheets. For example, the mineral *talc*, $\text{Mg}_3(\text{Si}_2\text{O}_5)_2(\text{OH})_2$, is a phyllosilicate. The weak interactions between silicate sheets give talc its slippery feel (this is similar to the way the weak interactions between sheets of carbon atoms give graphite its slippery feel). Table 22.2 summarizes the different kinds of silicate structures.

TABLE 22.2 Types of Silicate Structures

Tetrahedrons	Shared Vertices	Formula Unit	Si : O Ratio	Class Name	Example
Single tetrahedron	0	SiO_4^{4-}	1 : 4	Orthosilicates, nesosilicates	Olivine, Mg_2SiO_4
Double tetrahedron	1	$\text{Si}_2\text{O}_7^{6-}$	2 : 7	Pyrosilicates, sorosilicates	Hardystonite, $\text{Ca}_2\text{ZnSi}_2\text{O}_7$
Single chain	2	SiO_3^{2-}	1 : 3	Pyroxenes, inosilicates	Jadeite, $\text{NaAl}(\text{SiO}_3)_2$
Double chain	2 and 3	$\text{Si}_4\text{O}_{11}^{6-}$	4 : 11	Amphiboles	Tremolite, $\text{Ca}_2(\text{OH})_2\text{Mg}_5(\text{Si}_4\text{O}_{11})_2$
Sheet	3	$\text{Si}_2\text{O}_5^{2-}$	2 : 5	Phyllosilicates	Talc, $\text{Mg}_3(\text{Si}_2\text{O}_5)_2(\text{OH})_2$
Network covalent	4	SiO_2	1 : 2	Silicas, tectosilicates	Quartz, SiO_2
Network covalent	4	$\text{AlSi}_3\text{O}_8^-$ or $\text{Al}_2\text{Si}_2\text{O}_8^{2-}$	Variable	Feldspars	Albite, $\text{NaAlSi}_3\text{O}_8$

EXAMPLE 22.2 Composition and Charge Balance of Silicates

The silicate chrysotile is an amphibole with the formula $\text{Mg}_6\text{Si}_4\text{O}_{11}(\text{OH})_x$. Use charge balancing to calculate the value of x in the formula.

SOLUTION

The silicate unit for amphiboles is $\text{Si}_4\text{O}_{11}^{6-}$. The formula has six Mg^{2+} ions for a total charge of 12+. To balance, you need to add another 6– charge to the 6– charge for the silicate. Therefore, add 6 OH^- ions to the formula for chrysotile, giving a formula of $\text{Mg}_6\text{Si}_4\text{O}_{11}(\text{OH})_6$.

FOR PRACTICE 22.2

Use charge balancing to calculate how many hydroxide ions there are in the formula of the mineral pyrophyllite, $\text{Al}_2(\text{Si}_2\text{O}_5)_2(\text{OH})_x$.

PROCEDURE FOR...

Predicting Types of Silicate Structure and Accounting for Charge Balance

Determine the ratio of Si to O in the formula.

Match the Si : O ratio to the type of silicate in Table 22.2.

Determine the total anion charge.

Determine the total cation charge and show that it matches the total anion charge.

EXAMPLE 22.3

Predicting Silicate Structures

Predict the silicate structure for the mineral spudomene, $\text{LiAlSi}_2\text{O}_6$, and show that the formula is charge neutral.

SOLUTION

$$\text{Si:O} = 1:3$$

A 1 : 3 ratio is a single chain, a pyroxene (or inosilicate).

Each SiO_3 group has a charge of 2–, and there are two groups per formula, so the total anion charge is 4–.

The Li^+ cation has a 1+ charge and the Al^{3+} cation has a 3+ charge for a total of 4+, which matches the anion charge.

EXAMPLE 22.4

Predicting Silicate Structures

Predict the silicate structure for the mineral thortveitite, $\text{Sc}_2\text{Si}_2\text{O}_7$, and show that the formula is charge neutral.

SOLUTION

$$\text{Si:O} = 2:7$$

A 2 : 7 ratio is a double tetrahedron, a pyrosilicate (or sorosilicate).

Each Si_2O_7 group has a charge of 6–, and there is one group per formula, so the total anion charge is 6–.

Each scandium cation has a charge of 3+ for a total of 6+, which matches the anion charge.

FOR PRACTICE 22.3

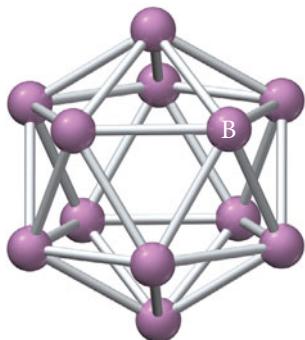
Predict the silicate structure for the mineral phenakite, Be_2SiO_4 , and show that the formula is charge neutral.

FOR PRACTICE 22.4

Predict the silicate structure for the mineral diopside, $\text{CaMgSi}_2\text{O}_6$, and show that the formula is charge neutral.

22.4 Boron and Its Remarkable Structures

The group 3A elements each have a filled *s* sublevel and one electron in the *p* sublevel. This electron configuration prevents these main-group elements, especially boron, from easily attaining a full octet. Most of the elements in the group are metals; however, because of its small size and higher electronegativity, boron behaves as a semimetal. These characteristics endow boron with some special properties and result in a wide array of structures not common to most elements.



▲ FIGURE 22.9 B_{12} Icosahedron An icosahedron contains 20 triangular faces that are connected at 12 vertices. Elemental boron forms several different structures, each based on the basic icosahedral unit.

Elemental Boron

The structure of elemental boron is complex. Boron has at least five different allotropes (different structures with the same elemental composition). The structure of each allotrope is based on an icosahedron (Figure 22.9 ▲), a geometrical shape, containing 20 triangular faces joined at 12 vertices, that is very roughly spherical. Twelve boron atoms occupy the 12 vertices. Each different allotrope connects the icosahedrons in different ways. They all have boron atoms outside the icosahedrons that bridge the icosahedrons together.

Boron is rare in Earth's crust, making up less than 0.001% by mass. Yet because it is highly concentrated at various deposits around the world, it can be mined in large quantities. The largest deposit occurs at a mine in Boron, California, which has operated continuously for over 135 years. Naturally occurring boron always occurs in compounds, and it is almost always bonded to oxygen. Among the major sources of boron are the sodium borates, which include borax, $Na_2[B_4O_5(OH)_4] \cdot 8 H_2O$, and kernite, $Na_2[B_4O_6(OH)_2] \cdot 3 H_2O$. Another major source of boron is calcium borate, or colemanite, $Ca_2B_6O_{11} \cdot 5 H_2O$. In all of these compounds, boron is bonded in polyatomic anions.

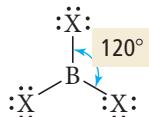
The primary use for boron today is in glass manufacture. Adding boron oxide to silicon oxide glass alters the thermal expansion of the glass, which is important for glassware intended for heating. When glass is heated, the outer edge of the glass warms and expands more quickly than the inner edge, creating stress that can result in cracking. Adding boron oxide to glass reduces its thermal expansion, allowing the glass (called borosilicate glass or Pyrex) to be heated without cracking.

Elemental boron is also used in the nuclear energy industry. Boron readily absorbs neutrons and is used in the control rods of nuclear reactors. When the nuclear reaction needs to be slowed down, the rods are inserted into the reactor to absorb the neutrons (see Section 19.7).

Boron-Halogen Compounds: Trihalides

Boron forms many covalently bonded compounds in which boron atoms bond to each other. In some ways, these compounds are similar to those in which carbon covalently bonds to itself; however, the structures are different because boron is less electronegative and has only three valence electrons. Recall from earlier in this section that elemental boron has a tendency to form polyhedral cluster structures. Boron also tends to form electron-deficient compounds (compounds in which boron lacks an octet).

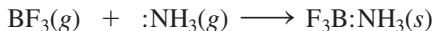
Boron halides have the general formula BX_3 and have a trigonal planar structure.



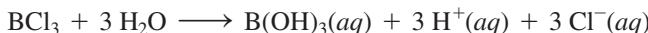
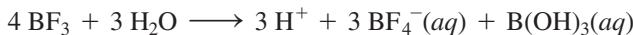
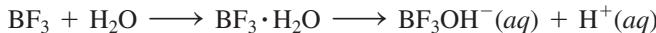
The bonds in the boron trihalides are stronger and shorter than a typical single bond, which we can explain using valence bond theory and hybridization. The boron atom uses sp^2 hybridized orbitals to form sigma bonds with the three halogen atoms. Because boron's three valence electrons are used to form the sigma bonds, the third *p* orbital of boron is an empty orbital that is perpendicular to the trigonal plane of the molecule. Each halogen atom has a filled *p* orbital, also perpendicular to the trigonal plane of the molecule. The empty *p* orbital on the boron atom can overlap with the full *p* orbitals on the halogens, forming a coordinate-covalent-type second bond. In BCl_3 ,

for example, the boron and chlorine are joined by bonds resembling a double bond. Like normal double bonds, the boron–chlorine bond is shorter and stronger than a single bond.

The boron trihalides are strong Lewis acids. For example, BF_3 reacts with NH_3 according to the following Lewis acid–base reaction:

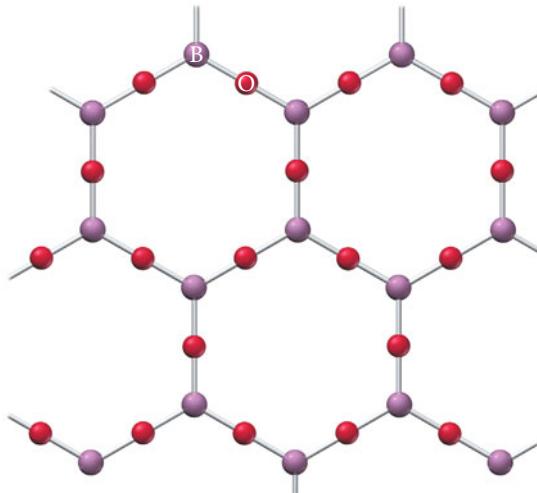


Boron trihalides act as Lewis acids in many organic reactions, such as those in which alcohols or acids are converted into esters. In water, the trihalides hydrolyze to form acidic solutions according to these reactions:



Boron–Oxygen Compounds

Boron forms very strong bonds with oxygen in structures that contain trigonal BO_3 structures. The formula for the crystalline structure of boron and oxygen is B_2O_3 . In this compound, the trigonal BO_3 structures hook together to form interlocking B_6O_6 hexagonal rings (Figure 22.10 ▶). Each hexagonal ring has a boron atom at each of its six corners and an oxygen atom in the middle of each of the six sides. The compound B_2O_3 melts at 450 °C. If the molten B_2O_3 cools quickly, it forms a glass (an amorphous solid). The glass still contains many interlocking B_6O_6 hexagonal rings but lacks the long-range order of the crystal. Molten boron oxide dissolves many metal oxides and silicon oxide to form glasses of many different compositions.



▲ FIGURE 22.10 B_2O_3 Structure

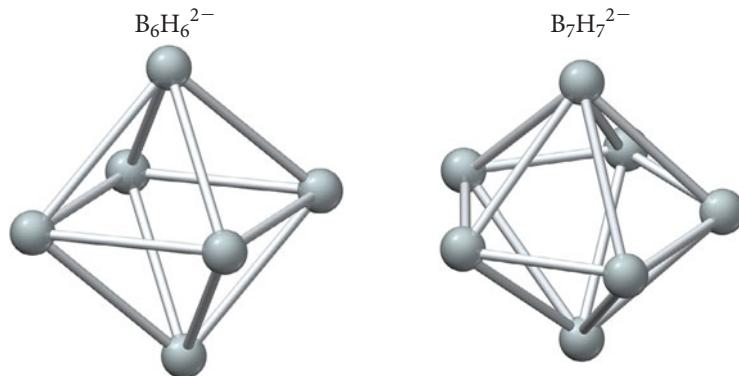
Crystalline B_2O_3 consists of BO_3 trigonal structures that form hexagonal rings of B_6O_6 .

Boron–Hydrogen Compounds: Boranes

Compounds composed of boron and hydrogen, called **boranes**, form many unique cluster, cagelike, and netlike structures. The **closo-boranes** have the formula $\text{B}_n\text{H}_n^{2-}$ and form fully closed polyhedrons with triangular sides; two of these structures are shown in Figure 22.11 ▼. A boron atom, with an attached hydrogen atom, occupies each of the vertices in the polyhedrons. The *closo*-borane with the formula $\text{B}_{12}\text{H}_{12}^{2-}$ forms the full icosahedral shape that elemental boron does, but it includes added hydrogen atoms.

If the borane polyhedron is missing one or more boron atoms, extra hydrogen atoms attach to the structure to make the borane neutral. Researchers have identified over 35 structurally different neutral boranes, ranging from B_2H_6 to $\text{B}_{20}\text{H}_{26}$. We can classify these neutral boranes on the basis of their different chemical formulas. The **nido-boranes**, named from the Latin word for *nest*, have the formula B_nH_{n+4} . They consist of a cage of boron atoms

closo-Boranes

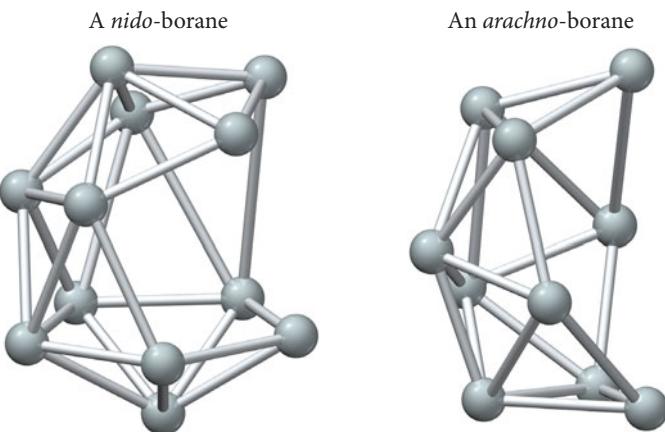


◀ FIGURE 22.11 *closo*-Borane

Structures *closo*-Borane structures form closed polyhedrons with triangular faces. In this figure, each sphere represents a BH unit. $\text{B}_6\text{H}_6^{2-}$ has an octahedral (square bipyramidal) shape. $\text{B}_7\text{H}_7^{2-}$ has a pentagonal bipyramidal shape.

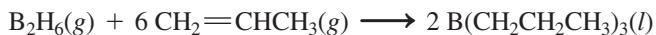
► **FIGURE 22.12** *nido-* and *arachno-*Boranes

Boranes The *nido*-borane structure forms a cage missing one boron atom from a corner. The *arachno*-borane structure forms a web missing more than one boron from a corner.



missing one corner. The ***arachno*-boranes**, named from the Greek word for *spiderweb*, have the formula B_nH_{n+6} . They consist of a cage of boron atoms that is missing two or three corners. Examples of a *nido*- and an *arachno*-borane are shown in Figure 22.12 ▲.

Boranes not only form interesting structures, but they are also valuable as catalysts in organic reactions. For example, adding an alkene to a diborane forms an alkane bonded to the boron atom. The alkane can be cleaved from the boron, resulting in a net hydrogenation reaction such as the one shown here that can be carried out under mild (lower temperature) conditions:



22.5 Carbon, Carbides, and Carbonates

The group 4A elements exhibit the most versatile bonding of all elements. As we saw in Chapter 20, carbon has the ability to bond with other carbon atoms and with a few other elements to form a great variety of organic compounds. These compounds are the molecules of life, which we examined in Chapter 21. Here we focus on elemental carbon and those compounds of carbon that are known as *inorganic* (rather than organic).

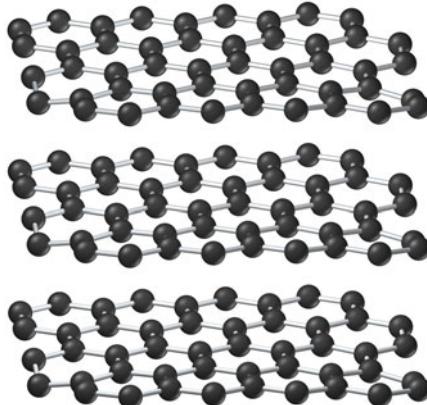
Carbon

Elemental carbon exists in several different forms. Two well-known naturally occurring crystalline forms of carbon are **graphite** and **diamond**. Graphite deposits occur mostly in mines in East Asia and Canada. Graphite's structure, shown in Figure 22.13 ▶, consists of flat sheets of carbon atoms bonded together as interconnected hexagonal rings. Although the covalent bonds *within* the sheets are strong, the interactions *between* the sheets are weak, allowing the layers of graphite to slip easily past each other and making graphite a good lubricant. The electrons in the extended pi bonding network within a sheet make graphite a good electrical conductor in the direction of the plane of the sheets. Because of its relative stability and electrical properties, graphite is used for electrodes in electrochemical applications and for heating elements in furnaces.

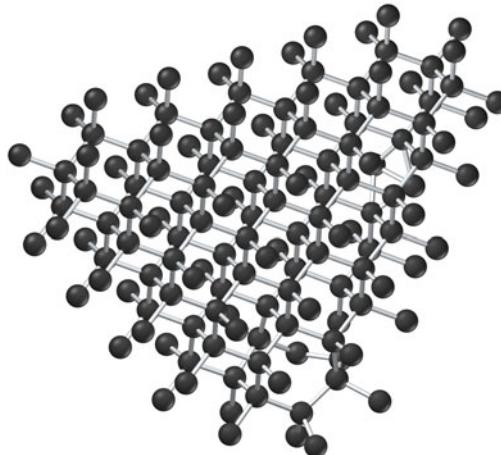
The density of graphite is 2.2 g/cm^3 . Under high pressure, the carbon atoms in graphite rearrange to form diamond, which has a higher density of 3.5 g/cm^3 . Diamond forms naturally when carbon is exposed to high pressures deep underground. Through movements in Earth's crust, diamond rises toward the surface. Most diamond is found in Africa, mainly in the Congo region and in South Africa. The first synthetic diamonds were produced in the 1940s, using pressures of 50,000 atm and a temperature of 1600°C . The diamond structure consists of carbon atoms connected to four other carbon atoms at the corners of a tetrahedron (Figure 22.14 ▶). This bonding extends throughout three dimensions, making giant molecules described as network covalent solids (see Section 11.12).

Conceptual Connection 22.1 Phase Changes and Pressure

Why do high pressures favor the formation of diamond from graphite?



▲ FIGURE 22.13 Graphite Structure The carbon atoms in graphite bond strongly within the plane of the carbon atoms but bond weakly between the sheets.



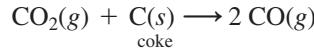
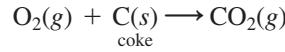
▲ FIGURE 22.14 Diamond Structure The diamond structure has carbon atoms at the corners of a tetrahedron, each connected to four other carbon atoms.

Diamond is very hard and is an excellent conductor of heat. Consequently, the largest use of diamonds is for abrasives and cutting tools. Small diamonds are used at the cutting edge of the tools, making the edges much harder and giving them a longer life. Natural diamonds are valued as gems for their brilliance and relative inertness.

Carbon also occurs naturally in noncrystalline forms. Noncrystalline **coal** forms from the decomposition of ancient plant material that has been buried for millions of years, during which time it undergoes a process called carbonization. The carbonization reaction, which occurs under high pressure in the presence of water and the absence of air, removes most of the hydrogen and oxygen (which are lost as volatile gases such as methane and water) from the original organic compounds that composed the plant. The resulting coal contains a mixture of various hydrocarbons and carbon-rich particles. It is extensively mined and employed as an energy source throughout the world. Coal types are classified by the amount of carbon and other elements that they contain, as shown in Table 22.3.

Among the types of coal listed in Table 22.3, anthracite has the highest carbon content and consequently yields the most energy per mass when burned. Bituminous coal also contains a relatively high amount of carbon but has in addition high levels of sulfur, which results in increased formation of sulfur oxides when this type of coal is burned. Sulfur oxides are the pollutants that create acid rain (see Sections 3.6 and 15.12).

Heating coal in the absence of air forms a solid called **coke** that is composed mainly of carbon and ash. Coke is used in the steel industry for the reduction of iron ore to iron. In a blast furnace, the carbon in the coke is oxidized to form carbon monoxide, which reduces the iron in iron oxide according to these reactions:



Heating wood in the absence of air produces **charcoal**. Like coal, charcoal contains a high amount of amorphous free carbon and is used as a common fuel for outdoor cooking grills. Charcoal retains the general overall shape of the original wood, but the process creates

TABLE 22.3 Approximate Composition of the Main Types of Coal

Type of Coal	Free C (mol %)	Total C (mol %)	H (mol %)	O (mol %)	S (mol %)
Lignite	22	71	4	23	1
Bituminous	60	80	6	8	5
Anthracite	88	93	3	3	1

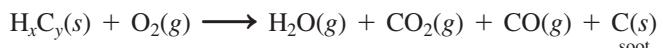


▲ Automobile tires are black because of the carbon black that is added to strengthen the tires and maintain flexibility.

many voids, resulting in a much lower density. The voids within charcoal create high surface area that makes the charcoal useful for filtration. The impurities in a liquid or gas adsorb on the charcoal surface as the liquid or gas flows through the pores in the charcoal.

Very fine carbon particles with high surface areas are called **activated carbon**, or *activated charcoal*. The large surface area of the particles, greater than $10^3 \text{ m}^2/\text{g}$, makes the particles extremely efficient at adsorbing other molecules onto their surfaces. Activated carbon is made by heating amorphous carbon in steam, which breaks the grains into smaller sizes and removes any other materials adsorbed on the surface. Activated carbon is used to filter impurities from gas and as a decolorizing agent, removing impurities that discolor organic products such as sugar or wheat flour.

Soot is an amorphous form of carbon that forms during the incomplete combustion of hydrocarbons; its presence is indicated by blue or black smoke. Toxic carbon monoxide also forms in the process.



Carbon black, a fine, powdered form of carbon, is a component of soot. Over a million tons of carbon black, a strengthener for rubber tires, is used in manufacturing each day. The black color of automobile tires is due to the several kilograms of carbon black within each tire, over 25% of the mass of the typical tire.

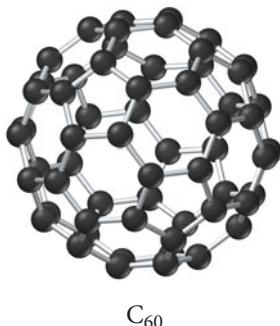
In the 1980s, researchers discovered a new form of carbon when they aimed a powerful laser at a graphite surface. This new form of carbon occurs as soccer-ball-shaped clusters of 60 carbon atoms (C_{60}). The atoms form 5- and 6-membered carbon rings wrapped into a 20-sided icosahedral structure (Figure 22.15 ▶). The compound was named *buckminsterfullerene*, honoring R. Buckminster Fuller, a twentieth-century engineer and architect who advocated the construction of buildings using a structurally strong geodesic dome shape that he patented.

Researchers have since identified carbon clusters similar to C_{60} containing from 36 to over 100 carbon atoms. As a class, all of these carbon clusters are called **fullerenes** and nicknamed *buckyballs*. At room temperature, fullerenes are black solids—the individual clusters are held together by dispersion forces. Fullerenes are somewhat soluble in nonpolar solvents, and the different fullerenes form solutions of different colors.

Researchers have also synthesized long carbon structures called **nanotubes**, which consist of sheets of interconnected C_6 rings that assume the shape of a cylinder (like a roll of chicken wire). A nanotube is featured in the image on the front cover of this book. The first nanotubes discovered consisted of tubes with double walls of C_6 rings with closed ends. The ends of the tubes can be opened when they are heated under the proper conditions. Researchers have also introduced salts and organometallic compounds into the nanotubes and have been able to form some generally not stable compounds inside nanotubes. The discovery of these materials opens a new synthetic route to making novel chemicals.

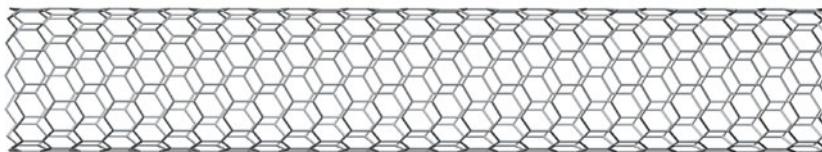
Today, two general types of nanotubes can be produced: (1) single-walled nanotubes (SWNT), which have one layer of interconnected C_6 rings forming the walls, and (2) multiwalled nanotubes (MWNT), which have concentric layers of interconnected C_6 rings forming the walls. In addition, researchers have been able to form *nanoribbons* by slicing open nanotubes. These three types of nanotubes are shown in Figure 22.16 ▷.

Nanotubes are 100 times stronger than steel and only one-sixteenth as dense. Consequently, carbon nanotubes are used commercially for lightweight applications that require strength, such as golf clubs and bicycle frames. When the nanotubes are lined up

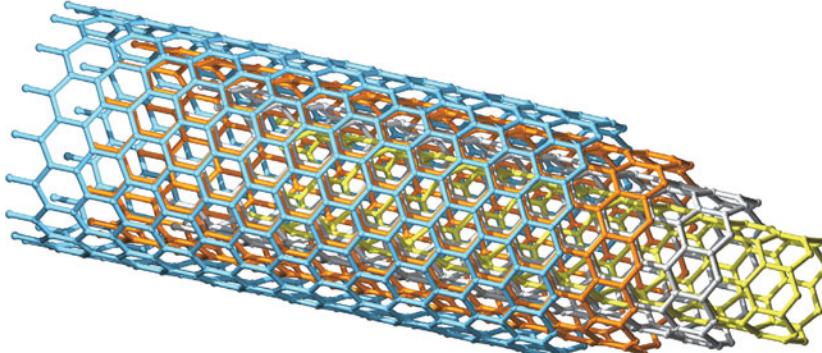


► FIGURE 22.15 C_{60} and a Geodesic Dome The C_{60} structure resembles Buckminster Fuller's geodesic dome.

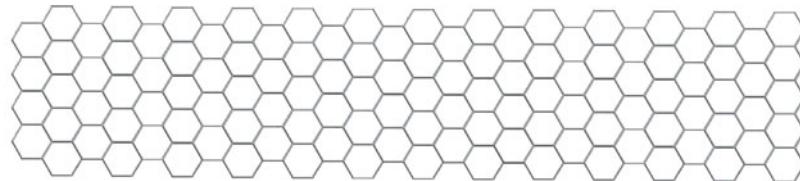
(a) Single-walled nanotube (SWNT)



(b) Multiwalled nanotube (MWNT)

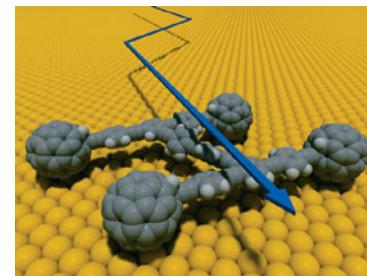


(c) Graphene nanoribbon



◀ FIGURE 22.16 Novel Carbon Structures (a) a single-walled nanotube, (b) a multiwalled nanotube, (c) a graphene nanoribbon

parallel to one another, a bundle of the tubes form a “wire” with very low electrical resistance. These tiny wires raise the possibility of making incredibly small electronic devices. For example, the front cover of this book depicts an image in which the conduction of electrical current through a nanotube is used to detect proteins and their interactions with other proteins in real time. Other applications include using nanotubes and buckyballs to make nanomachines. Figure 22.17▶ shows a nanocar that has buckyballs for wheels. The car can actually roll across an atomic surface and is so small that 20,000 of these cars laid end to end would span the thickness of a human hair.



▲ FIGURE 22.17 The Nanocar This nanocar has buckyballs for wheels and can actually roll across an atomic surface.

Carbides

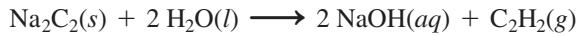
Binary compounds composed of carbon combined with less electronegative elements are **carbides**. We classify carbides into three general categories: ionic, covalent, and metallic. All types of carbides have some shared properties; they are extremely hard materials with high melting points.

Ionic Carbides Compounds composed of carbon and a low-electronegativity metal such as an alkali metal or an alkaline earth metal are **ionic carbides**. Most ionic carbides contain the dicarbide ion, C_2^{2-} , commonly called the *acetylide ion*. For example, calcium carbide has the formula CaC_2 and a structure similar to that of NaCl (Figure 22.18▶).

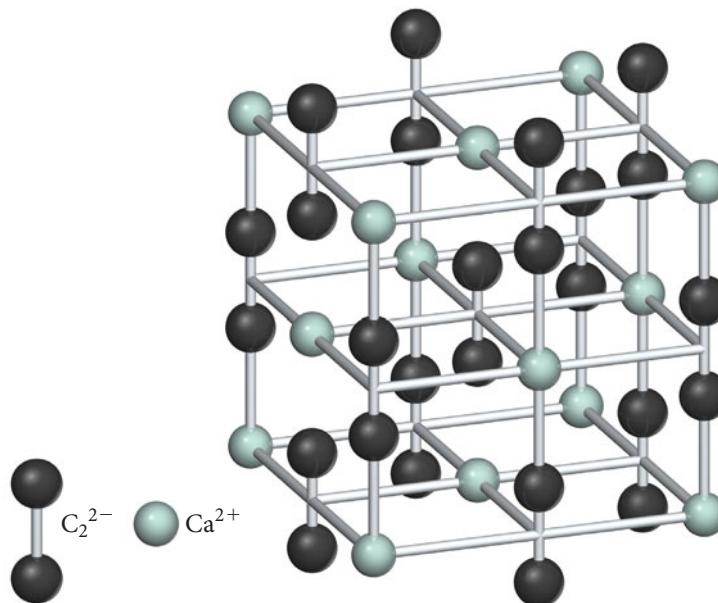
Calcium carbide forms by the reaction of calcium oxide with coke in an electric furnace.



Ionic carbides react with water, forming acetylene. For example, sodium carbide reacts with water according to the reaction shown here:



In the past, calcium carbide was used as a source of acetylene (which is highly flammable) for lighting. The solid CaC_2 reacts with water, releasing acetylene gas, which was burned in applications such as automobile headlights and lamps for mines. Transporting solid calcium carbide was more convenient and safer than transporting the flammable gas.



► FIGURE 22.18 Calcium Carbide

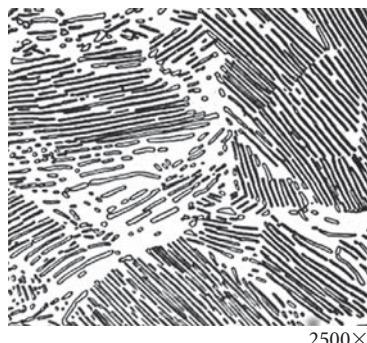
Structure In the NaCl-type structure for CaC_2 , the dicarbide ions are in the positions of the chloride ions, making the structure slightly noncubic.

Covalent Carbides Compounds composed of carbon and low-electronegativity *nonmetals* or *metalloids* are **covalent carbides**. The most important covalent carbide is silicon carbide (SiC), a very hard material. Over 500,000 tons of silicon carbide are produced annually, mostly for use as an abrasive material in the cutting and polishing of metals. In a process analogous to the formation of calcium carbide, silicon carbide forms by the reaction of silicon oxide with coke at high temperatures.



Recently, a gem-quality form of SiC , called *moissanite*, has been developed. Moissanite is described as being more brilliant than all other gems, including diamonds. Yet moissanite costs much less than diamond and is consequently sold as a diamond substitute (like the more common diamond substitute cubic zirconia, ZrO_2). Moissanite was first identified in small particles at the Diablo Canyon meteorite impact crater in Arizona and is sometimes advertised as “a gift from the stars.”

Metallic Carbides Compounds composed of carbon and metals that have a metallic lattice with holes small enough to fit carbon atoms are **metallic carbides**. Metallic carbides retain many metallic properties, such as high electrical conductivity, but they are stronger, harder, and less malleable than their corresponding metals. Adding carbon to steel, for example, increases its hardness by forming regions of cementite (Fe_3C) in the steel matrix. Tungsten carbide (WC) is a metallic carbide used in cutting tools.



▲ This micrograph shows cementite (dark regions) in steel.

Carbon Oxides

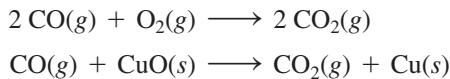
Carbon forms two stable oxides, carbon monoxide and carbon dioxide. Our atmosphere contains about 0.04% carbon dioxide by volume. Plants use atmospheric carbon dioxide to produce sugars during photosynthesis.



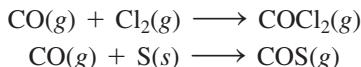
Carbon dioxide returns to the atmosphere via animal respiration, plant and animal decay, and (in modern history) fossil fuel combustion. Because carbon dioxide is highly soluble in water, the oceans of the world act as a reservoir for CO_2 , keeping the amount of CO_2 in the atmosphere generally stable. As we saw in Section 6.10, however, the increase in the combustion of fossil fuels in the last century has increased the amount of CO_2 in the atmosphere by about 25%.

Recall from Section 11.8 that CO_2 has a triple point at -57°C and 5.1 atm. At atmospheric pressure, therefore, the liquid phase of CO_2 does not exist. Solid carbon dioxide sublimes directly to the gas phase when heated, which is why solid CO_2 is called “dry ice.”

Carbon monoxide (CO) is a colorless, odorless, and tasteless gas. The boiling point of carbon monoxide is -192°C at atmospheric pressure, and CO is only very slightly soluble in water. Carbon monoxide is toxic because it interferes with the ability of hemoglobin to bind oxygen, as we saw at the very beginning of this book (see Section 1.1). Unlike carbon dioxide, which is very stable, carbon monoxide is relatively reactive and can be used as a reducing agent. For example, carbon monoxide reacts with oxygen and metal oxides to form carbon dioxide.



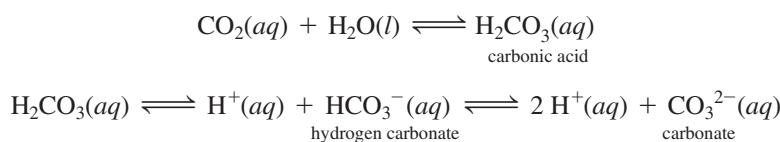
Carbon monoxide also reduces many nonmetals, producing compounds with the reduced form of the nonmetal.



The product of the first reaction listed is phosgene (COCl_2), also known as carbonyl chloride, a poisonous gas that was used in World War I as a chemical weapon. Phosgene is now an important industrial chemical used in the production of polycarbonates. The product of the second reaction, carbonyl sulfide (COS), is a fungicide (a substance that kills fungi).

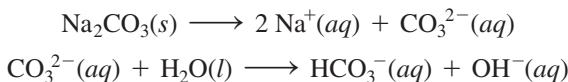
Carbonates

When carbon dioxide dissolves in water, it forms carbonic acid (H_2CO_3). As a weak acid, carbonic acid partially ionizes into hydrogen carbonate (or bicarbonate) and carbonate.



Recall from Section 12.4 that the solubility of carbon dioxide, like that of other gases, increases with increasing pressure. Carbon dioxide under high pressure carbonates soft drinks. Under most conditions, less than 0.5% of the dissolved carbon dioxide reacts with water to form carbonic acid. This leaves most of the carbon dioxide as dissolved gas molecules, so the soft drink does not acquire much of a sour acidic taste.

The hydrated crystal of sodium carbonate, $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$, is known as **washing soda**. When washing soda is heated, the waters of hydration are released, forming the stable anhydrous sodium carbonate, Na_2CO_3 . All of the alkali metal ions form stable carbonates that remain stable even when heated. The carbonates all make basic solutions when added to water because the carbonate ions readily ionize water (as described more fully in Section 15.8).



Sodium bicarbonate (NaHCO_3) is *baking soda*. When heated, baking soda gives off carbon dioxide gas, which is why its use in baking helps raise dough.



Baking powder is a mixture of NaHCO_3 and an acid. The two components of the mixture are kept from reacting by a starch filler. When water is added to the mixture, however, the two components dissolve and react, producing the carbon dioxide that forms pockets of gas in baked products. You can perform a simple test to determine if baking powder is still good (that is, whether the acid has not already slowly reacted with the sodium bicarbonate) by pouring some boiling water over a small sample of the baking powder. If the hot water produces bubbles, then the baking powder is still active. Alka-Seltzer is another common consumer product that employs sodium bicarbonate, in this case mixed with citric acid and aspirin. When immersed in water, the acid and carbonate react to produce carbon dioxide, producing the familiar fizz.



▲ Alka-Seltzer™ contains sodium bicarbonate mixed with citric acid and aspirin. When put in water, the acid and carbonate react.

Conceptual Connection 22.2
Carbonate Solubility

As we saw in Chapter 4, the carbonates of metal ions other than group 1A are insoluble in water. Which action would increase their solubility?

- adding acid to the solution
- adding base to the solution
- increasing the amount of the solid carbonate in the solution

22.6 Nitrogen and Phosphorus: Essential Elements for Life

The group 5A elements range from nonmetallic nitrogen and phosphorus to metallic bismuth. Both nitrogen and phosphorus are nonmetals; they do not conduct electricity and they form acidic oxides. Both have s^2p^3 electron configurations, and yet their chemical properties are very different. Phosphorus is much larger and less electronegative; it also has d orbitals available for bonding.

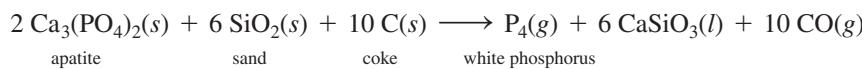
Elemental Nitrogen and Phosphorus

Nitrogen was identified in 1772 and phosphorus in 1669. Elemental nitrogen is a diatomic gas that composes about 78% of Earth's atmosphere by volume (see Section 5.6). To obtain elemental nitrogen, air is cooled below $-196\text{ }^\circ\text{C}$, which causes it to liquefy. When the liquid air is warmed slightly, the nitrogen boils off, leaving liquid oxygen (which boils at the higher temperature of $-183\text{ }^\circ\text{C}$). Passing the vaporized gas over hot copper metal purifies the nitrogen by removing residual oxygen (which reacts with the copper to form CuO). Nitrogen gas can also be separated from the other atmospheric gases by passing air through certain silicate materials called *zeolites*, which have channels of just the right diameter to separate gas molecules of different size. Some mineral sources for nitrogen are saltpeter (KNO_3) and Chile saltpeter (NaNO_3).

As we first saw in Section 9.5, nitrogen molecules have a triple bond between the two N atoms. The strength of the triple bond makes N_2 very stable, and attempts to break the bond have not been commercially successful. When nitrogen gas is heated with oxygen or hydrogen, nitric oxide (NO) or ammonia (NH_3), respectively, form with low yields. When nitrogen gas is heated with active metals, metal nitrides form. Aside from this, however, nitrogen gas is relatively unreactive.

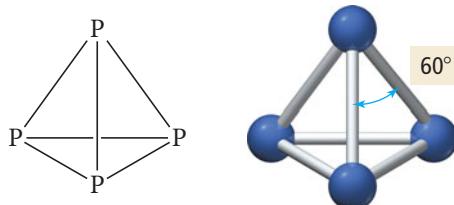
The stability of elemental nitrogen makes it useful in creating a protective atmosphere to prevent oxidation in many industrial processes. For example, industrial furnaces employ a nitrogen atmosphere to anneal (hold at elevated temperature below the melting point) products made of metal, and chemical reactions sensitive to oxygen are carried out in a nitrogen atmosphere. Nitrogen is also used to preserve a variety of foods.

Elemental phosphorus was first isolated by accident from urine when Henning Brand, a seventeenth-century physician and alchemist from Hamburg, Germany, was distilling urine in an ill-informed attempt to obtain gold from the golden liquid. The elemental form of phosphorus that he obtained instead was a white, waxy, flammable solid called **white phosphorus**. White phosphorus is highly toxic to humans. For over a hundred years, the phosphorus-containing compounds in urine were the main source for elemental phosphorus. Today, however, phosphorus is obtained from a calcium phosphate mineral called apatite, $[\text{Ca}_3(\text{PO}_4)_2]$. The mineral is heated with sand and coke in an electric furnace.



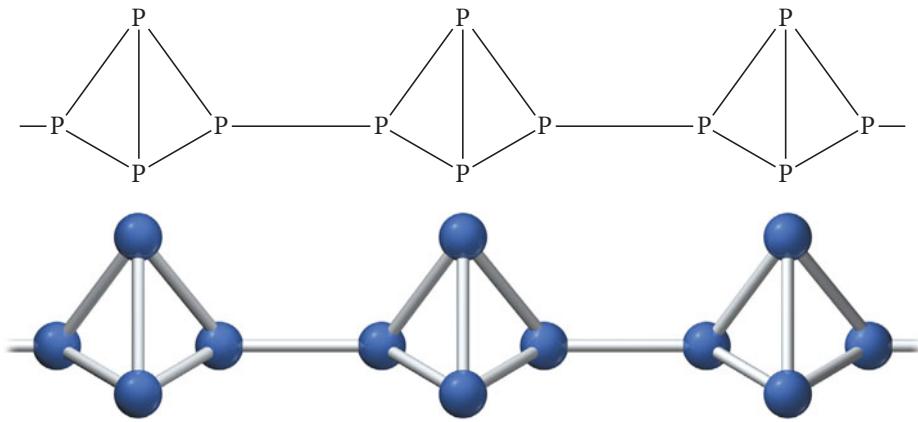
The desired product, white phosphorus, spontaneously burns in air; it is normally stored under water to prevent contact with air.

White phosphorus consists of P_4 molecules in a tetrahedral shape, with the phosphorus atoms at the corners of the tetrahedron (Figure 22.19 ▲). The bond angles between



▲ FIGURE 22.19 White Phosphorus

The small bond angle of 60° between the phosphorus atoms at the corners of the tetrahedron puts a great strain on the structure and makes the P_4 molecule unstable.



◀ FIGURE 22.20 Red Phosphorus
Red phosphorus consists of chains of phosphorus atoms that form amorphous structures.

the three P atoms on any one face of the tetrahedron is small (60°) and strained, making the P_4 molecule unstable and reactive.

When heated to about $300\text{ }^\circ\text{C}$ in the absence of air, white phosphorus slightly changes its structure to a different allotrope called **red phosphorus**, which is amorphous. The general structure of red phosphorus is similar to that of white phosphorus, except that one of the bonds between two phosphorus atoms in the tetrahedron is broken (Figure 22.20 ▲). The two phosphorus atoms then link to other phosphorus atoms, making chains that vary in structure.

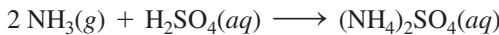
Red phosphorus is neither as reactive nor as toxic as white phosphorus, and even though it is also flammable, it can be stored in air. Red phosphorus is used commercially in applications such as match heads. Rubbing the match head onto a surface produces enough heat (through friction) to ignite the phosphorus. Most strike-anywhere matches feature the phosphorus compound tetraphosphorus trisulfide (P_4S_3) and an oxidizing agent, potassium chlorate ($KClO_3$).

A third allotrope of phosphorus is **black phosphorus**. Black phosphorus is obtained by heating white phosphorus under pressure. This form of phosphorus is the most thermodynamically stable form, and therefore the least reactive. Black phosphorus has a layered structure similar to that of graphite.

Nitrogen Compounds

Nitrogen, with a valence electron configuration of $2s^22p^3$, can gain three electrons or lose five electrons to obtain an octet. Nitrogen forms many covalent compounds with oxidation states from -3 to $+5$, as shown in Table 22.4.

Nitrogen Hydrides The most common nitrogen hydride is **ammonia** (NH_3), the strong-smelling compound in which nitrogen displays its lowest oxidation state (-3). Ammonia is important to humans because it reacts with sulfuric acid (or phosphoric acid) to produce ammonium salts for fertilizers.



For hundreds of years, natural biological materials such as animal manure were used as nitrogen-containing fertilizers. In the 1800s, however, the nitrogen-bearing nitrate mineral NaNO_3 was discovered in Chile (and named Chile saltpeter). This nitrate mineral became an important source of fertilizer and made the country of Chile very wealthy; yet it was a limited source so chemists were continually striving to develop a new source.

The obvious *unlimited* source of nitrogen is the atmosphere, but the strong triple bond in elemental nitrogen renders it unusable by plants. In order to be used as fertilizer, elemental nitrogen has to be *fixed*, which means that it has to be converted into a nitrogen-containing compound such as NH_3 . However, the direct reaction of nitrogen gas with hydrogen gas to form ammonia is very slow and produces low yields of ammonia under normal conditions.

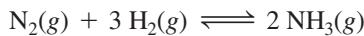
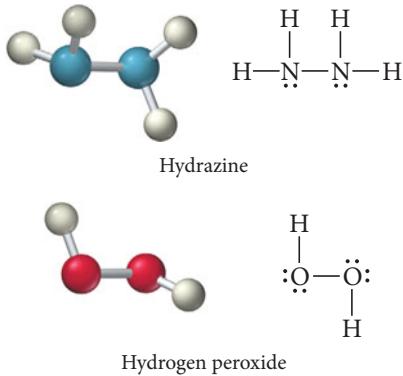
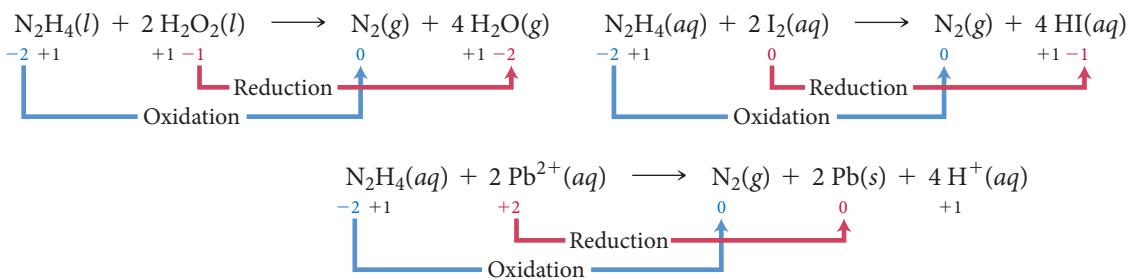


TABLE 22.4 Oxidation States of Various Nitrogen Compounds

Nitrogen-Containing Compound	Oxidation State
NH_3	-3
N_2H_4	-2
H_2NOH	-1
HN_3	$-\frac{1}{3}$
N_2	0
N_2O	$+1$
NO	$+2$
$\text{N}_2\text{O}_3, \text{NF}_3$	$+3$
$\text{NO}_2, \text{N}_2\text{O}_4$	$+4$
$\text{N}_2\text{O}_5, \text{HNO}_3$	$+5$

In the early 1900s, German chemist Fritz Haber studied the equilibrium conditions for this reaction and showed that high pressures and lower temperatures favored the product. Carrying out the reaction at a higher pressure, and using a catalyst to increase the reaction rate, the industrial process for producing ammonia from nitrogen gas and hydrogen gas—now called the **Haber–Bosch process**—became practical by the middle 1930s. This process is the main industrial process for making ammonia and fixing nitrogen for many uses, including fertilizers and explosives.

Hydrazine (N_2H_4) is another nitrogen and hydrogen compound in which nitrogen has a negative oxidation state (-2). Hydrazine is the nitrogen analog of hydrogen peroxide; it has a bond between nitrogen atoms that is similar to the bond between oxygen atoms in hydrogen peroxide (Figure 22.21 ▶). Hydrazine, like hydrogen peroxide, is a colorless liquid. However, while hydrogen peroxide is a powerful oxidizing agent, hydrazine is a powerful reducing agent, as shown in the following reactions:

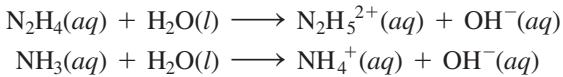


▲ FIGURE 22.21 Hydrazine and

Hydrogen Peroxide Hydrazine forms a structure similar to hydrogen peroxide with an $\text{N}=\text{N}$ bond in the place of the $\text{O}=\text{O}$ bond.

The oxidation state of each atom appears directly below its symbol. Notice that in each reaction, nitrogen is oxidized and causes the reduction of the other reactant.

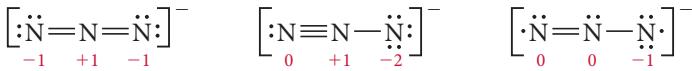
Hydrogen azide (HN_3) is a nitrogen and hydrogen compound with a higher nitrogen-to-hydrogen ratio than ammonia or hydrazine. Ammonia and hydrazine are both basic.



Hydrogen azide, by contrast, is acidic, ionizing in water to form the azide ion (N_3^-).



The N_3^- ion can be represented with the resonance structures shown here (formal charges indicated in red):



Since the rightmost structure has the least amount of formal charge, it contributes most to the hybrid structure.

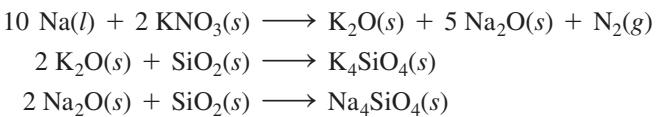
Hydrogen azide is thermodynamically unstable compared to its constituent elements and reacts explosively to produce hydrogen and nitrogen gas.



The sodium azide salt is a stable solid at room temperature, but at elevated temperatures, or with a spark, it quickly forms elemental sodium and nitrogen gas.

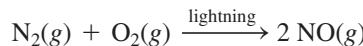


The large volume of N_2 gas that forms from a small volume of $\text{NaN}_3(s)$ is the basis for air bags in automobiles. However, pure sodium azide also forms liquid sodium, which is dangerous because of its high reactivity. Therefore, other components, such as KNO_3 and SiO_2 are added to the mixture in airbags to react with the liquid sodium.

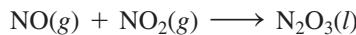
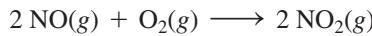


The overall reaction produces the large volume of nitrogen gas required to fill the air bag quickly, along with harmless potassium and sodium silicates.

Nitrogen Oxides Under certain conditions, especially high temperatures, nitrogen is oxidized by oxygen to form a number of different oxides. For example, during lightning storms, nitrogen monoxide (NO) gas forms in the upper atmosphere.



Other nitrogen oxides, such as nitrogen dioxide and dinitrogen trioxide, form from the further oxidation of nitrogen monoxide.

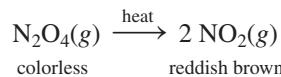


All nitrogen oxides are thermodynamically unstable and eventually decompose into their constituent elements or react to form more stable compounds. However, many of these reactions are kinetically slow, so some nitrogen oxides persist for long periods of time.

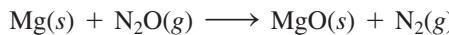
The most important nitrogen oxide, because of its significance in biological systems, is probably nitrogen monoxide (NO), also called nitric oxide. In 1987, nitrogen monoxide was named molecule of the year by the journal *Science* because of several discoveries related to its biological functions. For example, NO helps control blood pressure through blood vessel dilation, it is important in memory and digestion, and it plays major roles in inducing male erections and female uterine contractions. The ability to adjust NO levels is a key role of the medications that treat erectile dysfunction (such as Viagra).

Earlier in this section, we learned that lightning forms NO in the atmosphere. In Sections 3.6 and 15.12 we saw that NO and NO₂, formed as by-products of fossil fuel combustion, are among the important precursors of acid rain.

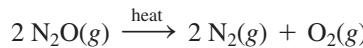
Nitrogen monoxide and nitrogen dioxide are both reactive free radicals (they contain unpaired electrons). At low temperature, two NO₂ molecules dimerize to form N₂O₄, pairing their two lone electrons. If N₂O₄ is heated it decomposes back to NO₂. Consequently, the equilibrium between NO₂ and N₂O₄ is highly temperature-dependent, as we saw in Section 14.9.



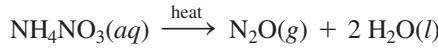
Dinitrogen monoxide (N₂O), also called nitrous oxide, is a good oxidizing agent. It can support the combustion of active metals.



Dinitrogen monoxide is unstable when heated, decomposing into nitrogen and oxygen gas.



Dinitrogen monoxide (often referred to as “nitrous” or laughing gas) is used as an anesthetic by dentists and to pressurize food dispensers (such as whipped-cream dispensers). Commercially, N₂O is produced by the decomposition of ammonium nitrate.

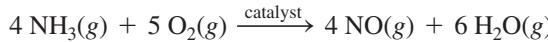


Nitric Acid, Nitrates, and Nitrides Nitric acid is an important commercial product of nitrogen. In an electric furnace, nitric acid forms from nitrogen and oxygen gas.



This reaction is thermodynamically favored, but it is kinetically slow. (What would happen to our atmosphere if this reaction were thermodynamically *and* kinetically favored?) Because of the slow speed of this reaction, a more efficient process, called the **Ostwald process**, is used to commercially produce nitric acid.

The first step of the Ostwald process involves passing ammonia gas over hot metal gauze at 600–700 °C to form NO gas. The gauze is made of metals such as platinum and rhodium that are good catalysts for this reaction.

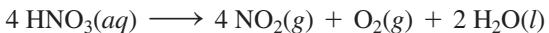


Next, additional oxygen is added to oxidize the NO to NO_2 gas, which is then passed through a water spray to form nitric acid.

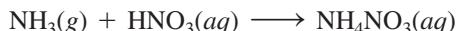


These steps are similar to the natural process that forms acid rain from NO and NO_2 gas in the atmosphere. The NO gas made during this last step can be recycled back to form more NO_2 and eventually more HNO_3 .

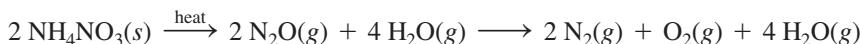
Nitric acid is a strong acid that completely ionizes in water. Concentrated nitric acid is 70% nitric acid by mass, or 16 M. A small fraction of the HNO_3 in a bottle of concentrated nitric acid will react with water to form NO_2 , a reddish brown gas that, in small amounts, gives the acid its characteristic pale yellow color.



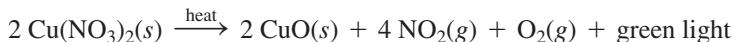
The main commercial uses of nitric acid are in the production of fertilizers and explosives. Over a million tons of ammonium nitrate fertilizer is produced annually by the reaction between ammonia and nitric acid.



Besides being a good fertilizer, ammonium nitrate (as well as some other nitrates) are also good explosives. Ammonium nitrate explodes according to the following reaction:



Metal nitrates are responsible for the various colors seen in fireworks displays. The different metal ions emit different colors as the nitrate explodes in air. For example, copper nitrate produces a green-colored light according to the reaction:



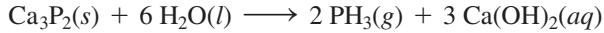
As we learned in Chapter 4, nitrates are very soluble in water. For reactions that need soluble metal cations, a nitrate compound is a good source for the cation without interference from the anion.

Nitrites are compounds containing the nitrite ion (NO_2^-). Sodium nitrite is used as a food preservative because it kills *Clostridium botulinum* bacteria, the cause of botulism, and because it keeps meat from discoloring when the meat is exposed to air. Consumers have voiced concerns over this practice, both because it hides the true age of the meat and because the nitrites can react with amines in the meat to form compounds called nitrosamines, which are suspected cancer-causing agents. However, no evidence exists to support the idea that nitrites at levels currently used in meats increase cancer risk in humans.

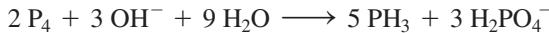
Phosphorus Compounds

Phosphorus has a valence electron configuration of $3s^23p^3$, similar to that of nitrogen. Phosphorus also forms many compounds with oxidation states ranging from -3 through $+5$. The most stable compounds have the $+5$ oxidation state.

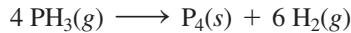
Phosphine Phosphine (PH_3) is a colorless, poisonous gas that smells like decaying fish and in which phosphorus has an oxidation state of -3 . Since phosphorus is less electronegative than nitrogen, phosphine is less polar than ammonia. Phosphine forms from the hydrolysis of metal phosphides.



The disproportionation of white phosphorus in a basic solution can also produce phosphine.



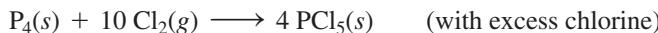
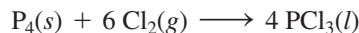
When heated, phosphine decomposes to phosphorus and hydrogen.



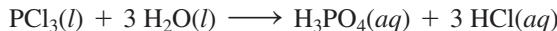
Like ammonia, phosphine can form phosphonium compounds such as PH_4Cl and PH_4I . Unlike ammonia, phosphine is not basic in aqueous solution.

Disproportionation is a reaction in which an element is both reduced and oxidized during the same reaction. In this equation the phosphorus in P_4 is both oxidized and reduced. Phosphorus has an oxidation number of 0 in P_4 and is reduced to -3 in PH_3 and oxidized to $+5$ in H_2PO_4^- .

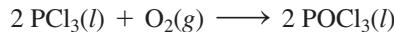
Phosphorus Halides When phosphorus reacts with the halogens, it forms phosphorus halides, the most important of which generally have the formulas PX_3 and PX_5 .



Phosphorus halides react with water to form phosphoric acid and the corresponding hydrogen halide. For example, PCl_3 reacts with water.



Reaction of PCl_3 with oxygen at room temperature forms phosphorus oxychloride.

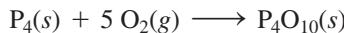


Other phosphorus oxyhalides form as a result of the reactions of POCl_3 with metal fluorides or iodides.



The phosphorus halides and oxyhalides are important compounds in organic chemistry and serve as starting materials for the production of many phosphorus-containing compounds. Many of the key compounds in pesticides, oil additives, fire retardants for clothing, and surfactants (agents that act at surfaces), for example, are commercially made from phosphorus oxyhalides.

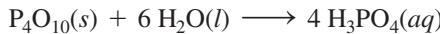
Phosphorus Oxides White phosphorus reacts directly with oxygen to form phosphorus oxides, as in the reaction shown here:



The product depends upon the amount of oxygen. Tetraphosphorus hexaoxide, $\text{P}_4\text{O}_6(s)$, forms when oxygen is limited, and tetraphosphorus decaoxide, $\text{P}_4\text{O}_{10}(s)$, forms when greater amounts of oxygen are available.

Phosphorus oxides form interesting cage structures (Figure 22.22 ▶). We can visualize the P_4O_6 structure as a tetrahedron with a phosphorus atom at each of the vertices and an oxygen atom between each pair of phosphorus atoms. The P_4O_{10} structure has four additional oxygen atoms bonded to each phosphorus atom at the vertices of each tetrahedron.

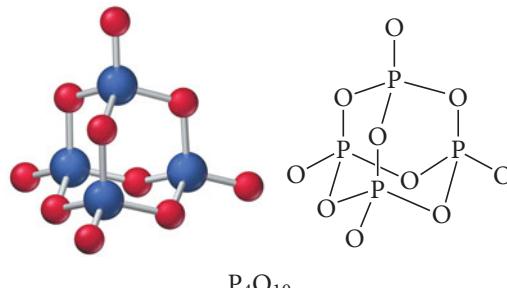
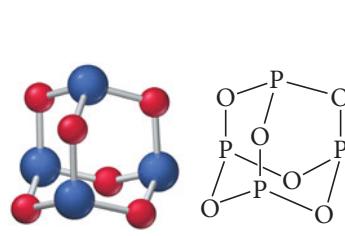
Phosphoric Acid and Phosphates Phosphoric acid and phosphates are among the most important phosphorus-containing compounds. Phosphoric acid is a colorless solid that melts at 42 °C. Concentrated phosphoric acid is 85% phosphoric acid by mass, or 14.7 M. Phosphoric acid is produced from the oxidation of white phosphorus to tetraphosphorus decaoxide (see previous reaction), which is then reacted with water.



This method produces a very pure phosphoric acid. A less pure product forms from the reaction of calcium phosphate (a mineral source of phosphate) with concentrated sulfuric acid.



One direct use of phosphoric acid is rust removal. In steel production, thick steel slabs must be heated and rolled into thinner ones. During this process, the hot steel is exposed



◀ **FIGURE 22.22** Tetraphosphorus Hexaoxide and Decaoxide, P_4O_6 and P_4O_{10} The P_4O_6 structure has the P atoms at the corners of a tetrahedron and the O atoms on the edges. The P_4O_{10} structure has O atoms also bonded to the P atoms at the corners.

to air, which oxidizes the surface. To remove this rust, the thin steel sheets pass through phosphoric or hydrochloric acid baths, which dissolve the rust from the metal.

A major use of phosphoric acid is fertilizer production. In the past, phosphorus-containing materials such as fish, bones, and bat guano were used as fertilizer. Sulfuric acid decomposes bones to make phosphorus compounds that are more readily taken up by plants. Today many different phosphorus compounds have been developed specifically as fertilizers for various types of plants.

Detergent manufacturers use sodium phosphate compounds as additives. Compounds such as sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$) and sodium tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$) remove metal ions such as Ca^{2+} and Mg^{2+} from hard water, increasing the effectiveness of the detergent and preventing scum rings on sinks and tubs. However, phosphate compounds in detergents are being replaced by other compounds because of the ecological problems—primarily the overfertilization of algae in bodies of water—associated with the phosphates.

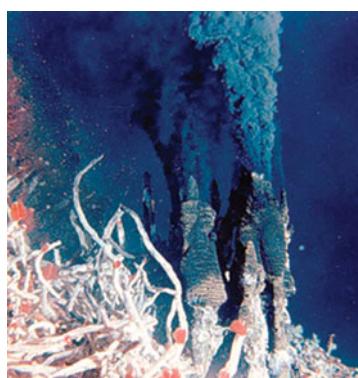
Phosphoric acid and phosphates are also important chemicals in the food industry. Phosphoric acid is a soft drink additive. At a low concentration, phosphoric acid is non-toxic and adds a tart, acidic taste to soft drinks. It also prevents bacterial growth in the soda. Table 22.5 summarizes the uses of phosphates in the food industry.

TABLE 22.5 Uses of Phosphates in the Food Industry

Phosphoric acid, H_3PO_4	Flavor agent in soda, yeast nutrient
Sodium dihydrogen phosphate (also Sodium phosphate monobasic), NaH_2PO_4	Emulsifier, pH buffering agent
Sodium hydrogen phosphate (also Sodium phosphate dibasic), Na_2HPO_4	Baking powder, fermentation auxiliary
Sodium hexametaphosphate, $(\text{NaPO}_3)_6$	Preservative, pH buffering agent
Sodium trimetaphosphate, $(\text{NaPO}_3)_3$	Starch modifier, juice dispersant
Iron(III) pyrophosphate nonahydrate, $\text{Fe}_4(\text{P}_2\text{O}_7)_3 \cdot 9 \text{ H}_2\text{O}$	Nutritional supplement
Sodium monofluorophosphate, $\text{Na}_2\text{PO}_3\text{F}$	Fluoride source for toothpaste
Pyrophosphate, $\text{P}_2\text{O}_7^{4-}$	Tartar control for toothpaste

22.7 Oxygen

The group 6A elements have an s^2p^4 valence electron configuration and a strong attraction for electrons. They can obtain a full octet by gaining only two more electrons. Because of its small size, oxygen is a much stronger oxidizing agent than the rest of the group 6A elements. Oxygen has the second highest electronegativity of any element (3.5), while the rest of the 6A elements range from 2.5 to 2.0. Because of its high abundance (almost half the mass of Earth's crust is composed of oxygen) and its high reactivity, oxygen occurs in many common compounds, including metal oxides, carbonates, silicates, hydrates, and water. Oxygen is also critical for life; the oxidation of biomolecules by oxygen provides energy for most living systems on Earth.



▲ Black smokers are vents found under the ocean that provide energy based on sulfur chemistry for life dwelling near the vents.

Elemental Oxygen

Oxygen exists naturally as a colorless, odorless, diatomic, nonpolar gas. It condenses to a pale blue liquid at -183°C . Oxygen is slightly soluble in water (0.04 g in 1 L or 0.001 M at 25°C). This rather low concentration of oxygen is enough to support life in aquatic environments. A few types of living systems that dwell deep in the ocean near vents that exude sulfur-containing fumes base their life processes on sulfur chemistry rather than oxygen chemistry.

Today, about 21% of Earth's atmosphere is composed of O_2 , but this was not always the case. Earth's early atmosphere was reducing (rather than oxidizing) and contained hydrogen, methane, ammonia, and carbon dioxide. About 2.7 billion

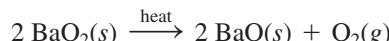
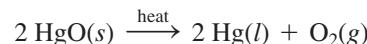
years ago, cyanobacteria (blue-green algae) began to convert the carbon dioxide and water to oxygen by photosynthesis. It took hundreds of millions of years to reach the current oxygen levels.

Joseph Priestley, an English scientist and minister, is credited with discovering oxygen. In 1774, he isolated oxygen by focusing sunlight on mercury(II) oxide and collecting the gas that was released as the red powder oxide formed liquid mercury. He tested the gas by using it to make a candle burn more brightly. He carried out a number of experiments with oxygen over the years, including bravely breathing his newfound gas. Antoine Lavoisier is credited with recognizing that oxygen is necessary for combustion. He described combustion as the reaction of a substance with oxygen (and not the loss of a substance). These discoveries and explanations were important steps in the development of modern chemistry.

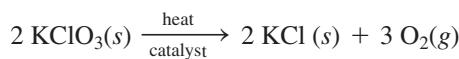
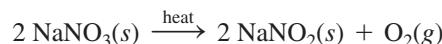
Oxygen is one of the most abundantly produced industrial chemicals. The major production method is the *fractionation* of air. Fractionation involves cooling air until its components liquefy. Then the air is warmed, and components such as N₂ and Ar are separated out, leaving oxygen behind. Most commercial oxygen is stored and transported as a gas in tanks under high pressure. Another method for the production of oxygen is the electrolysis of water. Passing an electric current through water containing a small amount of an electrolyte will form hydrogen gas at the cathode and oxygen gas at the anode (see Section 18.8). Because of the large amount of electricity needed, however, electrolysis is not a cost-efficient method for oxygen production.



In the laboratory, oxygen can be produced by heating and decomposing metal oxides and other oxygen-containing compounds. The oxides of mercury, silver, and gold lose all their oxygen when heated, while the oxides of other metals, such as barium, lose only some of their oxygen.



Metal nitrates and chlorates also yield oxygen when heated. A catalyst, such as manganese oxide or iron oxide, can make these reactions very fast and dangerous.



Uses for Oxygen

The greatest industrial use for oxygen is the enrichment of the air in a blast furnace for the conversion of high-carbon iron to steel. Large quantities of oxygen are also used in oxyhydrogen or oxyacetylene torches for the cutting of metals. Oxygen is also used to create artificial air for use underwater, during high-altitude travel, and in safety equipment.

Oxygen plays an important role in the treatment of a number of medical conditions, such as acute and chronic lung diseases and heart disorders. Generally, patients use masks or nasal catheters to receive oxygen from a tank of compressed oxygen. However, portable oxygen concentrators have been developed that use molecular sieves to separate and concentrate oxygen from air. Hyperbaric oxygen therapy is the application of high oxygen levels to patients with skin wounds, such as those with skin grafts or hard-to-heal wounds associated with diabetes. The high oxygen level kills anaerobic bacteria that can infect such wounds.

Oxides

As a strong oxidizing agent, oxygen reacts with most other elements to form oxides. We classify oxides according to the oxidation state of oxygen in the oxide (Table 22.6). The type of oxide that forms depends on the size and charge of the metal. Regular oxides

TABLE 22.6 Types of Oxides

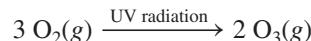
Class	Ion	Oxidation State of O	Example
Oxide	O^{2-}	-2	Li_2O , MgO
Peroxide	O_2^{2-}	-1	Na_2O_2 , BaO_2
Superoxide	O_2^-	$-\frac{1}{2}$	RbO_2 , CsO_2

are more stable for the smaller ions with a higher charge. Superoxides are more stable for the larger ions with a smaller charge.

Oxygen also reacts with many nonmetals to form covalent compounds. Many of these nonmetals form several different binary oxides. For example, we have already seen that carbon forms CO and CO_2 and that nitrogen forms N_2O , NO , N_2O_3 , NO_2 , N_2O_4 , and N_2O_5 .

Ozone

Ozone (O_3), an allotrope of oxygen, is a toxic blue diamagnetic gas with a strong odor. People can detect the smell at levels as low as 0.01 ppm, and the odor is often noticed in electrical storms or near electrical equipment because the gas forms from O_2 by an electrical discharge. Ozone is denser than O_2 and condenses to a deep blue liquid at $-112^\circ C$. Ozone is naturally made by the irradiation of O_2 with ultraviolet light in the upper atmosphere.



Ozone is also produced by passing O_2 gas through an electric field. The volume of gas decreases as the O_2 is converted to O_3 . Ozone is produced industrially by the electrolysis of cold concentrated sulfuric acid.

Thermodynamically unstable, ozone decomposes spontaneously to oxygen.



Ozone is used commercially as a strong oxidizing agent. For example, ozone can oxidize NO_2 to N_2O_5 or PbS to $PbSO_4$.



Ozone kills bacteria and is an environmentally safe replacement for chlorine in water-purification plants because the only by-product is O_2 . However, since ozone naturally decomposes, it must constantly be replenished, an economic drawback that limits its use.

The air we breathe contains ozone because it forms as a by-product of fossil fuel combustion. Since it is a strong oxidizing agent, it is a harmful substance. In the lower atmosphere, ozone damages the lungs and skin, stings the eyes, and damages most plant and animal tissues. Ozone also reacts with many types of plastic and rubber materials, causing them to become brittle and to crack.

As we also saw in Section 6.10, the layer of ozone in the upper atmosphere plays an important role in the absorption of harmful ultraviolet radiation from the sun. It absorbs the UV radiation and breaks apart to O_2 and O . This oxygen atom will often react with another O_2 molecule to re-form as ozone. During this cycle, each ozone molecule absorbs many ultraviolet photons. Recall also from Section 6.10 that the ozone layer has been depleted by chlorofluorocarbons (CFCs). However, legislation has banned CFCs in the hope that their reduction will help the ozone layer to recover.

22.8 Sulfur: A Dangerous but Useful Element

Like oxygen, sulfur is a nonmetal that belongs to the 6A family. However, sulfur's $3p$ orbitals extend farther out from the nucleus than do oxygen's $2p$ orbitals. Consequently, sulfur is larger and is a much weaker oxidizing agent than oxygen. Unlike oxygen, which

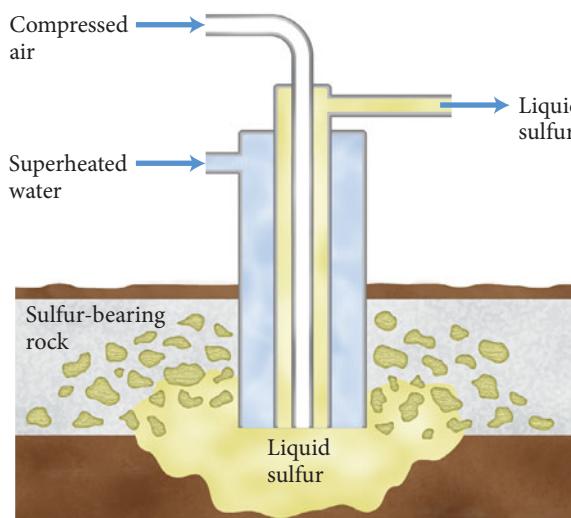
forms compounds with *only* negative oxidation states, sulfur forms compounds with both negative and positive oxidation states. Sulfur, selenium, and tellurium generally form covalent compounds with +4 or +6 oxidation states, forming anions only when bonding with highly electropositive metals. Sulfur is also much less abundant than oxygen, yet it still composes about 0.06% of the mass of Earth's crust.

Elemental Sulfur

Elemental sulfur occurs in a few natural deposits, mostly deep underground in the Gulf Coast area of the United States and in Eastern Europe. These deposits are believed to have formed as a by-product of anaerobic bacteria that decomposed sulfur-containing minerals over many years. The **Frasch process**, which allows us to recover sulfur from the earth, is diagrammed in Figure 22.23 ▼. Superheated water and compressed air are forced down long pipes into the sulfur deposits. The hot water melts the sulfur, which is pushed up to the surface along with the hot water through a third pipe. Some sulfur deposits also occur at Earth's surface—often in hot springs—where volcanic activity has made the sulfur accessible (Figure 22.24 ▶).

Sulfur has several allotropes; the most common naturally occurring allotrope of sulfur is composed of an S_8 ring structure called cyclooctasulfur. Most of the different allotropes have ring structures with rings ranging in size from S_6 to S_{20} . When heated above its melting point of 112 °C, cyclooctasulfur forms a straw-yellow liquid with low viscosity. Above 150 °C, the rings begin to break, and the sulfur becomes a darker, more viscous liquid as the broken rings entangle one another. The color is darkest at 180 °C when the liquid becomes very viscous and pours very slowly, as can be seen in the accompanying photo. Above this temperature, however, the intermolecular forces between the S_8 chains weaken, and the liquid becomes less viscous again. If the hot liquid is poured into cold water, the sulfur will quench into an amorphous solid (Figure 22.25 ►). Initially, this amorphous material is flexible like a plastic, but it hardens into a brittle solid.

The Frasch process, while important, provides less than one-third of the world's sulfur; sulfur is a by-product of a number of other industrial processes and is thus recovered from them. For example, dihydrogen monosulfide (H_2S), which is commonly called hydrogen sulfide, is a component of natural gas. The H_2S is separated from the other components by passing the gas through organic solvents such as ethanamine. The H_2S dissolves in the organic solvent.



▲ FIGURE 22.23 The Frasch Process The Frasch process extracts molten sulfur from the ground by forcing superheated water into beds of deposited solid sulfur.



▲ Molten sulfur below 150 °C (left) and nearing 180 °C (right).

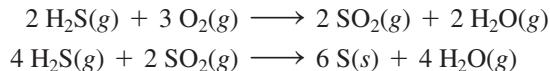


▲ FIGURE 22.24 Sulfur Deposits Some sulfur deposits can also be found at Earth's surface where volcanic activity has brought the element to the surface.

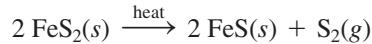


▲ FIGURE 22.25 Quenching Liquid Sulfur When hot liquid sulfur is poured into cold water, the sulfur quenches into an amorphous solid.

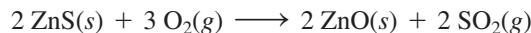
The H_2S is recovered and oxidized to elemental sulfur through a two-step process—the **Claus process**—that accounts for over 50% of all sulfur produced.



The third major source of sulfur production is metal sulfide minerals, such as the mineral iron(II) disulfide (also known as iron pyrite). Roasting iron pyrite in the absence of air causes the sulfur to disproportionate (react with itself) to form iron(II) sulfide and elemental sulfur.



Alternatively, the metal sulfide can be roasted in air to oxidize the metal sulfide. The sulfur is then removed as sulfur dioxide.



Hydrogen Sulfide and Metal Sulfides

Hydrogen sulfide, a component of natural gas, is toxic and forms by the reactions of anaerobic bacteria on organic substances. Rotting vegetation and bogs are natural sources of H_2S for the atmosphere. Fortunately, we can detect the odor of H_2S (a rotten egg smell) at concentrations as low as 0.02 ppm, which pose no threat to our health. Levels as low as 10 ppm can cause nausea, and 100 ppm can cause death. The smell of H_2S becomes more difficult to detect at high levels because H_2S also has an anesthetic effect that dulls the sense of smell. Consequently, the sudden onset of strong H_2S odor is a reason to move quickly to fresh air.

It might initially seem that hydrogen sulfide (H_2S) would share chemical properties with water (H_2O), but it does not. Water has a larger bond angle (104.5°) than hydrogen sulfide (92.5°) and is much more polar. Because of its polarity, water forms strong hydrogen bonds, but hydrogen sulfide does not. In addition, the O—H bond is much stronger than the S—H bond. These differences result in a far lower boiling point and greater reactivity for hydrogen sulfide compared to water. Water is a stable molecule in the presence of air and oxygen. Hydrogen sulfide burns in air, reacting with oxygen to form elemental sulfur or sulfur oxides.

EXAMPLE 22.5 Balancing of and Assigning Oxidation States to Sulfur Reactions

Write a balanced equation for the reaction of O_2 and H_2S to form elemental S (in the form of S_8). Identify the change of the oxidation state for S.

SOLUTION

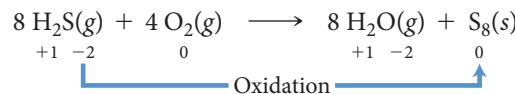
Write the skeletal equation. The products are elemental S_8 and H_2O .



Since hydrogen is initially balanced, balance S first, followed by H and O.



Assign oxidation states to each element (see Section 4.9).



The oxidation state of S changes from −2 in H_2S to 0 in S_8 ; therefore, S is oxidized.

FOR PRACTICE 22.5

Write a balanced equation for the reaction of oxygen with H_2S to form SO_2 . Identify the change of the oxidation state for S.

TABLE 22.7 Common Metal Sulfides

Sulfide	Formula	Common Name	K_{sp} (at 25 °C)
Iron(II) sulfide	FeS ₂	Pyrite	3.72×10^{-19}
Zinc sulfide	ZnS	Sphalerite	2.0×10^{-25}
Lead(II) sulfide	PbS	Galena	9.04×10^{-29}
Mercury(II) sulfide	HgS	Cinnabar	1.6×10^{-54}

Hydrogen sulfide forms from the reactions of metal sulfides with hydrochloric acid.

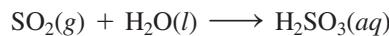


Only a few of the metal sulfides, those with group 1A and 2A metals and Al, are very soluble in water. Some common metal sulfides and their solubility product constants are listed in Table 22.7. The low solubility of these sulfides allows the use of H₂S as a good analytical method to determine whether metal ions are present in a solution. Sodium sulfide is used to precipitate toxic metals from industrial waste sources.

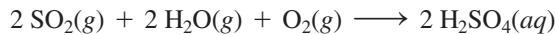
Metal sulfides have a number of industrial uses, mostly because they are toxic to bacteria. For example, SeS₂ is a shampoo additive that kills bacteria and controls dandruff, and As₂S₃ kills parasites.

Sulfur Dioxide

Sulfur dioxide is another toxic sulfur compound. Under standard conditions, it is a colorless, dense gas that has an acidic taste. The acidic taste results from the reaction of the gas with the water in your mouth.

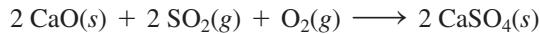
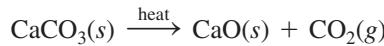


Sulfur dioxide forms naturally during volcanic activity when sulfides oxidize in the high volcanic temperatures. Sulfur dioxide is also a pollutant that forms during many industrial processes, such as coal and oil combustion and metal extraction. As we have seen, when the sulfur dioxide is emitted into the air, it reacts with oxygen and water to produce acid rain.



Sulfuric acid as a pollutant is destructive to plants, animals, and man-made structures (see Section 15.12).

To prevent the emission of SO₂ into the atmosphere, industrial processes “scrub” the gas to remove the SO₂. The exhaust gas flows through stacks lined with calcium carbonate that, when heated, capture sulfur oxides in the form of calcium sulfate dust.



The CaSO₄ dust is collected and disposed of. New uses for the tons of waste CaSO₄, such as discarded fireproof insulation, are needed.

One use for SO₂ again capitalizes on its toxicity. Food producers spray fruits and other vegetation with a solution containing SO₂ to kill mold and preserve the fruit. As a result, the fruits and vegetables can be shipped throughout the world, making it possible for inhabitants of the Northern Hemisphere to enjoy summer fruits (from the Southern Hemisphere) in the winter.

Sulfuric Acid

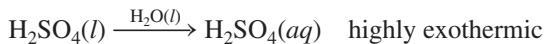
The most important use of sulfur and its compounds is the production of sulfuric acid. In fact, sulfuric acid is the most abundantly produced chemical in the world because it is a strong acid, a strong oxidizing agent, and a good dehydrating agent. It is also

**▲ FIGURE 22.26** Dehydration of

Sucrose Sulfuric acid dehydrates sucrose by removing the hydrogen and oxygen as water molecules and leaving carbon behind. The porous carbon foam forms because the reaction is very exothermic.

plentiful and inexpensive. Sulfuric acid is used in fertilizers, color dyes, petrochemicals, paints, plastics, explosives, battery, steel, and detergent industries, to name just a few.

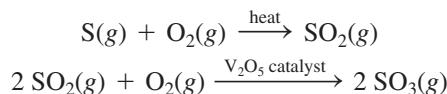
Pure H_2SO_4 melts at 10.4 °C and boils at 337 °C. At room temperature, it is an oily, dense liquid. Sulfuric acid reacts vigorously and exothermically with water. Pure or concentrated H_2SO_4 must be added to water slowly to avoid rapid heating, boiling, and splattering.



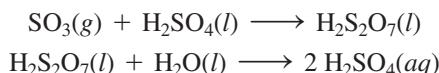
The strong attraction between sulfuric acid and water makes sulfuric acid a very strong dehydrating agent. As shown in Figure 22.26 ▲, its affinity for water is strong enough to decompose some organic materials, such as sucrose.



Sulfuric acid is produced industrially by a method known as the **contact process**, developed in the early twentieth century. In this method, elemental sulfur is first heated in air to form SO_2 gas, which is then heated in contact with a V_2O_5 catalyst to form SO_3 gas.



The SO_3 gas is absorbed into concentrated sulfuric acid, producing a dense form of sulfuric acid called oleum, $\text{H}_2\text{S}_2\text{O}_7$, which produces H_2SO_4 when dissolved in water.



As we have already seen, sulfuric acid is used in fertilizer production, which consumes a significant amount of the sulfuric acid produced.

22.9 Halogens: Reactive Elements with High Electronegativity

The halogens are all one electron short of a noble gas electron configuration. They are the most electronegative elements in their respective periods and are therefore very reactive. They do not naturally occur in their elemental form. The source of most of the halogens (except fluorine) is the dissolved salts present in seawater. The major sources for fluorine are several different minerals, including fluorspar (CaF_2) and fluoroapatite [$\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$].

We have already seen some of the properties of the halogens, especially those that exhibit periodic trends, in Section 8.9. For example, the atomic radius of the halogens increases regularly from fluorine to iodine, as shown in Table 22.8. Due partly to its small size, fluorine has the highest electronegativity of all elements and is always found in oxidation states of -1 or 0 . The other halogens can be found with oxidation states ranging from -1 to $+7$. The positive oxidation states occur when the halogen bonds to more electronegative elements such as fluorine or oxygen.

TABLE 22.8 Selected Properties of the Halogens

Element	Melting Point (°C)	Boiling Point (°C)	Atomic Radius (pm)	Electronegativity
Fluorine	-219	-188	72	4.0
Chlorine	-101	-34	99	3.0
Bromine	-7	60	113	2.8
Iodine	114	185	133	2.5

EXAMPLE 22.6 Determining the Oxidation State of Halogens in Compounds

Calculate the oxidation state of Cl in each compound.

- (a) ClO_3^- (b) HClO (c) Cl_2

SOLUTION

- (a) For ClO_3^- each O atom has an oxidation state of -2 for a total of -6 for all three O atoms. Therefore, the Cl atom has to have an oxidation state of $+5$ for the sum of the oxidation states to equal the charge of the ion ($5 - 6 = -1$).
- (b) For HClO , the O atom has an oxidation state of -2 and the H atom has an oxidation state of $+1$. Therefore the Cl atom has to have an oxidation state of $+1$ to have a neutral charge ($1 + 1 - 2 = 0$).
- (c) For Cl_2 the Cl atoms are in their elemental state, so they have an oxidation state of 0 .

FOR PRACTICE 22.6

Calculate the oxidation state of Cl in ClO_4^- and Cl^- .

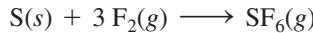
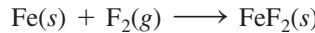
Elemental Fluorine and Hydrofluoric Acid

Fluorine is the most reactive element and forms binary compounds with all elements except He, Ne, and Ar. Fluorine even forms compounds with some of the noble gases, producing compounds such as XeF_2 , XeF_6 , and XeOF_4 . The high reactivity of fluorine is related to several factors. First, the F—F bond is among the weakest halogen–halogen bonds, as shown in Table 22.9. In order for a halogen to react with other substances, the halogen–halogen bond must break. The energy required to break that bond is small for F_2 , so the resulting reaction is more exothermic. Second, the small size of fluorine results in a high lattice energy for the ionic compounds that it forms. The high lattice energy means the compounds are very stable.

TABLE 22.9 Comparison of Halogen X—X Bond Energy

Halogen	F—F	Cl—Cl	Br—Br	I—I
Bond energy (kJ/mol)	159	243	193	151

The high reactivity of fluorine is illustrated by its ability to burn (or quickly oxidize) many substances, such as iron and sulfur, that do not readily burn with oxygen.



Fluorine gas even reacts with asbestos and glass, two materials commonly used as containers for reactive substances. Consequently, fluorine is normally held in metal containers made of iron, copper, or nickel. These metals also initially react with fluorine, but then a thin layer of the product coats the surface of the metal, protecting the underlying metal from further reaction.

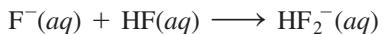
Elemental fluorine is produced from the electrolysis of hydrofluoric acid, forming F_2 and H_2 gases.



Gaseous hydrogen fluoride can be obtained from the reaction of the mineral fluorspar (CaF_2) with sulfuric acid.



In its solid form, HF has a crystal structure that contains zigzag chains of alternating H and F atoms. In aqueous solutions, HF is a weak acid ($K_a = 3.5 \times 10^{-4}$ for HF at 298 K). Like all anions in aqueous solution, the F^- ions from ionized HF are solvated by water molecules. However, the F^- ions can also associate with other HF molecules to form HF_2^- .



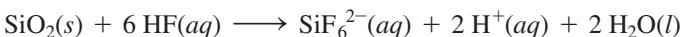
The structure of HF_2^- , shown here, is unique because it contains a bridging hydrogen atom (a hydrogen atom that essentially forms two bonds).



Hydrofluoric acid is a strong oxidizing agent and reacts with glass according to the following reactions:



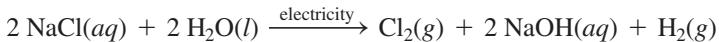
or



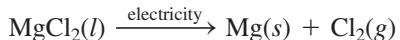
As a result, hydrofluoric acid cannot be held in a glass container and is generally stored in plastic. The ability of HF to react with glass makes it useful in etching glass. The parts of the glass to be etched are left exposed, and the rest of the surface is masked with a nonreactive substance such as plastic. The surface is then exposed to hydrofluoric acid and the nonmasked glass etches away, leaving the desired pattern. Hydrofluoric acid is particularly dangerous because it quickly penetrates into tissues, damaging internal organs and bones. Direct exposure of just 2% of body surface area to concentrated hydrofluoric acid can be fatal.

Elemental Chlorine

Historically, the primary source for chlorine has been seawater. Electrolysis of NaCl in seawater produces Cl_2 gas and H_2 gas.



Today, much Cl_2 gas is produced and collected as a by-product of the various metal processing methods, such as in the reduction of metal chlorides to form metals.



Halogen Compounds

Halogens form ionic compounds with most metals, they form covalent compounds with many nonmetals, and they can bond with themselves to form interhalogen compounds. Here we look at some of these halogen compounds.

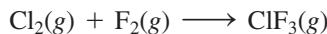
Interhalogen Compounds Covalent compounds composed of two different halogens are known as **interhalogen compounds** or *interhalides*. The general formula of these compounds is AB_n , where A is the larger halogen, B is the smaller halogen, and n is 1, 3, 5, or 7. The smaller halogens surround the larger halogen in the AB_3 compounds. The only known AB_5 compounds contain fluorine as the smaller halogen (because the other halogens are too large for five of them to fit around another halogen). The compound IF_7 is the only known interhalogen compound with $n = 7$. The large size of the iodine atom allows seven small fluorine atoms to surround it. The interhalides can be formed by reacting the elemental halogens with one another. Interhalide polyatomic ions, such as ICl_2^+ and ICl_4^- , also exist.

EXAMPLE 22.7 Formation of Interhalogen Compounds

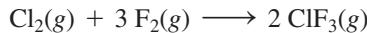
Write the balanced equation for the formation of ClF_3 gas from the elemental halogens.

SOLUTION

The unbalanced reaction is:



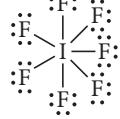
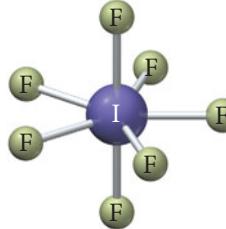
At least 2 ClF_3 molecules form from each Cl_2 molecule; therefore, add a 2 before ClF_3 and then a 3 before F_2 . The balanced equation is:



FOR PRACTICE 22.7

Write a balanced equation for the formation of IF_5 gas from the elemental halogens.

The geometry of the interhalides can be predicted from the valence shell electron pair repulsion model (VSEPR). Because the halogens do not form double or triple bonds, the shapes of these compounds are relatively straightforward to determine, as shown in Examples 22.8 and 22.9.

PROCEDURE FOR...	EXAMPLE 22.8	EXAMPLE 22.9
Determining the Shape of Interhalogen Compounds	Molecular Shapes of Interhalogen Compounds Determine the molecular geometry of IBr_2^- .	Molecular Shapes of Interhalogen Compounds Determine the molecular geometry of IF_7^- .
Identify the central atom.	SOLUTION I	SOLUTION I
Draw the Lewis structure (see Section 9.5).	$[\text{:Br}-\text{:I:}-\text{:Br:}]^-$	
Count the number of bonds and lone pairs on the central atom.	The I atom has two bonds and three lone pairs for a total of five electron groups.	The I atom has seven bonds on the central atom for a total of seven electron groups.
Determine the electron geometry from the number of electron groups (see Section 10.4).	With five electron groups, the electron geometry is <i>trigonal bipyramidal</i> .	With seven electron groups, the electron geometry is <i>pentagonal bipyramidal</i> .
Determine the molecular shape from the number of bonds and lone pairs.	With two bonds the molecular geometry is <i>linear</i> because the three lone pairs will occupy equatorial positions.	With seven bonds the molecular geometry will also be <i>pentagonal bipyramidal</i> .
		
	FOR PRACTICE 22.8 Determine the electron geometry and molecular geometry of ICl_2^+ .	FOR PRACTICE 22.9 Determine the electron geometry and molecular geometry of BrF_5 .

The only industrially useful interhalide is ClF_3 , employed in the nuclear energy industry to produce $\text{UF}_6(g)$, which is used to separate ^{235}U ($<1\%$ of naturally occurring uranium) from ^{238}U . Uranium ores react with gaseous hydrogen fluoride to form $\text{UF}_4(s)$, which reacts with $\text{ClF}_3(g)$ to form the gaseous uranium compound.



Because of the difference in mass between the two isotopes, $^{238}\text{UF}_6$ effuses more slowly than $^{235}\text{UF}_6$ (see Section 5.9 for a description of effusion). The mixture of gases is allowed to flow through barriers with very small pores. Since $^{235}\text{UF}_6$ effuses more quickly, the initial flow of gas that exits the pores is enriched in $^{235}\text{UF}_6$. By repeating the process, the two isotopes can be nearly completely separated.

Halogen Oxides Most halogen oxides are unstable and many are explosive. A unique halogen oxide is OF_2 ; oxygen usually has a negative oxidation state in its compounds but has a +2 oxidation state in OF_2 (due to the high electronegativity of fluorine).

A number of different chlorine oxides are known, including Cl_2O , ClO_2 , Cl_2O_6 , and Cl_2O_7 . Chlorine dioxide is a powerful oxidizing agent used to bleach flour and wood pulp (to make white paper). Because ClO_2 is explosive, the gas is diluted with CO_2 or N_2 for safety. Some water treatment plants use ClO_2 for water disinfection in place of Cl_2 . ClO_2 is produced by the reduction of sodium chlorite with Cl_2 or by the reduction of sodium chlorate with hydrochloric acid.

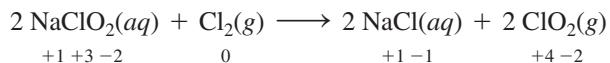


EXAMPLE 22.10 Identifying Changes in Oxidation States

Identify the change of oxidation state for Cl in the production of chlorine dioxide from sodium chlorite. Identify the oxidizing agent and the reducing agent.

SOLUTION

First determine the oxidation state of Cl in each compound.



The Cl in the NaClO_2 was oxidized from +3 to +4 by the oxidizing agent Cl_2 , which was reduced from 0 to -1 by the reducing agent NaClO_2 .

FOR PRACTICE 22.10

Identify the change of oxidation state for Cl in the production of chlorine dioxide from sodium chlorate. Identify the oxidizing agent and the reducing agent.

CHAPTER IN REVIEW

Self Assessment Quiz

- Q1.** An aluminosilicate is composed of a crystal in which Al atoms substitute for three-fourths of the Si atoms in the silica structure. The negative charge of the AlO_2^- groups is balanced by Na^+ ions. What is the formula of the aluminosilicate?
- a) $\text{Na}(\text{AlSi}_3\text{O}_8)$
 - b) $\text{Na}_2(\text{Al}_2\text{Si}_2\text{O}_8)$
 - c) $\text{Na}_3(\text{Al}_3\text{SiO}_8)$
 - d) NaSiO_2
- Q2.** Use charge balance to determine x in the formula for the sorosilicate bertrandite, $\text{Be}_4\text{Si}_2\text{O}_7(\text{OH})_x$.
- a) 1
 - b) 2
 - c) 3
 - d) 4

- Q3.** Which element is important in the manufacturing of glassware intended for heating?
- carbon
 - nitrogen
 - phosphorus
 - boron
- Q4.** Fertilizers commonly contain compounds of which element?
- nitrogen
 - aluminum
 - fluorine
 - boron
- Q5.** What is the oxidation state of bromine in the compound NaBrO_3 ?
- +2
 - 3
 - 4
 - +5
- Q6.** What is the molecular geometry of ICl_4^- ?
- tetrahedral
 - square planar
 - octahedral
 - seesaw
- Q7.** Which element is oxidized in the reaction?
- $$2 \text{CaO}(s) + 2 \text{SO}_2(g) + \text{O}_2(g) \longrightarrow 2 \text{CaSO}_4(s)$$
- Ca
 - O
 - S
 - None of the above (no element is oxidized in the reaction)
- Q8.** Which carbon oxide does not exist?
- CO
 - CO_2
 - CO_3^{2-}
 - CO_4
- Q9.** Which element is extracted from the ground primarily in its elemental form?
- boron
 - phosphorus
 - sulfur
 - fluorine
- Q10.** Which substance forms when carbon dioxide dissolves in water?
- CO
 - H_2CO
 - CH_4
 - H_2CO_3

Answers 1. (c) 2. (b) 3. (d) 4. (a) 5. (d) 6. (b) 7. (c) 8. (d) 9. (c) 10. (d)

Key Terms

Section 22.2

main-group elements (1036)

Section 22.3

silicates (1038)
quartz (1038)
silica (1038)
aluminosilicates (1038)
mineral (1038)
orthosilicates (1039)
pyrosilicates (1039)
pyroxenes (1039)

Section 22.4

boranes (1043)
closو-boranes (1043)
nido-boranes (1043)
arachno-boranes (1044)

Section 22.5

graphite (1044)
diamond (1044)

coal (1045)

coke (1045)
charcoal (1045)
activated carbon (1046)
soot (1046)
carbon black (1046)
fullerenes (1046)
nanotubes (1046)
carbides (1047)
ionic carbides (1047)
covalent carbides (1048)
metallic carbides (1048)
washing soda (1049)

Section 22.6

white phosphorus (1050)
red phosphorus (1051)
black phosphorus (1051)
ammonia (1051)
Haber–Bosch process (1052)
hydrazine (1052)

hydrogen azide (1052)

Ostwald process (1053)
phosphine (1054)

Section 22.7

ozone (1058)

Section 22.8

Frasch process (1059)
Claus process (1060)
contact process (1062)

Section 22.9

interhalogen compounds (1064)

Key Concepts

Bonding and Properties (22.2)

- ▶ Main-group elements are defined by their electron configurations and their location on the periodic table.
- ▶ The properties of the main-group elements show great diversity. Metals, nonmetals, and metalloids are all found among the main-group elements.
- ▶ Some of the main-group elements form covalent bonds while others form ionic bonds.

The Most Common Matter: Silicates (22.3)

- ▶ Silicates (found in rocks, clays, and soils) are covalent atomic solids that contain silicon, oxygen, and various metal atoms.
- ▶ Silicate structures consist of four oxygen atoms bonded to silicon, forming a negatively charged polyatomic anion with a tetrahedral shape. Various metal ions within the structure balance the charge of the compound.
- ▶ The SiO_4 tetrahedrons can link to form chains, double chains, sheets, or even extended three-dimensional structures.
- ▶ The properties of the silicates depend on the connections between the silicate tetrahedrons. Because of the wide variety of combinations of tetrahedron connections and the many different metal ions that fit within the structure, an enormous variety of different silicate minerals exist in nature, making the silicate materials the most common structures found on Earth.

Boron (22.4)

- ▶ Because of its small size and high electronegativity, boron behaves as a metalloid.
- ▶ The structure of elemental boron consists of icosahedron structures bonded together in various ways.
- ▶ Boron tends to form electron-deficient compounds.
- ▶ Compounds of boron and hydrogen form cluster compounds resembling spheres, cages, and nets.

Carbon (22.5)

- ▶ Organic chemistry is based on the chemistry of carbon, yet carbon is also very important in many inorganic compounds and applications.
- ▶ Graphite and diamond are two well-known structures of elemental carbon, but many other forms of elemental carbon, such as carbon black, coke, and the more recently discovered fullerenes and nanotubes have many industrial applications.
- ▶ Important types of inorganic carbon compounds include carbides and carbonates. Carbon can form carbides with metallic, covalent, or ionic properties.

- ▶ Carbon and its oxygen compounds are intimately involved in the functions of life.

Nitrogen and Phosphorus (22.6)

- ▶ Nitrogen and phosphorus have been known for over 200 years; both form compounds with oxidation numbers ranging from -3 up to $+5$.
- ▶ Both nitrogen and phosphorus compounds are critical for plant growth, so not surprisingly, their most important use is as fertilizers. The strong triple bond between nitrogen atoms in N_2 makes nitrogen from the atmosphere inaccessible to most plants, so ingenious chemical processes have been devised to make nitrogen compounds that are more available to plants.

Oxygen (22.7)

- ▶ Oxygen is the most common element on Earth. It is found in the atmosphere as the elemental gas and as many oxide gases.
- ▶ Oxygen is found in ocean water and in Earth's crust as silicate and oxide compounds. Oxygen is a strong oxidizing agent and forms compounds with $-\frac{1}{2}$, -1 , or -2 oxidation states.
- ▶ Ozone, O_3 , is a helpful molecule in the upper atmosphere, where it absorbs harmful ultraviolet radiation, but it is a harmful molecule at Earth's surface.

Sulfur (22.8)

- ▶ More sulfuric acid is produced than any other chemical; most of it is used to make fertilizers. Other uses take advantage of its strong oxidation and dehydration properties.
- ▶ Elemental sulfur has several allotropes ranging from ring structures to chain structures and amorphous materials, depending upon temperature.

Halogens (22.9)

- ▶ The halogens are the most electronegative elements, so they are always found as compounds, usually ionic. When they bond with other electronegative elements, however, they can form covalent compounds.
- ▶ Fluorine has special chemical properties because it is the most electronegative element and is very small, making it a very strong oxidizing agent.
- ▶ Interhalogen compounds are formed between two halogens, with the larger halogen as the central atom of the structure.

Key Learning Outcomes

Chapter Objectives	Assessment
Determining the Composition, Charge Balance, and Type of Silicates and Aluminosilicates (22.3)	Examples 22.1, 22.2, 22.3, 22.4 For Practice 22.1, 22.2, 22.3, 22.4 Exercises 17–26
Writing Equations for Reactions and Assigning Oxidation States (22.8, 22.9)	Examples 22.5, 22.6, 22.10 For Practice 22.5, 22.6, 22.10 Exercises 43–46, 55–58, 73–74, 77–78
Formation of Interhalogen Compounds and Their Structures (22.9)	Examples 22.7, 22.8, 22.9 For Practice 22.7, 22.8, 22.9 Exercises 75–76, 80



EXERCISES

Review Questions

1. Why does BN form compounds similar to those formed by elemental carbon?
2. What is the main characteristic that determines whether or not an element is a main-group element?
3. Does the metallic characteristic of a main-group element increase or decrease as we move down a family? Explain why.
4. Why does silicon form only single bonds with oxygen but carbon, which is in the same family as silicon, form double bonds with oxygen in many compounds?
5. What is the difference between SiO_2 that is cooled slowly and SiO_2 that is cooled quickly?
6. What is the difference between a rock and a mineral?
7. Briefly define each term.
 - a. orthosilicate
 - b. amphibole
 - c. pyroxene
 - d. pyrosilicate
 - e. feldspar
8. Why is boron oxide often added to silica glass?
9. Why does boron form electron-deficient bonds? Provide an example.
10. List three allotropes of crystalline carbon.
11. Explain why solid CO_2 is referred to as dry ice.
12. Nitric acid and phosphoric acid are two major chemical products of the chemical industry. Describe some of their uses.
13. What is the typical concentration of oxygen in dry air?
14. Describe how nitrogen can be separated from the other components of air.
15. Earth's atmosphere originally did not contain oxygen. Explain how the atmosphere gained oxygen.
16. Name a benefit, a hazard, and a useful commercial application of ozone.

Problems by Topic

Silicates: The Most Abundant Matter in Earth's Crust

17. Silicon bonds to oxygen to form a tetrahedral shape in both the network covalent silica compound, SiO_2 , and in ionic silicate compounds. What is the oxidation state of Si in each of these structures?
 - a. silica compound, SiO_2
 - b. orthosilicates, SiO_4^{4-}
 - c. pyrosilicates, $\text{Si}_2\text{O}_7^{6-}$
18. What is the oxidation state of Si in each of these structures?
 - a. pyroxenes, SiO_3^{2-}
 - b. amphiboles, $\text{Si}_4\text{O}_{11}^{6-}$
 - c. phyllosilicates, $\text{Si}_2\text{O}_5^{2-}$
19. In the orthosilicate garnet, the formula unit has three SiO_4^{4-} units and is balanced by Ca^{2+} and Al^{3+} cations. Determine the formula unit of garnet.
20. In the pyroxene kanoite, the formula unit has two SiO_3^{2-} units and is balanced by manganese and magnesium ions. Determine the formula unit of kanoite. Assume that the oxidation state of Mn is +2.
21. Kaolin is a clay material that is a phyllosilicate. Use charge balancing to determine how many hydroxide ions are in the formula for kaolin, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_x$.
22. Tremolite is a double-chain silicate in the amphibole class. Use charge balancing to determine how many hydroxide ions are in the formula for tremolite, $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_x$.
23. How are the silica tetrahedrons linked for ZrSiO_4 ? Which class of silicates does this compound belong to?
24. How are the silica tetrahedrons linked for CaSiO_3 ? Which class of silicates does this compound belong to?
25. Predict the structure and give the charges on the cations in one of the minerals in the hornblende family, $\text{Ca}_2\text{Mg}_4\text{FeSi}_7\text{AlO}_{22}(\text{OH})_2$.
26. Predict the structure and label the charges on the cations in the mineral hedenbergite, $\text{CaFeSi}_2\text{O}_6$.

Boron and Its Remarkable Structures

27. A major source of boron is the mineral kernite, $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 3 \text{H}_2\text{O}$. Calculate how many grams of boron can be produced from 1.0×10^3 kg of a kernite-bearing ore if the ore contains 0.98% kernite by mass and the process has a 65% yield.
28. An uncommon mineral of boron is ulexite, $\text{NaCaB}_5\text{O}_9 \cdot 8 \text{H}_2\text{O}$. How many grams of boron can be produced from 5.00×10^2 kg of ulexite-bearing ore if the ore contains 0.032% ulexite by mass and the process has an 88% yield?
29. Explain why the bond angles in BCl_3 and NCl_3 are different.
30. Explain why the bond between B and Cl in the molecule BCl_3 is shorter than would be expected for a single B—Cl bond.
31. Predict the number of vertices and faces on each *closo*-borane.
 - a. $\text{B}_6\text{H}_6^{2-}$
 - b. $\text{B}_{12}\text{H}_{12}^{2-}$
32. Predict the number of vertices and faces on each *closo*-borane.
 - a. $\text{B}_4\text{H}_4^{2-}$
 - b. $\text{B}_9\text{H}_9^{2-}$
33. Describe the differences among a *closo*-borane, a *nido*-borane, and an *arachno*-borane.
34. Describe how boron is used in the nuclear industry.

Carbon, Carbides, and Carbonates

35. Explain why the graphite structure of carbon allows graphite to be used as a lubricant, but the diamond structure of carbon does not.
36. Explain why graphite can conduct electricity, but diamond does not.
37. Describe the difference between regular charcoal and activated charcoal.
38. Explain why the structure of charcoal allows carbon to act as a good filter while the diamond structure does not.

- 39.** Describe the difference between an ionic carbide and a covalent carbide. Which types of atoms will form these carbides with carbon?
- 40.** Silicon carbide is produced by heating silicone polymers, forming methane gas, hydrogen gas, and silicon carbide. Balance the reaction of heating $[(\text{CH}_3)_2\text{Si}]_8$ to form silicon carbide.
- 41.** Referring to the phase diagram in Section 11.8, describe what happens to the phase of CO_2 during each process.
- reducing the pressure on solid CO_2 that is at -80°C
 - decreasing the temperature on CO_2 gas that is held at a pressure of 20 atm
 - increasing the temperature on solid CO_2 that is held at a pressure of 0.8 atm
- 42.** Referring to the phase diagram in Section 11.8, describe what happens to the phase of CO_2 during each process.
- reducing the temperature from the critical point
 - increasing the pressure on CO_2 gas that is held at a temperature of -50°C
 - increasing the temperature on solid CO_2 that is held at a pressure of 20 atm
- 43.** Predict the products for each reaction and write a balanced equation.
- $\text{CO}(g) + \text{CuO}(s)$
 - $\text{SiO}_2(s) + \text{C}(s)$
 - $\text{S}(s) + \text{CO}(g)$
- 44.** Predict the products for each reaction and write a balanced equation.
- $\text{CO}(g) + \text{Cl}_2(g)$
 - $\text{CO}_2(g) + \text{Mg}(s)$
 - $\text{S}(s) + \text{C}(s)$
- 45.** Give the oxidation state for carbon in:
- CO
 - CO_2
 - C_3O_2
- 46.** Write a balanced reaction for the gas release reaction of Alka-Seltzer, sodium bicarbonate with citric acid, $\text{C}_6\text{H}_8\text{O}_7$. (The acid is a triprotic acid and consists of a chain of three carbon atoms, each with a carboxylic acid group, COOH .)

Nitrogen and Phosphorus: Essential Elements for Life

- 47.** Explain the process of fixing nitrogen.
- 48.** Explain why the diatomic nitrogen atom is unusable by most plants. Where do plants get nitrogen?
- 49.** Describe the differences in the allotropes of white and red phosphorus. Explain why red phosphorus is more stable.
- 50.** Describe how red and black phosphorus are made from white phosphorus.
- 51.** Saltpeter and Chile saltpeter are two important mineral sources for nitrogen. Calculate the mass percent of nitrogen in each mineral.
- 52.** Apatite is a main mineral source for the production of phosphorus. Calculate the atomic and mass percent of P in the mineral apatite.
- 53.** Referring to the tables in Appendix IIB, determine whether or not hydrogen azide is stable at room temperature compared to its elements, H_2 and N_2 . Is hydrogen azide stable at any temperature?

- 54.** Referring to the tables in Appendix IIB, determine if dinitrogen monoxide is stable at room temperature compared to its elements, O_2 and N_2 . Is dinitrogen monoxide stable at any temperature?
- 55.** Predict the products for each reaction and write a balanced equation.
- $\text{NH}_4\text{NO}_3(aq) + \text{heat}$
 - $\text{NO}_2(g) + \text{H}_2\text{O}(l)$
 - $\text{PCl}_3(l) + \text{O}_2(g)$
- 56.** Predict the products for each reaction and write a balanced equation.
- $\text{NO}(g) + \text{NO}_2(g)$
 - heating PH_3
 - $\text{P}_4(s) + 5 \text{O}_2(g)$
- 57.** Rank the nitrogen ions from the one with N in the highest oxidation state to the one with N in the lowest.
- $$\text{N}_3^-, \text{N}_2\text{H}_5^+, \text{NO}_3^-, \text{NH}_4^+, \text{NO}_2^-$$
- 58.** Determine the oxidation state of N in the compounds in the reaction for the formation of nitric acid. Identify the oxidizing agent and the reducing agent.
- $$3 \text{NO}_2(g) + \text{H}_2\text{O}(l) \longrightarrow 2 \text{HNO}_3(l) + \text{NO}(g)$$
- 59.** Draw the Lewis structures for the phosphorus halides PCl_3 and PCl_5 . Describe their VSEPR shape.
- 60.** Dinitrogen pentoxide is an ionic compound formed from the ions NO_2^+ and NO_3^- . Give the oxidation state of N in each ion and the VSEPR shape for each of the ions.
- 61.** Ammonium carbonate is produced from the reaction of urea, $\text{CO}(\text{NH}_2)_2$ with water. Write a balanced equation for this reaction and determine how much urea is needed to produce 23 g of ammonium carbonate.
- 62.** Explain why phosphine, PH_3 , is less polar than ammonia.
- 63.** Reacting oxygen with white phosphorus can form either P_4O_6 or P_4O_{10} . State the conditions that determine which product forms.
- 64.** P_4O_{10} is one of the most effective drying agents, having the ability to extract water from other molecules. The P_4O_{10} forms phosphoric acid. Write balanced reactions for the reaction of P_4O_{10} with:
- HNO_3 , forming N_2O_5
 - H_2SO_4 , forming SO_3

Oxygen

- 65.** Name the major source of the element oxygen and describe how it is produced.
- 66.** Explain why either greatly decreasing or increasing the percentage of oxygen in the atmosphere is dangerous.
- 67.** Identify each compound as an oxide, peroxide, or superoxide.
- LiO_2
 - CaO
 - K_2O_2
- 68.** Identify each compound as an oxide, peroxide, or superoxide.
- MgO
 - Na_2O_2
 - CsO_2

Sulfur: A Dangerous but Useful Element

- 69.** Explain why the viscosity of liquid sulfur increases with increasing temperature initially, but then decreases upon further increases in temperature.
- 70.** Sulfur dioxide is a toxic sulfur compound. List one natural source and one industrial source that produces SO_2 .
- 71.** Calculate the maximum mass (in grams) of each metal sulfide that will dissolve in 1.0 L of a solution that is 5.00×10^{-5} M in Na_2S .
- PbS
 - ZnS
- 72.** A coal source contains 1.1% sulfur by mass. If 2.0×10^4 kg of coal is burned and forms oxides, calculate the mass of $\text{CaSO}_4(s)$ that is produced from “scrubbing” the SO_2 pollutant out of the exhaust gas. Assume that all of the sulfur in the coal is converted to calcium sulfate.
- 73.** Write the equation for roasting iron pyrite in the absence of air to form elemental sulfur. Calculate the volume of S_2 gas that can be produced from roasting 5.5 kg of iron pyrite. Assume that all of the sulfur in the iron pyrite is converted to S_2 gas. (Assume STP to calculate the gas volume.)
- 74.** Write an overall reaction from the two steps in the Claus process. Calculate the volume of H_2S gas needed to produce 1.0 kg of $\text{S}(s)$. (Assume STP to calculate the gas volume.)

Halogens

- 75.** Determine the oxidation state of Xe and give the VSEPR structure for each compound.
- XeF_2
 - XeF_6
 - XeOF_4
- 76.** Describe the shape of each halogen compound.
- BrF_4^-
 - IF_3
 - BrO_2^-
 - ClO_4^-
- 77.** When chlorine is bubbled through a colorless aqueous solution containing bromide ions, the solution turns red and the chlorine is reduced. Write a balanced equation for this reaction and identify the oxidizing and reducing agent.
- 78.** Carbon tetrachloride is produced by passing chlorine gas over carbon disulfide in the presence of a catalyst. The reaction also produces S_2Cl_2 . Write the balanced reaction and identify which element is oxidized and which element is reduced.
- 79.** If 55 g of $\text{SiO}_2(s)$ glass is placed into 111 L of 0.032 M HF, is there enough HF to dissolve all of the glass? Determine which substance is the limiting reagent and calculate how much of the other reagent is left if the reaction proceeds to completion.
- 80.** Describe the difference in the types of bonds (single, double, triple) and the shapes of the following two iodine ions: ICl_4^- and IO_4^- .

Cumulative Problems

- 81.** From the compositions of lignite and bituminous coal, calculate the mass of sulfuric acid that could potentially form as acid rain from burning 1.00×10^2 kg of each type of coal.
- 82.** Calculate the volume of CO_2 released from heating and decomposing 88 g of sodium bicarbonate. (Assume standard pressure and temperature.)
- 83.** All of the halogens form oxoacids. The perhalic acids have the general formula of HXO_4 . Explain why HClO_4 is a much stronger acid than HIO_4 .
- 84.** The halogens form oxoacids with different amounts of oxygen. Explain why HClO_4 is a stronger acid than HClO_2 .
- 85.** Determine the ratio of effusion rates of HCl compared to each gas.
- Cl_2
 - HF
 - HI
- 86.** Calculate the ratio of effusion rates for each pair of gases.
- $^{238}\text{UF}_6$ and ClF
 - $^{238}\text{UF}_6$ and $^{235}\text{UF}_6$
- 87.** Sodium peroxide is a very powerful oxidizing agent. Balance the reaction of sodium peroxide with elemental iron to give sodium oxide and Fe_3O_4 .
- 88.** Sulfur dioxide is a reducing agent. When it is bubbled through an aqueous solution containing Br_2 , a red-colored solution, it reduces the bromine to colorless bromide ions and forms sulfuric acid. Write a balanced equation for this reaction and identify the oxidizing and reducing agent.

- 89.** Using the molecular orbital model for a diatomic molecule, explain the different bond lengths for the ions of oxygen. Also state which ion is diamagnetic.

Ion	O—O Bond Length (pm)
O_2^+	112
O_2	121
O_2^-	133
O_2^{2-}	149

- 90.** The *closo*-borane with the formula $\text{B}_6\text{H}_6^{2-}$ has the six B atoms at vertices, forming an octahedron structure with eight faces. The formula for the number of sides is $2n - 4$, where n is the number of boron atoms. Determine the number of vertices and faces for each *closo*-borane.
- $\text{B}_4\text{H}_4^{2-}$
 - $\text{B}_{12}\text{H}_{12}^{2-}$
- 91.** Find the amount (in moles) of C—C bonds that must be broken when 1.0 mole of $\text{C}(g)$ is formed from C(diamond). Calculate the ΔH of sublimation of diamond from the data in Appendix II, Table B. Then do the calculation using the C—C bond energy in Table 9.3. Suggest a reason for the difference between the two values.

92. Breathing air that contains 0.13% CO by volume for 30 minutes will cause death. CO can form by incomplete combustion of carbon-containing compounds. Calculate the minimum volume of octane (C_8H_{18} , a component of gasoline, which has a density of 0.70 g/mL) that must burn to produce this composition of CO in a garage of volume 40 m³ at 298 K and 1.0 atm.

93. Given that the ΔH_f° of 1 M H_2SO_3 is -633 kJ, use the data in Appendix II, Table B to calculate the ΔH° for the formation of a 1 M solution of SO_2 in water from $SO_2(g)$.
94. Use the data in Appendix II, Table B to calculate ΔH° for the formation of a 1 M solution of H_2SO_4 from $SO_3(g)$.

Challenge Problems

95. Calculate the standard enthalpy of reaction for reducing the different forms of iron oxide to iron metal and CO_2 from the reaction of the oxide with CO. Identify which reaction is the most exothermic per mole of iron and explain why.

- a. Fe_3O_4
- b. FeO
- c. Fe_2O_3

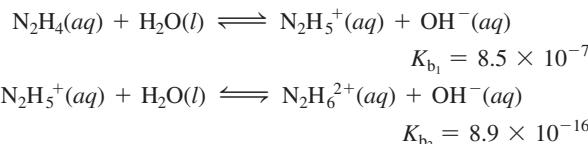
96. Balance the equation for the production of acetylene (C_2H_2) from the reaction of calcium carbide with water. If the acetylene is burned to form water and carbon dioxide, how many kilojoules of energy are produced from the complete reaction of 18 g of calcium carbide?

97. Carbon suboxide, C_3O_2 , is a linear molecule with the two oxygen atoms at the end and double bonds between each carbon and oxygen atom.

- a. Draw the Lewis structure for C_3O_2 .
- b. State the type of hybridization of each carbon atom.
- c. Calculate the heat of reaction for the reaction of carbon suboxide with water to form malonic acid ($HO_2CCH_2CO_2H$). Hint: Each end of malonic acid has a carbon double bonded to an oxygen and bonded to a hydroxide.

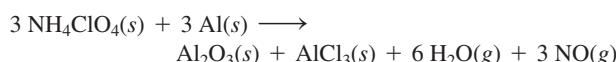
98. Calcium carbonate is insoluble in water. Yet, it dissolves in an acidic solution. Calculate the standard enthalpy, entropy, and Gibbs free energy change for the reaction between solid calcium carbonate and hydrochloric acid. What drives the reaction, the enthalpy change, or the entropy change?

99. When hydrazine is dissolved in water it acts like a base.



- a. Calculate the K_b for the overall reaction of hydrazine forming $N_2H_6^{2+}$.
- b. Calculate K_{a_1} for $N_2H_5^+$.
- c. Calculate the concentration of hydrazine and both cations in a solution buffered at a pH of 8.5 for a solution that was made by dissolving 0.012 mol of hydrazine in 1 L of water.

100. Solid fuel in the booster rockets for spacecraft consists of aluminum powder as the fuel and ammonium perchlorate as the oxidizing agent.



If a rocket launch burns 2.200×10^3 kg of aluminum, calculate the energy produced in joules. Calculate the volume of the gas produced assuming it was cooled back to 298 K at 1 atm. The standard enthalpy of formation of solid ammonium perchlorate is -295.3 kJ/mol.

101. Two known compounds have the formula $H_2N_2O_2$. One of them is a weak acid and one is a weak base. The acid, called hyponitrous acid, has two O—H bonds. The base, called nitramide, has no O—H bonds. Draw Lewis structures for these compounds. Predict whether the acid is stronger or weaker than nitrous acid and whether the base is stronger or weaker than ammonia.

Conceptual Problems

102. Explain why fine particles of activated charcoal can absorb more (as a filter) than large briquettes of charcoal.

103. The two major components of the atmosphere are the diatomic molecules of nitrogen and oxygen. Explain why pure nitrogen is used as a protective atmosphere in the laboratory and pure oxygen is much more reactive.

104. Explain why nitrogen can form compounds with many different oxidation numbers.

105. Describe how sodium dihydrogen phosphate can be used as a pH buffering agent.

106. Explain why H_2S has a different bond angle and is much more reactive than H_2O .

107. Explain why fluorine is found only with the oxidation state of -1 or 0, while the other halogens are found in compounds with other oxidation states.

108. Why do some substances burn in fluorine gas even if they do not burn in oxygen gas?

109. Explain why SO_2 is used as a reducing agent but SO_3 is not.

110. Explain why the interhalogen molecule $BrCl_3$ exists but $ClBr_3$ does not.

Answers to Conceptual Connections

Phase Changes and Pressure

22.1 An increase in pressure favors the denser phase, in this case diamond.

Carbonate Solubility

22.2 (a) Since the carbonate ion is basic, adding acid to the solution drives the dissolution reaction to the right because the acid reacts with the carbonate ion. (Recall from Section 16.5 that the solubility of an ionic compound with a basic anion increases with increasing acidity.)

23

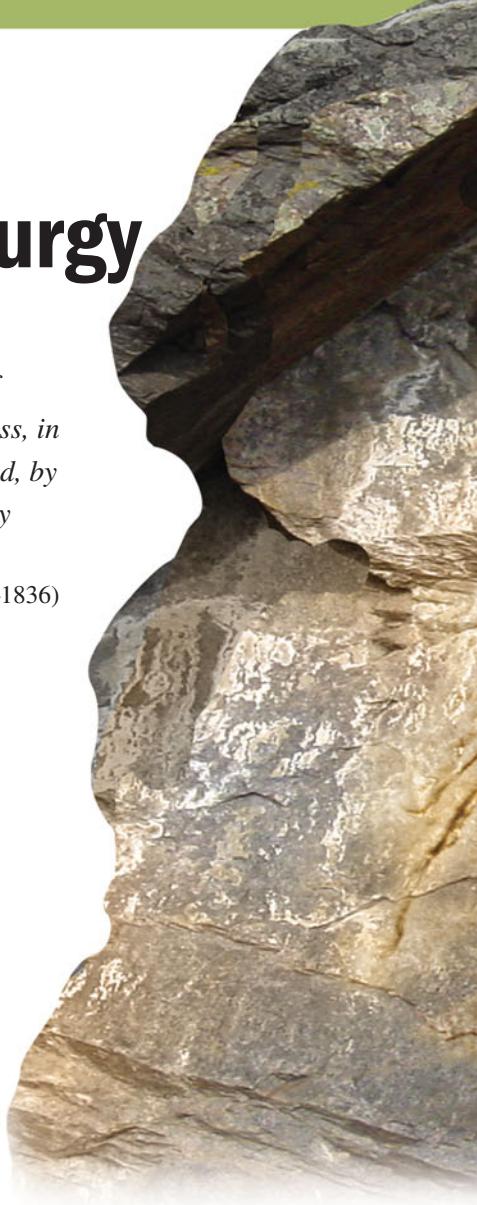
Metals and Metallurgy

The metals are not presented immediately to the hand of man . . . but they are, for the most part, buried in darkness, in the bowels of the earth, where they are so much disguised, by combination and mixture with other substances, that they often appear entirely unlike themselves.

—William Henry (1774–1836)

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IF YOU LOOK AROUND YOUR HOUSE, classroom, or neighborhood, much of what you see is made of metal or at least has some metal parts. Can you imagine life without metals? Without metals, we would have no skyscrapers, which need the rigid framework of steel beams; no automobiles, which need metal engines and bodies; and no electricity, which needs copper and aluminum wire for transmission. Metallurgy is both a very old and a very new science. We find the roots of metallurgy in the distant past, when our primitive ancestors began to search for and process metals. Of the three prehistoric ages of humankind—the Stone Age, the Bronze Age, and the Iron Age—two are named after our quest for metals. But we do not commonly find metals as elements on Earth; instead we find them in compounds, often scattered within other compounds. The mining, separating, and refining of the vast array of metals is a fairly new science. Many modern metals were not available even as recently as 200 years ago. In the middle of the nineteenth century, gold was cheaper than aluminum because aluminum was so difficult to refine, and titanium, which is important in the aerospace industry, could not even be manufactured. In this chapter, we cover the area of chemistry known as metallurgy.





Vanadium

Oil is sometimes contaminated with vanadium, which is thought to have been the metal used for oxygen transport by some ancient life forms.

23.1 Vanadium: A Problem and an Opportunity

Recently, some members of a university's chemistry and engineering departments met with representatives of an oil company to discuss how the faculty and students could cooperate on industrial research. One major topic they discussed was vanadium contamination in oil, a serious problem of continuing concern. Because vanadium is toxic, the U.S. government regulates the quantity of vanadium that can be emitted by industrial processes and oil companies have to figure out environmentally acceptable ways to remove vanadium from oil.

Vanadium is a rare element, making up only about 0.015% of Earth's crust (by mass). It is a soft white metal with high ductility and malleability, which means that it can be easily drawn into narrow wires or rolled into thin sheets. Because of the high reactivity of pure vanadium, this element occurs naturally within compounds (not in its elemental form). However, vanadium compounds are not normally found in the rocks or soils near oil fields, so why does this rare, reactive metal occur in oil? The answer lies in the biology of ancient life-forms. Most modern animals use iron in hemoglobin to transport oxygen through their bloodstreams (see Sections 1.1 and 14.1), and a few (such as lobsters) use copper for this function. It appears that some extinct animals used vanadium. Even today,



▲ Vanadium is a soft white metal.

one group of simple marine organisms, the tunicates or sea squirts, are believed to employ vanadium compounds for oxygen transport. The source of vanadium in some crude oil may be the very animals from which the oil was formed.

During refining, crude oil is heated to carry out the reactions that form the different petroleum products. If some of the vanadium-containing oil burns during heating, the vanadium forms vanadate compounds, ionic compounds with vanadium oxide polyatomic ions such as VO_4^{3-} and VO_3^- . These compounds, which have low melting points, can dissolve the protective oxide coatings on stainless steel containers, causing the steel to corrode and ruining the containers in which the oil is stored. If the vanadium compounds are not removed from the oil before storage, the customer inherits the problem. In addition, vanadium and many of its compounds are toxic, so oil companies cannot simply dump the extracted vanadium compounds into the environment.

The presence of vanadium in crude oil may, however, turn out to be profitable for the oil companies. If vanadium can be economically recovered from oil, then oil could become a major source of vanadium, a valuable metal with several important industrial uses, including the production of iron alloys and sulfuric acid.

The recovery of vanadium from oil involves metallurgy, the topic of this chapter. **Metallurgy** includes all the processes associated with mining, separating, and refining metals and the subsequent production of pure metals and mixtures of metals called *alloys* (which we define in Section 23.4). In this chapter we explore the general properties and natural distribution of metals; several different categories of metallurgical processes, including pyrometallurgy, hydrometallurgy, electrometallurgy, and powder metallurgy; the structures and alloys formed by metals; and the metallic products and applications for several selected materials.

23.2 The General Properties and Natural Distribution of Metals

Metals share several common properties. All metals are opaque (we cannot see through them), and they are good conductors of heat and electricity. They generally have high malleability (the ability to be bent or hammered into desired forms) and ductility (the ability to be drawn into wires). We can explain these properties by the bonding theories that we have already examined for metals: the electron sea model and band theory. In the electron sea model, discussed in Section 9.11, each metal atom within a metal sample donates one or more electrons to an *electron sea*, which flows within the metal. In band theory, discussed in Section 11.13, the atomic orbitals of the metal atoms are combined, forming *bands* that are delocalized over the entire crystalline solid; electrons move freely within these bands. The mobile electrons in both of these models endow metals with many of their shared properties.

Each metal, however, is also unique, and even their shared properties may vary within a range. For example, some metals, such as copper, silver, and aluminum, have much higher thermal and electrical conductivities than do other metals. Table 23.1 lists the thermal conductivity and electrical resistivity (a low resistivity corresponds to a high conductivity) of a few metals. Notice that both properties can vary by factors of 10 or more. Most metals are very strong, malleable, and ductile. But lead is a soft, weak metal, and chromium is a brittle metal that will not bend without breaking. When we think about the shared properties of metals, we must allow for a range of properties as well as some unique ones.

Over 75% of the elements in the periodic table are metals, yet metals make up only about 25% of the mass of Earth's crust (see Figure 22.2 for the composition of Earth's crust). Earth's core is thought to be composed of iron and nickel, but because the core

TABLE 23.1 Thermal Conductivity and Electrical Resistivity of Several Metals

Metal	Thermal Conductivity (W/cm · K)	Electrical Resistivity ($\mu\Omega \cdot \text{cm}$)
Ag, silver	4.29	1.59
Cu, copper	4.01	1.67
Fe, iron	0.804	9.71
V, vanadium	0.307	24.8

is so far from the surface, these metals are not accessible. The most abundant metal on Earth is aluminum, a main-group metal. Several alkali and alkaline earth metals (calcium, sodium, potassium, and magnesium) make up more than 1% of Earth's crust. Iron, which makes up about 5% of the crust, is the only transition metal that accounts for more than 0.1% of the crust. Of the first-row transition metals, titanium, chromium, iron, nickel, copper, and zinc are all plentiful enough to be important industrial materials.

Only a few metals occur naturally as elements, including nickel, copper, palladium, silver, platinum, and gold. Because of their low reactivity, these metals are often called the *noble metals*. They are usually concentrated within mountainous or volcanic regions in small, isolated veins within a rock matrix.

Most of the rest of the metals occur naturally in positive oxidation states within mineral deposits. **Minerals** (as we saw in Chapter 22) are homogeneous, naturally occurring, crystalline inorganic solids. A rock that contains a high concentration of a specific mineral is called an **ore**. Metallurgical processes separate useful minerals from other, unusable material in the ore.

The main sources for the alkali metals are chloride minerals, such as halite (sodium chloride) and sylvite (potassium chloride). Halite occurs in large deposits in sites that were once ancient oceans, or it can be precipitated by evaporating ocean water. The main source for some other metals are oxide minerals, such as hematite (Fe_2O_3), rutile (TiO_2), and cassiterite (SnO_2). The ores containing these minerals are unevenly distributed throughout the earth. For example, North America has large deposits of hematite, but no substantial deposits of cassiterite. Sulfides are the most important minerals for many metals, such as galena (PbS), cinnabar (HgS), sphalerite (ZnS), and molybdenite (MoS_2).

The main mineral source for some other metals can be complex. For example, the primary *mineral* sources for vanadium are vanadinite [$\text{Pb}_5(\text{VO}_4)_3\text{Cl}$] and carnotite [$\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3 \text{H}_2\text{O}$], which is also a main mineral source for uranium. Vanadium, as we have seen, is also found in crude oil. No specific minerals contain the metal radium. Yet radium sometimes substitutes for uranium within uranium-containing minerals. The small amount of radium that replaces uranium in carnotite is also the major source of radium. Tantalum and niobium, named after the Greek god Tantalus and his daughter Niobe, always occur together in mixed deposits of columbite [$\text{[Fe}(\text{NbO}_3)_2]$] and tantalite [$\text{[Fe}(\text{TaO}_3)_2]$]. The minerals are mined together and the elements are later separated by recrystallization (see Section 12.4).



▲ Gold is one of the few metals that can be found as an element in nature, often in veins like the one shown here.



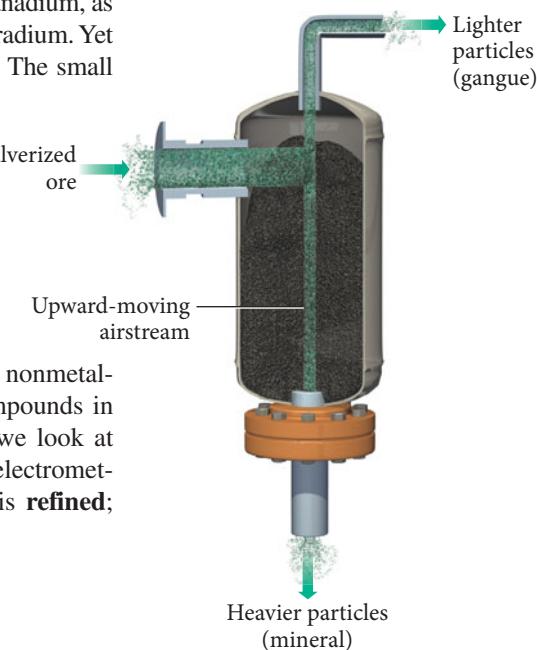
▲ Most NaCl salt is produced by trapping ocean water in shallow basins and letting the water evaporate.

23.3 Metallurgical Processes

Mined ores are first physically *separated* into their metal-containing and nonmetal-containing components. Then, the elemental metal is extracted from the compounds in which it is found, a process called **extractive metallurgy**. In this section, we look at several metallurgical processes, including pyrometallurgy, hydrometallurgy, electrometallurgy, and powder metallurgy. After separation and extraction, the metal is **refined**; refining is the process in which the crude material is purified.

Separation

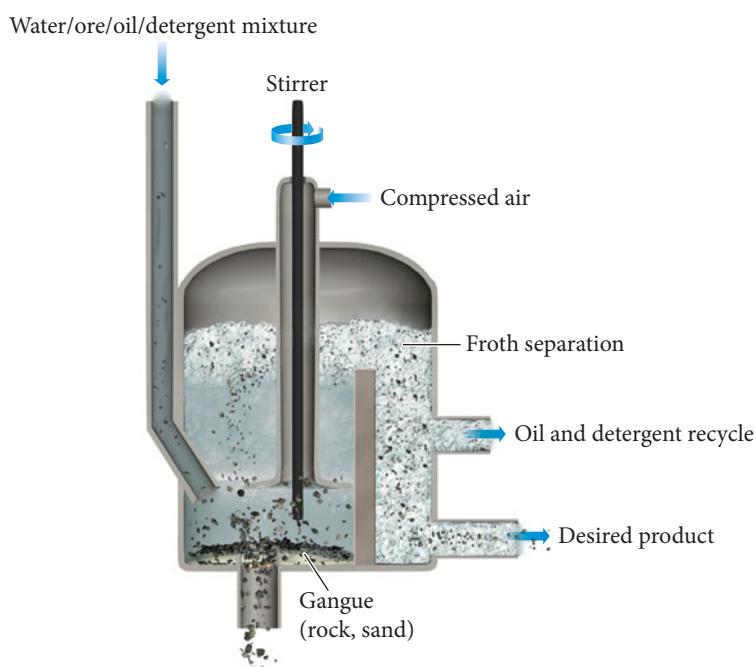
The first step in processing metal-containing ores is crushing the ore into smaller particles. The particles that contain the minerals are then separated from the undesired material, called **gangue** (pronounced “gang”), usually by physical methods. For example, in some cases, a cyclone of wind is used to lift the gangue away from the metal-containing particles, as shown in Figure 23.1 ▶. If the minerals are magnetic, magnets can separate the minerals. Electrostatic forces are also used to separate polar minerals from nonpolar gangue.



▲ FIGURE 23.1 Separation by Air
An industrial cyclone separates the crushed light particles of gangue from the heavier metal-bearing particles.

► FIGURE 23.2 Separation by Using a Solution

A wetting agent helps the minerals attach to the froth in a bubbled solution. The minerals in the froth are separated from the gangue remaining in the solution.



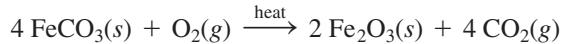
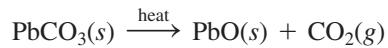
Sometimes solutions are used to separate the minerals from the gangue, as shown in Figure 23.2 ▲. A *wetting agent* (or detergent) that preferentially attaches to the mineral surfaces is added to a mixture of the mined material and water. Air is then blown through the mixture, forming bubbles and a froth. Because they are attached to the wetting agent, the minerals segregate into the froth, where they can be collected. The gangue separates into the solution.

Pyrometallurgy

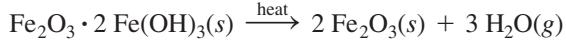
Pyrometallurgy contains the Greek stem *pyro*, meaning fire or heat.

Once the mineral is separated from the gangue, the elemental metal is extracted from the mineral. Several different techniques can achieve this separation. In **pyrometallurgy**, heat is employed to extract a metal from its mineral. Different heating conditions have different effects on the mineral.

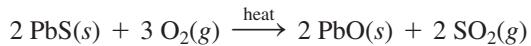
Calcination is the heating of an ore in order to decompose it and drive off a volatile product. For example, when carbonate minerals are heated, carbon dioxide is driven off, as shown in these examples:



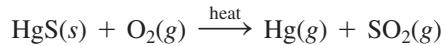
Many minerals occur in a hydrated form (that is, they contain water). Calcination can also drive off water.



Heating that causes a chemical reaction between the furnace atmosphere (the gases in the furnace) and the mineral is called **roasting**. Roasting is particularly important in processing sulfide ores. The ores are heated in the presence of oxygen, converting the sulfide into an oxide and emitting sulfur dioxide. For example, the roasting of lead(II) sulfide occurs by the reaction:

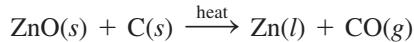


In some cases, especially with the less active metals such as mercury, roasting the sulfide produces the pure metal.

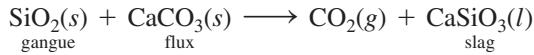


Hydrated compounds are discussed in Section 3.5.

When roasting forms a liquid product, which makes separation easier, it is called **smelting**. Consider, for example, the smelting of zinc oxide:



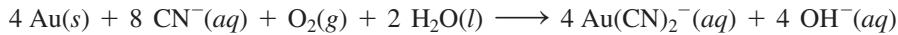
The gaseous carbon monoxide separates from the liquid zinc, allowing the metal to be readily recovered. In some cases, a flux must be added to the mixture during smelting to help separate the two materials. The **flux** is a material that will react with the gangue to form a substance with a low melting point. For example, oxides of silicon within gangue can be liquefied by reaction with calcium carbonate according to the reaction:



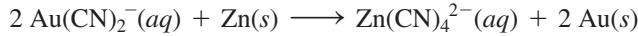
The waste liquid solution that forms from the flux and gangue is usually a silicate material called a **slag**. The liquid metal and the liquid slag have different densities and therefore separate. Holes tapped at different heights into the side of the container holding the liquid metal and slag allow the more dense liquid to flow out of the lower tap holes and the less dense liquid to flow out of the higher tap holes.

Hydrometallurgy

The use of an aqueous solution to extract metals from their ores is known as **hydrometallurgy**. One early example of hydrometallurgy is a process used to obtain gold. Gold occurs in its elemental state, but often as very small particles mixed with other substances. The gold can be separated out of the mixture by selectively dissolving it into solution, a process called **leaching**. In this process, solid gold reacts with sodium cyanide to form a soluble gold complex.

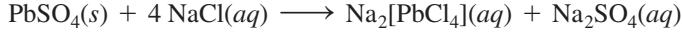


The impurities are filtered out of the solution and the gold is reduced back to elemental gold with a reactive metal such as zinc.



Leaching has been practiced for many years and often results in the contamination of streams and rivers with cyanide. New alternatives, using the thiosulfate ion ($\text{S}_2\text{O}_3^{2-}$), are being investigated to replace it.

Different acid, base, and salt solutions are sometimes used to selectively separate out metal-bearing minerals. For example, sulfuric acid is used to separate the copper and iron from the mineral chalcopyrite, CuFeS_2 , and a sodium chloride solution is used to separate the lead from the insoluble mineral anglesite, PbSO_4 .



Hydrometallurgy is often more economical than pyrometallurgy, due to the high energy costs associated with the elevated temperatures needed for calcination and roasting.

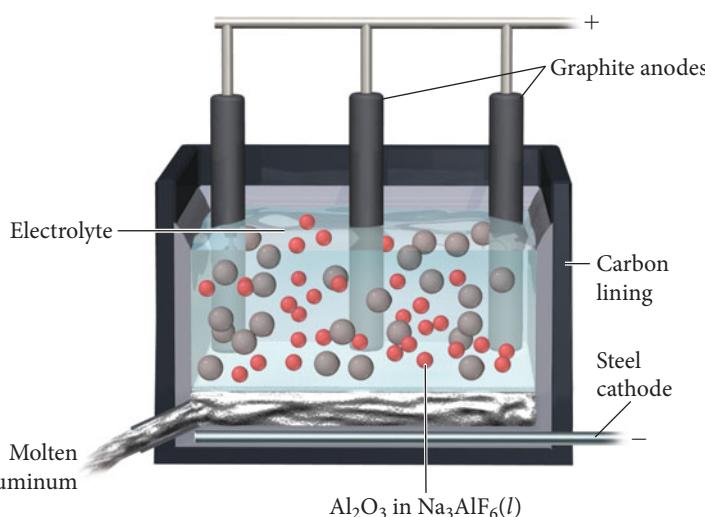
Electrometallurgy

In **electrometallurgy**, electrolysis is used to produce metals from their compounds. For example, the *Hall process* is an electrometallurgical process crucial to aluminum production. The main source of aluminum is bauxite, $\text{Al}_2\text{O}_3 \cdot n \text{ H}_2\text{O}$. A hydrometallurgical process, the *Bayer process*, separates bauxite from the iron and silicon dioxide with which it is usually found. In this process, the bauxite is heated in a concentrated aqueous NaOH solution under high pressure. The aluminum oxide dissolves, leaving the other oxides behind in solid form.

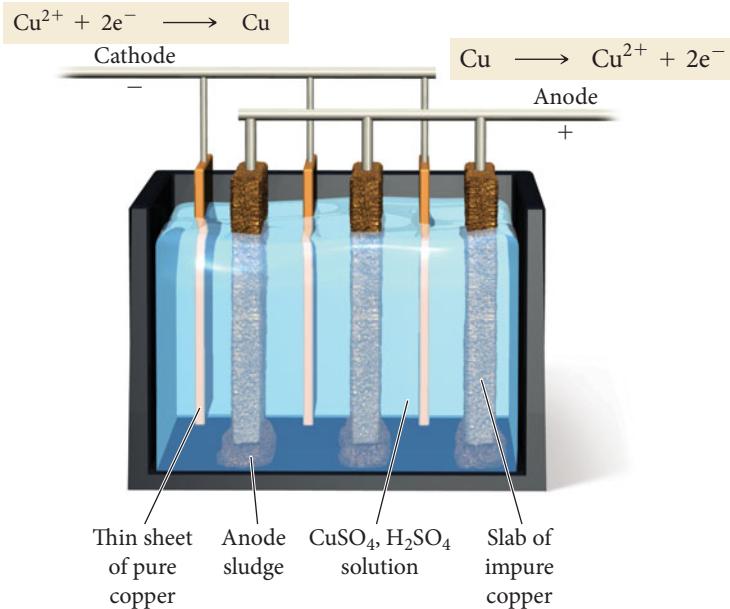
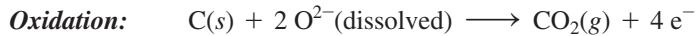
See Section 18.8 for a description of electrolysis.



► FIGURE 23.3 The Hall Process The Hall process produces aluminum metal by reducing the aluminum ions in alumina. Graphite electrodes act as reducing agents. Dissolved oxygen ions in the molten cryolite oxidize the carbon in the graphite electrodes to form carbon dioxide.



The basic aluminum solution is separated from the oxide solids, and then the aluminum oxide is precipitated out of solution by neutralizing it (recall the pH dependence of the solubility of $\text{Al}(\text{OH})_3$ from Section 16.8). Calcination of the precipitate at temperatures greater than 1000°C yields anhydrous alumina (Al_2O_3). Electrolysis is then used to reduce the aluminum out of the aluminum oxide. Because Al_2O_3 melts at such a high temperature (greater than 2000°C), however, the electrolysis is not carried out on molten Al_2O_3 . Instead, in the Hall process the Al_2O_3 is dissolved into molten cryolite (Na_3AlF_6), and graphite rods are used as electrodes to carry out the electrolysis in the liquid mixture (Figure 23.3 ▲). The carbon that composes the graphite electrodes is oxidized by the dissolved oxygen ions in the molten salt and converted to carbon dioxide. The aluminum ions dissolved in the molten salt reduce to molten aluminum, which sinks down to the bottom of the cell and is removed.



▲ FIGURE 23.4 Copper Electrolysis Cell

Copper is refined by electrolysis. The impure copper is oxidized at the anode and then reduced to form pure metal on the cathode. Many precious metals collect in the sludge at the bottom of the electrolysis cell.

Another important example of metallurgy is the refinement of copper. The most abundant copper source is the mineral chalcopyrite, CuFeS_2 . First, the chalcopyrite is converted to CuS by roasting. During this process, the iron also forms oxides and sulfides. Silica is added to form an iron silicate slag, which is then removed. The remaining copper(II) sulfide is reacted with oxygen to form sulfur dioxide gas and copper metal, but the metal is not very pure. Electrolysis is employed to refine the copper.

In the electrolysis cell used to refine copper, both the anode and the cathode are made of copper (Figure 23.4 ▲). The anode is the impure copper (that needs to be refined) and the cathode is a thin sheet of pure copper. As the current flows through the cell, the copper from the anode oxidizes and dissolves in a copper sulfate solution. It then plates out as pure copper on the cathode. The impurities in the copper anode separate from the copper during electrolysis because, even though the more active metals also

oxidize from the anode, they stay in solution and do not plate out on the cathode. The less active metals do not oxidize at all and simply fall to the bottom of the cell as the copper is dissolved from the anode. The sludge at the bottom of the electrolysis cell contains many precious metals, including gold and silver. About one-quarter of the silver produced in the United States is from the impurities recovered from the refinement of copper.

Powder Metallurgy

Powder metallurgy, first developed in the 1920s, is used to make metallic components from powdered metal. In powder metallurgy, micron-sized metal particles are pressed together under high pressures to form the desired component. The component is then heated (*sintered*). The sintering process occurs below the melting point of the powder but at a temperature high enough to cause the metal particles to fuse together, strengthening the metal and increasing its density.

Originally, iron powder from mill scrap was used in powder metallurgy. The scrap was primarily iron oxide that would fall off the steel as it was being milled. The iron oxide dust was heated in a hydrogen atmosphere to reduce the oxide to iron particles. Manufacturers called the powdered metal *iron sponge* because numerous holes form in the particles when the oxygen escapes.

In the 1960s the A. O. Smith Company in the United States introduced a new method for the development of powdered metal, called water atomization. In this method, the pure metal is melted and a small stream of the liquid is allowed to flow from the bottom of the container of molten metal. A high-pressure blast of cold water hits the stream of metal, breaking it into small droplets that quickly solidify. Powdered metal particles made in this way are more smooth and dense than the sponge powder particles from oxide scrap. In addition to powdered iron metal, many copper, bronze, carbide, and brass parts are made through powder metallurgical processes.

Powder metallurgy offers several advantages over traditional casting or milling of metal. For example, waste is almost eliminated because the part can be pressed directly into the desired shape. Intricate teeth on gears and multiple holes can be designed into the press and therefore do not have to be machined after production. Making cast metal objects from metals with high melting points, such as molybdenum and tungsten, can be difficult because of the high temperatures necessary to melt the metal. Using the powder avoids the need for high temperatures.



▲ These metal products were all made by powder metallurgy.

23.4 Metal Structures and Alloys

We can describe the structures of metals as the closest packing of spheres, first discussed in Section 11.11. Elemental metals generally crystallize in one of the basic types of crystal lattices, including face-centered cubic, body-centered cubic, and hexagonal closest packed. The crystal structure of a metal may change, however, as a function of temperature and pressure. Table 23.2 lists the crystal structures for the 3d transition metals at atmospheric pressure.

TABLE 23.2 The Crystal Structures of the 3d Elements

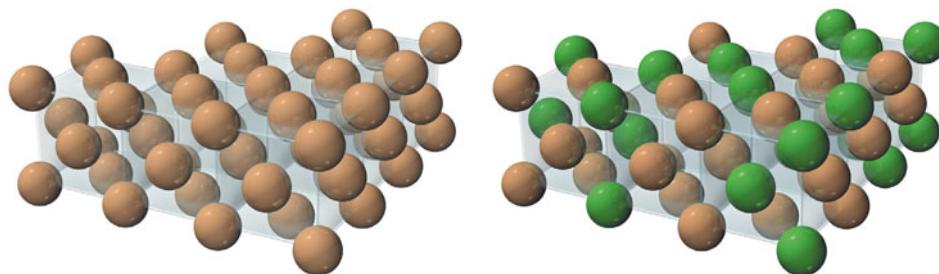
Metal	Natural Crystal Structure at Room Temperature	Other Crystal Structures at Different Temperatures and Pressures
Sc	Hexagonal closest packed	Face-centered cubic, body-centered cubic
Ti	Hexagonal closest packed	Body-centered cubic above 882 °C
V	Body-centered cubic	
Cr	Body-centered cubic	Hexagonal closest packed
Mn	Alpha complex body-centered cubic form	Beta simple cubic form above 727 °C Face-centered cubic above 1095 °C Body-centered cubic above 1133 °C
Fe	Body-centered cubic	Face-centered cubic above 909 °C Body-centered cubic above 1403 °C
Co	Hexagonal closest packed	Face-centered cubic above 420 °C
Ni	Face-centered cubic	
Cu	Face-centered cubic	
Zn	Hexagonal closest packed	

Alloys

An **alloy** is a metallic material that contains more than one element. Some alloys are simply solid solutions, while others are specific compounds with definite ratios of the component elements. Alloys have metallic properties, but they can consist of either two or more metals or a metal and a nonmetal. We broadly classify alloys as substitutional or interstitial. In a **substitutional alloy**, one metal atom substitutes for another in the crystal structure. The crystal structure may either stay the same upon the substitution, or it may change to accommodate the differences between the atoms. In an **interstitial alloy**, small, usually nonmetallic atoms fit in between the metallic atoms of a crystal. The alloy maintains its metallic properties with these interstitial atoms in the structure.

Substitutional Alloys

For two metals to form a substitutional alloy, the radii of the two metal atoms must be similar, usually within 15% of each other. For example, the atomic radii of copper and nickel are both 135 pm, and both of the elements form the face-centered cubic structure. Therefore, either metal can easily replace the other in the metal crystal structure.

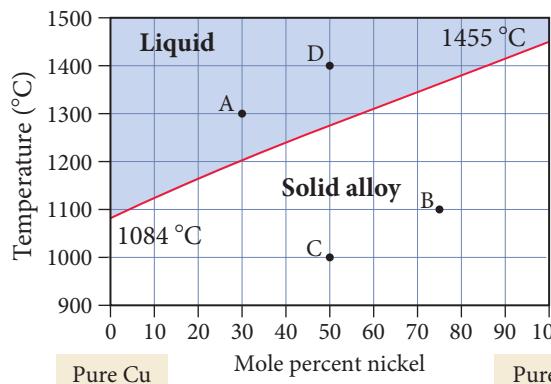


▲ Copper crystallizes in the face-centered structure shown here.

▲ In a nickel and copper alloy, nickel atoms substitute for some of the copper atoms.

Figure 23.5 ▼ is a phase diagram for a copper and nickel alloy. This phase diagram, called a *binary* phase diagram, is different from the diagrams that we discussed in Section 11.8, which show the phases of a pure substance at different pressures and temperatures. This diagram shows the different phases for a mixture at different *compositions* and temperatures. The *x*-axis indicates the composition (in this case, the mole percent of nickel in the alloy, with the left side representing pure copper and the right side representing pure nickel). The *y*-axis indicates the temperature.

Pure copper melts at 1084 °C, as indicated by the change from solid to liquid at 0% nickel. Pure nickel melts at 1455 °C, as indicated by the change from solid to liquid at 100% nickel. The area on the diagram above the line connecting the melting points of copper and nickel represents a liquid solution of the two metals. The area below that line represents a solid solution of the two metals. Any ratios of copper and nickel can form the face-centered cubic structure.

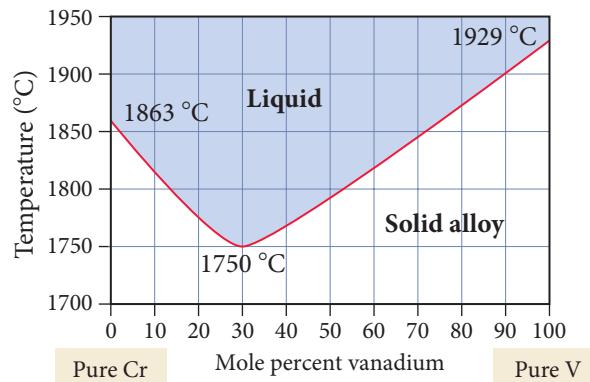


► FIGURE 23.5 Cu-Ni Phase Diagram

Because copper and nickel have similar crystal structures and similar size, they can form a solid solution. A solution forms at all compositions from pure copper to pure nickel.

GUIDELINES FOR...	EXAMPLE 23.1	EXAMPLE 23.2
Interpreting a Binary Phase Diagram	Determining Alloy Compositions from a Phase Diagram Determine the composition and phase present at point A on Figure 23.5.	Determining Alloy Compositions from a Phase Diagram Determine the composition and phase present at point B on Figure 23.5.
Locate the temperature and composition of the alloy on the binary phase diagram.	Point A represents 30 mol % Ni at 1300 °C.	Point B represents 75 mol % Ni at 1100 °C.
Identify the phase.	The point is above the melting point line, so the phase is liquid.	The point is below the melting point line, so the phase is solid.
Identify the amount of copper and nickel in the phase.	This liquid phase is made up of 30 mol % Ni, so it is 70 mol % Cu.	This solid phase is made up of 75 mol % Ni, so it is 25 mol % Cu.
	FOR PRACTICE 23.1 Determine the composition and phase present at point C on Figure 23.5.	FOR PRACTICE 23.2 Determine the composition and phase present at point D on Figure 23.5.

The phase diagrams of some alloys are more complex. Consider the phase diagram for Cr and V, shown in Figure 23.6 ▶. Both Cr and V form the body-centered cubic crystal, and the atoms are close in size. Yet this phase diagram reveals an important difference between this alloy and the Cu and Ni alloy: the melting temperature does not vary in a uniform way from the lower melting point of Cr to the higher melting point of V. Instead we see that the alloys with intermediate compositions melt at lower temperatures than either pure metal. The lowest melting point is 1750 °C at a composition of 30 mol % vanadium. Solid compositions that melt at temperatures lower than either of the pure metals, as well as compositions that melt at temperatures higher than either of the two metals, are common in these types of alloys.

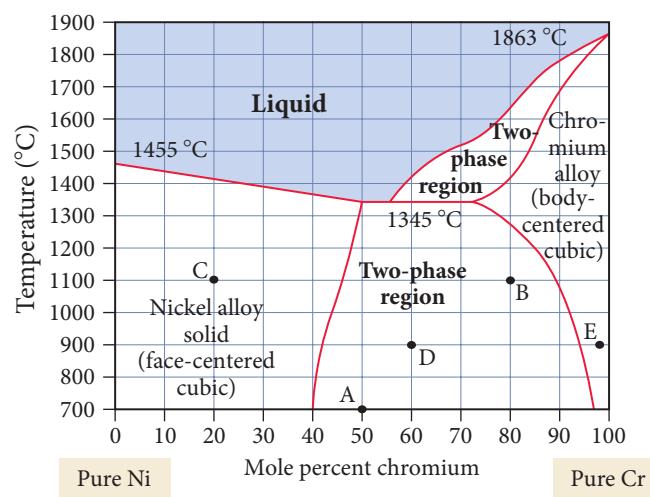


Alloys with Limited Solubility

Some alloys are composed of metals that have different crystal structures. For example, nickel crystallizes in the face-centered cubic structure and chromium in the body-centered cubic structure. Because of their different structures, these two metals do not form a miscible solid solution at all compositions. At some intermediate composition, the structure has to change from that of one of the metals to that of the other. Figure 23.7 ▼ shows the nickel and chromium phase diagram from 700 °C to 1900 °C. Notice that the diagram has two different solid phases: face-centered cubic and body-centered cubic. From pure nickel (0 mol % chromium) to about 40–50 mol % chromium, the structure is face-centered cubic. In this structure, Cr atoms substitute for Ni atoms in the face-centered cubic structure of nickel. However, beyond a certain percentage of chromium (which depends on temperature), that structure is no longer stable. At 700 °C about 40 mol % Cr can fit in the crystal and at 1200 °C about 50 mol % Cr can fit in. Adding additional Cr beyond these points results in a different phase.

► **FIGURE 23.7 Cr-Ni Phase Diagram** Because chromium and nickel form solids with crystal structures that differ from each other, an alloy mixture of the two metals does not form a solid solution at all compositions. A two-phase region exists at compositions between the possible compositions of the two different structures. In the two-phase region, both crystal structures coexist in equilibrium.

▲ **FIGURE 23.6 Cr-V Phase Diagram** In a binary phase diagram of two metals that form a solid solution, an intermediate composition can have either the highest or lowest melting point. In the chromium and vanadium phase diagram an intermediate composition has the lowest melting point.



At the other end of the diagram (nearly pure chromium) and at 700 °C, only a small amount of nickel can be substituted into the body-centered cubic structure of the chromium. As the temperature rises to 1300 °C, however, about 20 mol % nickel can be accommodated into the chromium structure. The region in between the two phases is called a **two-phase region**. At these compositions, the two phases (nickel-rich face-centered cubic and chromium-rich body-centered cubic) exist together. The amount of each phase depends upon the composition of the alloy.

We can determine the composition and relative amounts of the two different phases that coexist in a two-phase region from a phase diagram. Point A on Figure 23.7 in the Cr–Ni phase diagram represents 50% composition at 700 °C, and both phases are present. Some of the Cr atoms have substituted into the nickel-rich face-centered cubic structure, but there is too much Cr to all fit into the crystal. The leftover Cr atoms form the chromium-rich body-centered cubic structure with a small number of Ni atoms in the crystal.

The two crystals that exist at point A are (1) the nickel-rich face-centered cubic structure with 40 mol % Cr; and (2) the chromium-rich body-centered cubic structure with 5 mol % Ni. The 50% composition on the phase diagram has just slightly more Cr atoms than can fit into the nickel structure. Thus most of the crystals in the two-phase region are the nickel-rich face-centered cubic structure with only a small amount of the chromium-rich body-centered cubic structure, as determined by a method called the *lever rule*. The **lever rule** tells us that in a two-phase region, whichever phase is closest to the composition of the alloy is the more abundant phase. In this example, the 50 mol % Cr composition on the phase diagram is closer to the 40 mol % Cr composition of the nickel-rich face-centered cubic phase than the 95 mol % Cr composition of the chromium-body-centered cubic phase, so more face-centered cubic crystals are present than body-centered cubic crystals.

GUIDELINES FOR...

Interpreting the Phases and Compositions in a Binary Phase Diagram as Described by the Lever Rule

Locate the temperature and composition of the alloy on the binary phase diagram.

Identify the phases(s).

Identify the amount of Ni and Cr in the phases.

Identify the relative amounts of the phases.

EXAMPLE 23.3

Alloy Compositions in a Solid Solution with Limited Solubility

Determine the composition, relative amounts, and phases present at point B on Figure 23.7.

Point B represents 80 mol % Cr at 1100 °C.

Point B is located in the two-phase region, consisting of the nickel-rich face-centered cubic structure and the chromium-rich body-centered cubic structure.

The nickel-rich face-centered cubic structure has 45 mol % Cr and 55 mol % Ni, and the chromium rich body-centered cubic structure has 90 mol % Cr and 10 mol % Ni.

At a composition of 80 mol % Cr, the composition is closer to the Cr-rich body-centered cubic phase, so there is more of this phase than there is of the Ni-rich face-centered cubic phase.

FOR PRACTICE 23.3

Determine the composition, relative amounts, and phases present at point D on Figure 23.7.

EXAMPLE 23.4

Alloy Compositions in a Solid Solution with Limited Solubility

Determine the composition, relative amounts, and phases present at point C on Figure 23.7.

Point C represents 20 mol % Cr at 1100 °C.

Point C is located in the one-phase region of the nickel-rich face-centered cubic structure.

The nickel-rich face-centered cubic structure at this point has 20 mol % Cr and 80 mol % Ni.

There is only one phase. It is 100 mol % of the Ni face-centered cubic phase.

FOR PRACTICE 23.4

Determine the composition, relative amounts, and phases present at point E on Figure 23.7.

Interstitial Alloys

Recall that in contrast to substitutional alloys, where one metal atom substitutes for another in the lattice, interstitial alloys contain atoms of one kind that fit into the holes, or interstitial sites, of the crystal structure of the other. In metals with the interstitial elements hydrogen, boron, nitrogen, or carbon, the alloy that results retains its metallic properties.

Closest-packed crystal structures have two different types of holes between the atoms in the crystalline lattice. An **octahedral hole**, shown in Figure 23.8 ▶, exists in the middle of six atoms on two adjacent closest-packed sheets of metal atoms. The hole is located directly above the center of three closest-packed metal atoms in one sheet and below the three metal atoms in the adjacent sheet. This configuration of metal atoms is identical to a regular octahedral configuration that consists of four atoms in a square plane with one atom above and one atom below the square. We can calculate the size of an octahedral hole by determining the size of a hole on a square of four atoms in a plane (Figure 23.9 ▷). Any of the four corners of the square is the 90° angle of a right triangle formed from the adjacent two sides and the diagonal line that runs across the center of the square. According to the Pythagorean theorem, the length of the diagonal line (c) is related to the length of the sides (a and b) as follows:

$$c^2 = a^2 + b^2 \quad [23.1]$$

If we let r_m equal the metal atom radius, the lengths of the sides are $2r_m$. We can then substitute $2r_m$ for both a and b .

$$\begin{aligned} c^2 &= (2r_m)^2 + (2r_m)^2 \\ c^2 &= 8r_m^2 \\ c &= 2.828r_m \end{aligned} \quad [23.2]$$

We can see from Figure 23.9 that the length of the diagonal (c) is twice the radius of the atoms plus twice the radius of the hole.

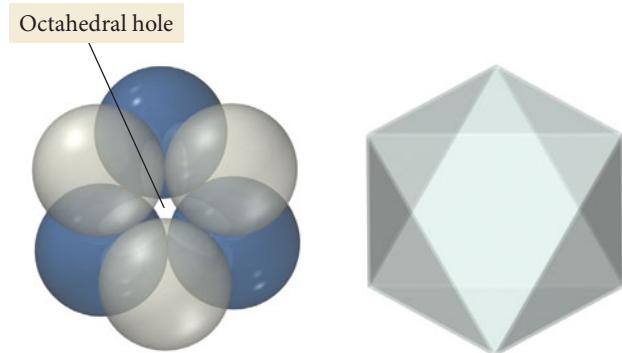
$$c = 2r_m + 2r_{\text{hole}} \quad [23.3]$$

Combining Equations 23.2 and 23.3, we get the important result:

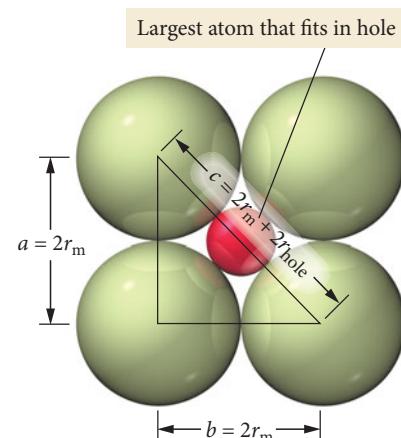
$$\begin{aligned} 2.828r_m &= 2r_m + 2r_{\text{hole}} \\ 0.828r_m &= 2r_{\text{hole}} \\ r_{\text{hole}} &= 0.414r_m \end{aligned} \quad [23.4]$$

The octahedral hole, surrounded by six metal atoms, has a radius that is 41.4% of the metal atom radius. By contrast, the hole in the center of a cube in the *simple cubic* structure has a radius that is 73% of the metal atom radius. The *number* of octahedral holes in a closest-packed structure is equal to the number of metal atoms.

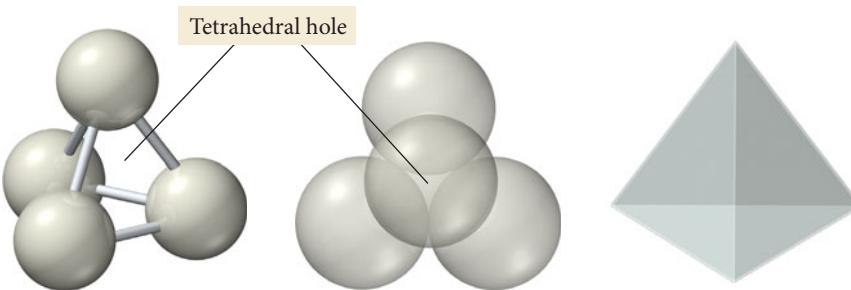
The second type of interstitial hole in a closest-packed structure is a **tetrahedral hole** (first introduced in Section 11.12), which forms directly above the center point of three closest-packed metal atoms in one plane and below a fourth metal atom located directly above the center point in the adjacent plane (Figure 23.10 ▼). The number of tetrahedral holes in a closest-packed structure is equal to *twice* the number of metal atoms.



▲ FIGURE 23.8 Octahedral Holes in Closest-Packed Crystals Octahedral holes are found in a closest-packed structure. The octahedral hole is surrounded by six of the atoms in the closest-packed structure.



▲ FIGURE 23.9 A Different View of an Octahedral Hole An octahedral hole can be viewed as the area in the middle of a square plane of atoms, with one additional atom above the hole and one additional atom below the hole, accounting for the six close atoms. The diagonal of the square is equal to the radius of the two corner atoms plus the diameter of the hole. The length of the diagonal is related to the lengths of the sides of the square by the Pythagorean theorem.



◀ FIGURE 23.10 A Tetrahedral Hole in a Closest-Packed Crystal Tetrahedral holes are found in a closest-packed structure. The tetrahedral hole is surrounded by four of the atoms in the closest-packed structure.

TABLE 23.3 Formulas of Several Interstitial Alloys

Compound	Type of Interstitial Hole Occupied	Fraction of Holes Occupied	Formula
Titanium carbide	Octahedral	All	TiC
Molybdenum nitride	Octahedral	One-half	Mo ₂ N
Tungsten nitride	Octahedral	One-half	W ₂ N
Manganese nitride	Octahedral	One-quarter	Mn ₄ N
Palladium hydride	Tetrahedral	One-quarter	Pd ₂ H
Titanium hydride	Tetrahedral	All	TiH ₂

Because this hole is surrounded by only four atoms, the hole is smaller than the octahedral interstitial hole. We can apply geometric considerations similar to those used previously for the octahedral hole to determine that the tetrahedral hole has a radius that is 23% of the metal atom radius.

Interstitial alloys form when small nonmetallic atoms fit within the octahedral or tetrahedral holes of the crystalline lattice of the metal. The formulas for these alloys depend both on the type of hole occupied by the nonmetallic atom and on the fraction of holes occupied. For example, titanium and carbon form an alloy with a closest-packed structure for titanium in which all of the octahedral holes are filled with carbon atoms. Since the number of octahedral holes in a closest-packed structure is equal to the number of atoms in the structure, the ratio of carbon atoms to titanium atoms must be 1:1 and the corresponding formula is TiC. In the compound formed between molybdenum and nitrogen, by contrast, only one-half of the octahedral holes in the closest-packed structure of Mo are filled with N. Therefore, the formula for this compound is Mo₂N. Table 23.3 lists the formulas and relative number of holes filled for several different interstitial alloys.

Conceptual Connection 23.1 Interstitial Alloys

An interstitial alloy contains a nonmetal (X) that occupies one-eighth of the tetrahedral holes of the closest-packed structure of the metal (M). What is its formula?

23.5 Sources, Properties, and Products of Some of the 3d Transition Metals

In this section we examine major sources, interesting properties, and important products of several of the 3d transition metals, specifically, titanium, chromium, manganese, cobalt, copper, nickel, and zinc. We also survey the different metallurgical methods used to separate and refine them. The variety of uses for these metals reflects their varied properties.

Titanium

Titanium is the ninth most abundant element in Earth's crust, and the fourth most abundant metal. Titanium was discovered in 1791, but the pure metal was not isolated until 1910. The principal minerals of titanium are rutile (TiO_2) and ilmenite (FeTiO_3). Another source of titanium is coal ash, the residue from burned coal. Black shiny ilmenite is found in granite deposits along the North Atlantic coast, often within silica sand. The mineral is magnetic due to the presence of Fe^{2+} ions, so it can be separated with a magnet from the nonmagnetic silica. The separated mineral is heated in the presence of carbon under an atmosphere of chlorine gas, forming TiCl_4 , a volatile gas that can be isolated.



The TiCl_4 gas is reacted with hot magnesium metal turnings (shaved pieces of magnesium), forming elemental titanium—a solid sponge material.



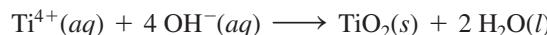
Titanium is very reactive, readily oxidizing in the presence of oxygen and even nitrogen. Consequently, the elemental titanium is **arc-melted**—a method in which the solid metal is melted with an arc (an electrical discharge) from a high-voltage electric source in a controlled atmosphere to prevent oxidation—and then collected in a water-cooled copper pot. Because of titanium's high reactivity, any further processing must be done in a protective atmosphere of an inert gas, such as Ar, to prevent oxidation.

Despite its reactivity, solid titanium is highly resistant to corrosion in air, acid, and seawater because it quickly reacts with oxygen to form an oxide that coats the surface, preventing further oxidation of the underlying metal. Consequently, titanium is often used in the production of ship components such as propeller shafts and rigging. Titanium is also very strong and light; it is stronger than steel and less than half as dense. It is denser than aluminum but twice as strong. For these reasons, titanium is used in the airline industry for the production of jet engine parts. When titanium is alloyed with 5% aluminum and trace amounts of Fe, Cr, and Mo, the resulting metal retains its strength under higher temperature.

The most common use of titanium, however, is as titanium(IV) oxide (TiO_2), which forms a clear crystal but a brilliant white powder. Most white paints include TiO_2 , which is far less toxic than PbO_2 , which was used in older paints. Titanium(IV) oxide is made by reacting sulfuric acid with ilmenite, which dissolves the titanium into solution.



Neutralizing the solution with strong base forms titanium(IV) oxide.



Calcination of the oxide dries it to form TiO_2 rutile crystals. Large rutile crystals are sometimes used as gems because they resemble diamonds.

Chromium

The name *chromium* comes from the Greek root *chroma*, which means color. The different compounds of chromium are brightly colored (Table 23.4; Figure 23.11 ▶). The main ore source of chromium is chromite, FeCr_2O_4 . No appreciable sources of chromium ores exist in the United States. Chromium metal is produced by reducing chromium ore with aluminum.



Metallic chromium is a white, hard, lustrous, and brittle metal. The metal readily dissolves in acids such as hydrochloric acid and sulfuric acid, but it does not dissolve in concentrated nitric acid (because nitric acid forms an oxide on the surface of the chromium that resists further reaction). The primary use of chromium is in the production of steel alloys called *stainless steels*. Reducing chromite with carbon produces ferrochrome, an alloy that is added to steel.

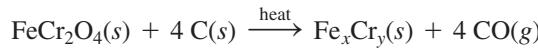


TABLE 23.4 The Colors of Various Chromium Compounds

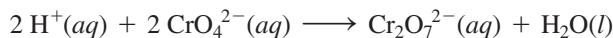
Compound	Color
Chromates (CrO_4^{2-})	Yellow
Chromium(II) iodide	Red-brown
Chromium(III) iodide	Green-black
Chromium(II) chloride	White
Chromium(III) chloride	Violet
Dichromates ($\text{Cr}_2\text{O}_7^{2-}$)	Orange
Chromium(III) oxide	Deep green
Chrome alum	Purple
Chromium(VI) oxychloride (CrO_2Cl_2)	Dark red
Chromium(II) acetate	Red

▼ FIGURE 23.11 Chromium Compounds
Chromium compounds tend to be brightly colored.

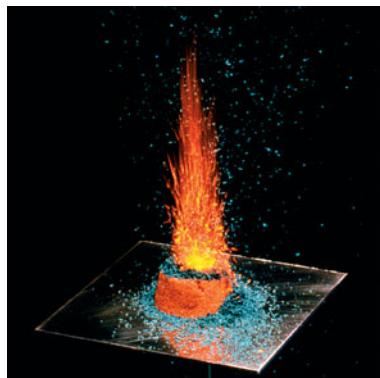
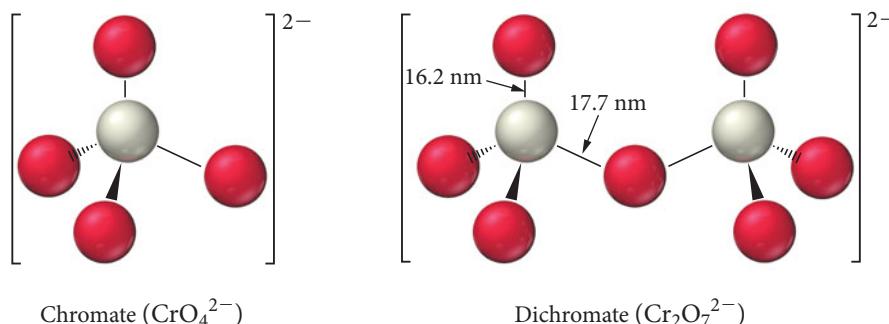


The chromium reacts with any oxygen in the steel to protect the iron from rusting. Chromium compounds were also used extensively in metal coatings such as paints, because the chromium helps to rustproof the underlying metal, and in wood preservatives, because these compounds kill many of the bacteria and molds that rot wood. Chromium compounds are finding less use today, however, because of their toxicity and potential carcinogenicity. Nonetheless, because of their great corrosion resistance, chromate coatings are still used on large outdoor steel structures such as bridges, and chromate paints are used to mark streets (on the pavement) and on street signs.

Because chromium has the electron configuration $[Ar] 4s^1 3d^5$, with six orbitals available for bonding, it can have oxidation states from +1 to +6. Low-oxidation-state chromium exists primarily as the *cation* in salt compounds such as $Cr(NO_3)_3$ and $CrCl_3$. High-oxidation-state chromium occurs within the polyatomic *anions* of salts. The most important compounds with chromium in the +6 oxidation state are the chromates and dichromates. In an acidic solution (below pH 6), the orange-red dichromate ion $Cr_2O_7^{2-}$ is more stable. In more basic solutions (above pH 6), the yellow chromate ion CrO_4^{2-} dominates. Adding acid to a solution containing the chromate ion produces the dichromate ion.

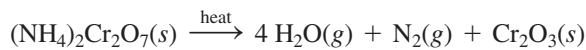


The chromate ion has a tetrahedral arrangement of oxygen atoms around a chromium atom. The dichromate ion has one bridging oxygen between the two tetrahedrons surrounding the chromium ions.



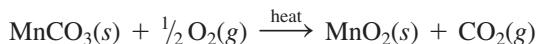
▲ Ammonium dichromate does not require additional oxygen to burn.

The high-oxidation-state chromates and dichromates are very strong oxidizing agents (that is, they are easily reduced). Consequently, they are used as coatings on other metal surfaces to prevent oxidation. The chromates react with the atoms on the surface of the other metals, forming a strongly bonded gel-like film. The film is non-metallic and bonds very effectively with paint and resins that are applied over the film. We can see evidence of the oxidizing power of dichromate in the ability of ammonium dichromate to sustain combustion without any additional oxygen. Once ignited, ammonium dichromate burns with visible flames, giving off a smoke of green chromium oxide dust.



Manganese

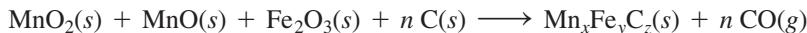
Manganese, with the electron configuration $[Ar] 4s^2 3d^5$, exhibits the widest range of oxidation states, from +1 to +7. The most common natural sources of manganese are pyrolusite (MnO_2), hausmannite (Mn_3O_4), and rhodochrosite ($MnCO_3$) minerals. Calcination of rhodochrosite produces manganese (IV) oxide.



The manganese (IV) oxide or pyrolusite minerals can react with active metals such as Al or Na to produce the elemental metal.

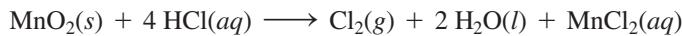


Pyrolusite, however, is often found as an impure mineral, containing mixtures of MnO and Fe₂O₃. Heating the mineral in the presence of carbon can reduce the mineral, forming an alloy of manganese and iron called ferromanganese.

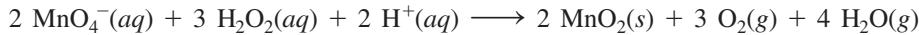


Ferromanganese generally contains about 5–6% carbon and is used as an alloying material in steel production. Manganese is added to steel alloys to change the physical properties of the steel. For example, manganese makes the steel easier to deform at high temperatures. Adding manganese to steel helps the rolling and forging steps of steel production. Steel alloys containing about 12% manganese are used in military armor and industrial applications such as bulldozer blades. Manganese also strengthens copper, aluminum, and magnesium alloys.

Manganese is a reactive metal that dissolves in most acids. When heated in the presence of air, it forms the various manganese oxides, including MnO, Mn₃O₄, and MnO₂. When heated in pure oxygen, the high-oxidation-state oxide Mn₂O₇ also forms. At high oxidation states, the manganese compounds are good oxidizing agents. Dissolving MnO₂ into a solution of hydrochloric acid oxidizes the chloride and produces chlorine gas.



The permanganate ion (MnO₄⁻) has an oxidation state of +7 for Mn and is also an important oxidizing agent. The permanganate ion can even oxidize hydrogen peroxide, which is itself used as an oxidizing agent.



The compound MnO₂ is a glass additive. By itself, MnO₂ is either a brown or black crystal, depending on the degree of hydration. Yet, when added to a silica glass, it imparts a pink color to the glass. The pink color is useful because it counteracts the green color often seen in glass, which is due to small concentrations of impure iron oxides. In other words, MnO₂ is added to glass to “decolorize” it. Old manganese-containing glass that has been exposed to UV light for over 100 years develops a slight purple tint. This purple color is due to the oxidation of MnO₂ to Mn(VII) oxides.

Cobalt

Cobalt ore is often found within the ores of other metals, such as iron, nickel, lead, and silver. Cobalt's most common ores are sulfide minerals, such as cobaltite (CoAsS), which is collected as a by-product in the extraction processes of the other metal ores. No large deposits of cobalt ores occur in the United States, but surveys indicated that there are cobalt-rich deposits in the Pacific Ocean near the Hawaiian Islands.

Cobalt, like iron and nickel, is **ferromagnetic** and is important in the production of magnets. Like in the paramagnetic materials described in Section 8.7, the atoms in ferromagnetic materials contain unpaired electrons. In ferromagnetic materials, however, these electrons can all align with their spins oriented in the same direction, creating a permanent magnetic field.

Magnets are increasingly important in industrial and military applications. In the United States, concerns have arisen over the lack of domestic sources of cobalt for these applications. New and stronger magnetic materials that do not require cobalt have been developed, but these require neodymium, which is found mostly in China.

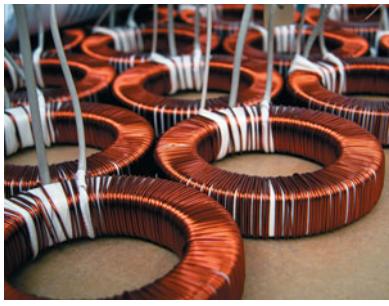
Cobalt is also an important additive for high-strength steels. Carbaloy, a mixture composed primarily of cobalt metal with grains of tungsten carbide, is a very tough material. The strength of the cobalt and hardness of the carbides make this a good material for industrial cutting and abrasion. In addition, cobalt forms many compounds with brilliant blue colors and is used in making pigments and inks. Cobalt compounds are also essential for health, because cobalt is the metal in vitamin B₁₂, which prevents anemia.

Copper

Copper, which can be found in its elemental form, was one of the first elements to be isolated and used by humans—copper products have been known for over 10,000 years. Ancient civilizations used copper to form tools. The earliest known artifacts produced



▲ Copper wiring is used to conduct electricity in wires.



▲ Copper is used in a variety of applications.

by the smelting of copper are at a site in Tepe Yahya, Iran, dating from about 3800 b.c. The discovery of **bronze**, a copper and tin alloy, improved tool making because copper's bronze alloys are stronger, and they resist wear and corrosion better than pure copper.

The most important copper ores are chalcopyrite (CuFeS_2) and malachite [$\text{Cu}_2(\text{OH})_2\text{CO}_3$]. Copper ores often occur near deposits of elemental copper, providing early humans with an easy way to locate copper ores. The electrometallurgical production of pure copper from chalcopyrite is described in Section 23.3.

The high natural abundance and generally high concentration of copper and copper ores makes copper an economical choice for many industrial applications. Today over 40% of copper products are made from recycled copper. The ease and low cost of recycling copper has allowed copper to remain an important industrial metal.

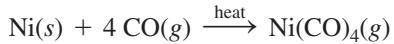
The high conductivity of copper is second only to that of silver, making copper the most important metal for electrical wires. Along with iron in steel, copper is now among the most widely-used metals; it is used in electrical motors and devices, the electrical wiring that snakes though the walls of houses, and the electrical transmission network linking power sources to homes and industries all over the world. Because of its high heat conductivity, copper is also used as a heat exchange material—for example, in car radiators. In addition, copper is used to make pipes for water distribution. Copper pipes can be readily connected to each other with watertight seals by soldering. Copper displaced lead for use as water pipes because of the toxicity of lead. Today, because of its lower price and lighter weight, plastic is used for many water pipes.

Copper has a distinctive reddish color that can be polished to a beautiful metallic luster; it has been used in architecture, as a decorative metal in jewelry, and as a material for sculpture. Copper composes the decorative sheathings on many domes and roof-top art works. When exposed to the atmosphere and rain, copper can oxidize, forming a number of different compounds, such as malachite and brochanite ($\text{Cu}_4\text{SO}_4(\text{OH})_6$), that have beautiful blue or green colors. Copper roofing shingles can be purchased as polished copper sheets or as sheets that have already been oxidized and exhibit a beautiful weathered *patina* (a coating that comes with age and use). Chemical compounds speed up the aging process and produce the desired patina, which takes 20 or more years to develop naturally.

Even though copper has many useful properties, it is not a very strong metal; therefore, alloys of copper with improved strength have been developed. Bronze was one of the first alloys ever produced. This alloy of copper and tin has been used for thousands of years because it could be made even in the low heat of a Stone Age campfire. **Brass**, another widely used alloy, contains copper and zinc. Many brass and bronze alloys also contain other metals to achieve certain physical properties. Some of the most important applications of bronze and brass are for plumbing fixtures, bearings, and art decorations. In addition, the tendency of brass and bronze alloys (unlike those of iron) not to spark when struck make them useful in applications where sparks could be dangerous.

Nickel

Most of the world's nickel comes from deposits in Ontario, Canada. These deposits are believed to have formed from a meteorite impact (most meteorites have high nickel content). The nickel occurs as a sulfide compound mixed with copper and iron sulfides. To produce nickel, the sulfides are roasted in air to form metal oxides, and then they are reduced to the elemental metals with carbon. The metal mixture is heated in the presence of carbon monoxide, forming nickel carbonyl, which has a boiling point of 43 °C and can be collected as a gas.



When the nickel carbonyl is heated past 200 °C, it decomposes back to nickel metal and carbon monoxide. This method of refining nickel is called the *Mond process*.

Nickel metal is fairly unreactive and resistant to corrosion, characteristics that it shares with platinum and palladium. Consequently, nickel is used as an alloying metal in the production of stainless steels. Many nickel alloys are used for applications where corrosion resistance is important. For example, the alloy Monel contains 72% Ni,

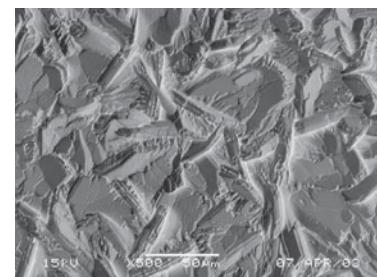
25% Cu, and 3% Fe and is resistant to reaction with most chemicals. Monel does not react even with fluorine gas at room temperature. Nickel–steel alloys are used for armor plates, and elemental nickel is often plated onto other metals as a protective coating.

Zinc

Elemental zinc was officially discovered in Europe in 1746 when calamine (zinc silicate) was reduced with charcoal to produce the metal. However, zinc had been used for many hundreds of years before this discovery because zinc ores and copper ores were used to form copper–zinc brass alloys. The main sources of zinc are ores composed of sphalerite (ZnS), smithsonite (ZnCO_3), and an oxide mixture of zinc, iron, and manganese called franklinite. These ores are roasted to form the oxides of the metals and then reduced with carbon to produce the elemental metals. Zinc combines with many different metals to form useful alloys. As we have seen, the combination of zinc and copper produces the brass family of alloys. The combination of zinc and nickel with copper produces alloys with a silver color called *German* or *silver brass*. Zinc is also used in solder alloys with low melting points.

Galvanizing a steel object (such as a nail) involves dipping the object into a molten bath of zinc. The zinc, which is more reactive than the iron in steel, preferentially oxidizes, forming a tough protective coating. Zinc compounds are also used to coat steel before applying other coatings. The zinc compounds, such as zinc phosphate, adhere strongly to the steel surface, forming rough crystals onto which other coatings, such as paint, adhere very well. If a painted steel surface is scratched, the underlying exposed metal is susceptible to rust, but the added zinc ions prevent this by migrating toward the defect and forming a protective zinc oxide coating.

Zinc and zinc compounds have generally been considered safe. Zinc additives in coatings have replaced many of the chromium and lead additives (both of which are toxic) that were previously used. Today, however, even zinc additives in coatings are being studied for environmental hazards. In Europe, all substances that contain zinc compounds must be labeled as potential polluters of environmental water. More environmentally safe organic compounds have been developed to replace the metallic anticorrosion additives, but these compounds are more expensive to produce. Opportunities abound for chemists to develop needed products that are both environmentally safe and economically viable.



▲ Zinc phosphate adheres strongly to steel surfaces, forming rough crystals onto which other coatings, such as paint, can be applied.

CHAPTER IN REVIEW

Self Assessment Quiz

Q1. Which metal is naturally found in its elemental state?

- gold
- titanium
- chromium
- iron

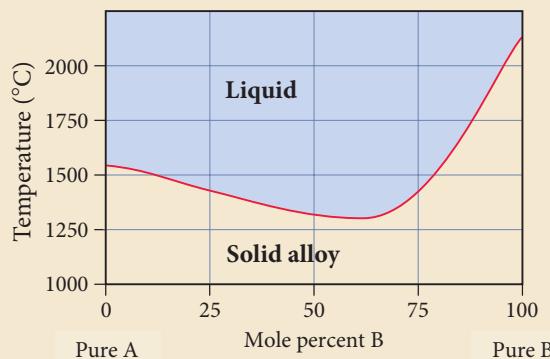
Q2. Which reaction is an example of pyrometallurgy?

- $\text{Ti}^{4+}(aq) + 4 \text{OH}^-(aq) \longrightarrow \text{TiO}_2(s) + 2 \text{H}_2\text{O}(l)$
- $2 \text{MnCO}_3(s) + \text{O}_2(g) \xrightarrow{\text{heat}} 2 \text{MnO}_2(s) + 2 \text{CO}_2(g)$
- $\text{Ni}(s) + 4 \text{CO}(g) \longrightarrow \text{Ni(CO)}_4(g)$
- $3 \text{MnO}_2(s) + 4 \text{Al}(s) \longrightarrow 3 \text{Mn}(s) + 2 \text{Al}_2\text{O}_3(s)$

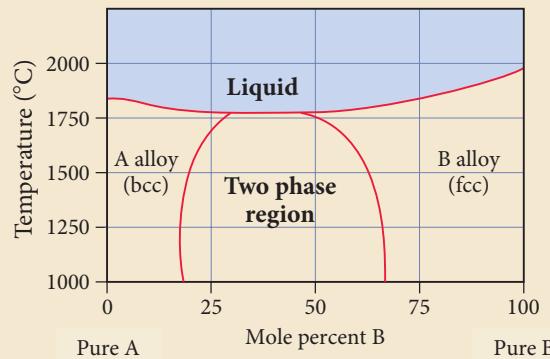
Q3. Based on the data in the table, which pair of metals is likely to form a substitutional alloy?

Metal	Atomic Radius	Crystal Structure
Sc	162 pm	Hexagonal closest packed
W	135 pm	Body-centered cubic
Cu	128 pm	Face-centered cubic
Cr	128 pm	Body-centered cubic
a) Sc and W		
b) Cu and Cr		
c) Cu and Sc		
d) Cr and W		

- Q4.** Two metals, A and B, form a substitutional alloy with the binary phase diagram shown here. What is the melting point of the alloy at a composition that is 75% A and 25% B?



- a) 1000 °C
 - b) 1300 °C
 - c) 1450 °C
 - d) 2000 °C
- Q5.** Two metals, A and B, form a substitutional alloy with the binary phase diagram shown here. Determine the composition and relative amounts of the two phases present at 50% composition and 1500 °C.



- a) The A-rich bcc phase is 80% A and 20% B; the B-rich fcc phase is 37% A and 63% B; the mixture contains more of the A-rich fcc phase.
- b) The A-rich bcc phase is 20% A and 80% B; the B-rich fcc phase is 63% A and 37% B; the mixture contains more of the B-rich fcc phase.
- c) The A-rich bcc phase is 50% A and 50% B; the B-rich fcc phase is 50% A and 50% B; the mixture contains equal amounts of both phases.
- d) The A-rich bcc phase is 80% A and 20% B; the B-rich fcc phase is 37% A and 63% B; the mixture contains more of the B-rich fcc phase.

- Q6.** An interstitial alloy contains a nonmetal (X) that occupies one-fourth of the octahedral holes in the closest-packed lattice of the metal (M). What is the formula for the alloy?
- a) M_4X
 - b) MX_4
 - c) M_2X
 - d) MX_2

- Q7.** Which metal is commonly used to make electrical wires?
- a) zinc
 - b) cobalt
 - c) manganese
 - d) copper
- Q8.** Which metal is commonly used to make parts for aircraft engines?
- a) zinc
 - b) titanium
 - c) nickel
 - d) silver

- Q9.** Calculate the mass percent of chromium in the mineral chromite ($FeCr_2O_4$).
- a) 83.97%
 - b) 46.46%
 - c) 86.78%
 - d) 36.13%

- Q10.** What is a common use for zinc?
- a) galvanization of steel
 - b) lightweight aircraft parts
 - c) paint pigments
 - d) production of magnets

Key Terms

Section 23.1

metallurgy (1076)

Section 23.2

minerals (1077)
ore (1077)

Section 23.3

extractive metallurgy (1077)
refining (1077)

gangue (1077)

pyrometallurgy (1078)

calcination (1078)

roasting (1078)

smelting (1079)

flux (1079)

slag (1079)

hydrometallurgy (1079)

leaching (1079)

electrometallurgy (1079)

powder metallurgy (1081)

octahedral hole (1085)

tetrahedral hole (1085)

Section 23.4

alloy (1082)

substitutional alloy (1082)

interstitial alloy (1082)

two-phase region (1084)

lever rule (1084)

Section 23.5

arc-melting (1087)

ferromagnetic (1089)

bronze (1090)

brass (1090)

Key Concepts

General Properties (23.2)

- Metals have many common physical properties, such as high conductivity of electricity and heat and high malleability and ductility. These properties vary among the different metals.

Natural Distribution of Metals (23.2)

- Metals are unevenly distributed throughout Earth's crust. All the metals together compose about 25% of the mass of Earth's crust, but just a few key metals are abundant enough to each individually compose more than 1% of the crust.
- Few metals exist naturally in their elemental state; most are found in ores, rocks that contain a high concentration of metal-containing minerals.
- Most metal-containing minerals are oxides, sulfides, chlorides, carbonates, or more complex compounds.

Metallurgical Processes (23.3)

- To be useful, metals have to be separated from the gangue, the unusable part of the ores, reduced to the elemental metals, and refined to be more pure.
- Extractive metallurgy is the general term for the processes such as pyrometallurgy, hydrometallurgy, and electrometallurgy that separate metal from ore.
- A new method of forming metal components from micron-sized metal particles is powder metallurgy.

Phase Diagrams (23.4)

- Elemental metals tend to crystallize in three main crystalline structures: face-centered cubic, body centered cubic, and hexagonal closest packed.
- When two types of metal atoms bond together, they form an alloy.
- A binary phase diagram is a graphical representation of the phases and crystal types of alloys present at different compositions and temperatures.
- If the two metals in an alloy are similar in size and have the same crystal structure, they tend to form a miscible solid solution, which means that they can form an alloy at any composition ratio. If the two metals are dissimilar in size or crystal structure, the solubility of one atom in the other's crystal structure is often limited. At certain compositions two different crystals can coexist in equilibrium; this is called a two-phase region. The lever rule determines which phase is present in a greater proportion.

Types of Alloys (23.4)

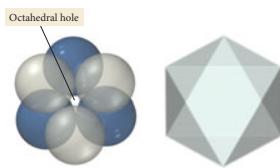
- There are two different types of alloys, substitutional and interstitial.
- A substitutional alloy is a mixture in which one type of metal atom replaces another type of metal atom in the crystal structure.
- In an interstitial alloy, one type of atom (either a metal or non-metal) fits into the holes within the crystal structure of the metal. Interstitial alloys can be made with different atoms filling different fractions of the different types of holes.

Key Equations and Relationships

Lever Rule (23.4)

In a two-phase region on a phase diagram, two different crystal structures coexist in equilibrium. Whichever phase has a composition closer to the overall composition of the alloy is the phase present in the larger relative amount.

Key Learning Outcomes

Chapter Objectives	Assessment
Using a Phase Diagram to Determine the Composition, Relative Amounts, and Phases Present (23.4)	Examples 23.1, 23.2, 23.3, 23.4 For Practice 23.1, 23.2, 23.3, 23.4 Exercises 35–38
Determining the Composition of an Interstitial Alloy from the Occupancy of the Interstitial Holes (23.4)	 Exercises 41, 42

EXERCISES

Review Questions

- Why is vanadium present in oil from some sources?
- List three categories of metallurgical processes.
- Why is Ni not considered a common metal even though it composes over 2% of the total mass of Earth and only Fe and Mg have a higher percent composition of Earth's total mass?
- Metal elements are found in both minerals and ores. Describe the difference between a mineral and an ore.
- Ores contain minerals and gangue. Describe the difference between a mineral and gangue.
- Calcination, roasting, and smelting are three pyrometallurgical processes. Compare and contrast the processes.
- What compound has been historically used to leach gold from gold ores? Why is this process being discontinued?
- Name three advantages of making metal components from the powder metallurgical process.
- Describe the difference between body-centered cubic and face-centered cubic structures.
- Describe the difference between a substitutional alloy and an interstitial alloy.
- Why was copper one of the first metals that humans used?
- Describe why bronze was one of the first alloys that humans used.
- Both brass and bronze contain copper. Describe the difference between these two alloys.
- List the properties of copper that make it appropriate for electric wires and the properties that make it appropriate for water pipes.

Problems by Topic

The General Properties and Natural Distribution of Metals

- Describe three typical properties of metals.
- Describe whether each property is generally higher or lower for metals compared to nonmetals.
 - thermal conductivity
 - electrical resistivity
 - transparency
 - ductility
- List four metal elements that each individually compose more than 1% of Earth's crust.
- List four metals that occur as elements in their natural state.
- List the name and formula of one important mineral source for each of these metals: Fe, Hg, V, and Nb.
- List the name and formula of one important mineral source for each of these metals: Ti, Zn, U, and Ta.

Metallurgical Processes

- Two ores of magnesium are MgCO_3 and Mg(OH)_2 . Write balanced equations for the calcination of these two minerals to form MgO .
- Two ores of copper are CuO and CuS . Write balanced equations for the roasting of CuO with C to form Cu metal and the roasting of CuS with O_2 to form CuO .
- Give the definition of a flux and identify the flux in the reaction.

$$\text{SiO}(s) + \text{MgO}(s) \longrightarrow \text{MgSiO}_3(l)$$
- Give the definition of a slag and identify the slag in the reaction.

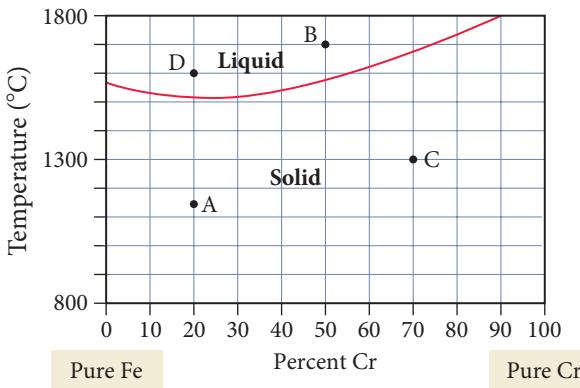
$$\text{SiO}_2(s) + \text{MgO}(s) \longrightarrow \text{MgSiO}_3(l)$$
- Provide a general description of how hydrometallurgy is used to extract metals from ores.

26. Provide a general description of how electrometallurgy is used to extract metals from ores.
27. How is Al_2O_3 separated from other oxides using the Bayer process? What soluble form of aluminum forms from Al_2O_3 during the Bayer process?
28. When copper is purified using an electrochemical cell, which electrode has the pure copper and which electrode has the impure copper? Explain how gold is obtained from this process.
29. Describe the difference between sponge powdered iron and water-atomized powdered iron.
30. Describe the difference in the processing of sponge powdered iron and water-atomized powdered iron.

Metal Structures and Alloys

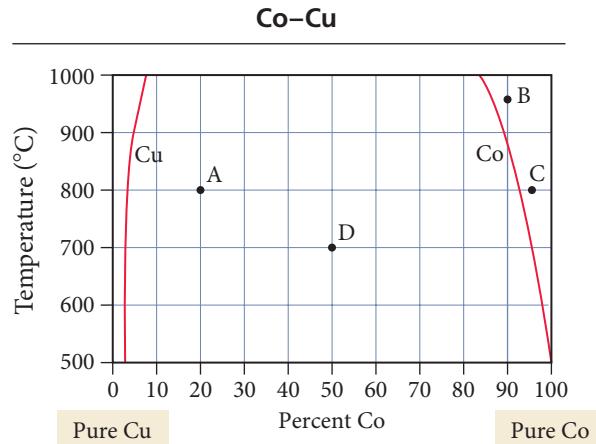
31. Determine the composition of each vanadium alloy.
- One-half of the V atoms are replaced by Cr atoms.
 - One-fourth of the V atoms are replaced by Fe atoms.
 - One-fourth of the V atoms are replaced by Cr atoms, and one-fourth of the V atoms are replaced by Fe atoms.
32. Determine the composition of each cobalt alloy.
- One-third of the Co atoms are replaced by Zn atoms.
 - One-eighth of the Co atoms are replaced by Ti atoms.
 - One-third of the Co atoms are replaced by Zn atoms, and one-sixth of the Co atoms are replaced by Ti atoms.
33. Referring to Table 23.2, explain why you might expect Cr and Fe to form miscible alloys.
34. Referring to Table 23.2, explain why you might expect Co and Cu to not form miscible alloys.
35. Determine the composition and phases present at points A and B on the Cr–Fe phase diagram.

Cr–Fe



36. Determine the composition and phase present at points C and D on the Cr–Fe phase diagram (see previous problem for diagram).

37. Determine the composition, relative amounts, and phases present at points A and B on the Co–Cu phase diagram.



38. Determine the composition, relative amounts and phases present at points C and D on the Co–Cu phase diagram (see previous problem for phase diagram).
39. The elements Mn and Si are added to steel to improve its properties in electric motors, and some C is often found as a detrimental impurity. Which of these elements fills interstitial holes in the Fe lattice and which substitutes for the Fe in the lattice?
40. The elements Si and P are added to steel to improve its properties in electric motors, and some N is often found as a detrimental impurity. Which of these elements fills interstitial holes in the Fe lattice and which substitutes for the Fe in the lattice?
41. Determine the formula for each interstitial alloy.
- Nitrogen occupies one-half of the octahedral sites of a closest-packed Mo structure.
 - Hydrogen occupies all of the tetrahedral sites of a Cr closest-packed structure.
42. Determine the formula for each interstitial alloy.
- Nitrogen occupies one-fourth of the octahedral sites of a closest-packed Fe structure.
 - Hydrogen occupies one-half of the tetrahedral sites of a Ti closest-packed structure.

Sources, Properties, and Products of Some of the 3d Transition Metals

43. Identify the metal found in each mineral.
- sphalerite
 - malachite
 - hausmannite
44. Name at least one important mineral that is a source for each metal.
- Fe
 - Co
 - Cr

- 45.** Calculate the heat of reaction (ΔH_{rxn}°) for the calcination of rhodochrosite. (ΔH_f° for rhodochrosite is -894.1 kJ/mol .)
- 46.** The extraction of Mn from pyrolusite with aluminum produces pure Mn metal and Al_2O_3 . Calculate the heat of reaction (ΔH_{rxn}°).
- 47.** Describe the effects of adding Cr to steel and give a use for chromium–steel alloys.
- 48.** Describe the effects of adding Mn to steel and give a use for manganese–steel alloys.
- 49.** Calculate the mole percent and mass percent of Ti in the minerals rutile and ilmenite.
- 50.** Calculate the mole percent and mass percent of Mn in the minerals pyrolusite and rhodochrosite.
- 51.** Why is it important to use an inert atmosphere to surround the metal when arc-melting titanium?
- 52.** Titanium is a very reactive metal. Explain why titanium has a high corrosion resistance to seawater and can be used for the production of ship components.
- 53.** Which compound of Ti is the most important industrial product of titanium metal? Describe an application for this compound.
- 54.** Describe how Zn is used to protect the surface of steel products. What is the name of this process?
- 55.** Describe the Bayer process.
- 56.** Describe the Mond process.
- 57.** Which metals are found in carbaloy steel?
- 58.** Which metals are found in Monel steel?

Cumulative Problems

- 59.** After $2.0 \times 10^4\text{ kg}$ of an ore that contains 0.051% ilmenite is mined, the percent yield from extracting and refining the metals from the mineral is 87% for the iron and 63% for the titanium. Calculate the mass of iron and titanium produced from the ore.
- 60.** Calculate the mass of aluminum metal that is needed to produce Cr metal from $5.00 \times 10^2\text{ g}$ of chromite. Calculate how many grams of Cr metal are produced from $5.00 \times 10^2\text{ g}$ of chromite.
- 61.** How many lattice atoms surround a tetrahedral hole and an octahedral hole in a closest-packed structure? Describe which hole site is larger and explain why.
- 62.** Explain why the crystal structure and atomic size of the two elements are important factors in a two-component phase diagram.
- 63.** Why does Mn form compounds with higher oxidation states than Cr?
- 64.** Why is MnO_2 added to silica glass?
- 65.** Co, Fe, and Ni are ferromagnetic. What is the difference between ferromagnetic and paramagnetic?
- 66.** Is the chromate ion or dichromate ion more stable in an acidic solution? Which ion has a higher Cr:O ratio? Which ion has a higher oxidation state for Cr?
- 67.** The first ionization energies of iron, cobalt, nickel, and the first three platinum metals are all about the same, but the first ionization energies of osmium, iridium, and platinum are substantially greater. Suggest an explanation for this observation.
- 68.** Although both the Group IA and IB metals have a half-filled s subshell, the IB metals have markedly higher first ionization energies, densities, and melting points, and markedly lower second and third ionization energies than the corresponding IA metals. Explain these observations.

Challenge Problems

- 69.** Iron powder is placed into a tall cylinder-shaped die and pressed from the top and bottom to make a cylinder-shaped pressed part with a height of 5.62 cm and radius of 4.00 cm. The density of the iron powder before it was pressed was 2.41 g/mL . The density of a pressed iron part is 6.85 g/mL . The density of pure solid iron is 7.78 g/mL .
- Calculate the original height of the powder before it was pressed.
 - Calculate the theoretical height of the pressed component if it could be pressed to the same density of pure iron.
 - What percentage of the component is composed of voids between the iron particles?
- 70.** When a part is made by pressing together powdered metal, no metal is wasted. In contrast, metal is typically scrapped after a metal part is cut from a solid metal plate. If a circular part with a diameter of 10.0 cm is made from an original shape of a square with a side length of 10.0 cm, calculate the percentage of the metal that is thrown away as scrap. If the circular shape also has a circular hole with a diameter of 6.0 cm, calculate the percentage of the metal that is thrown away as scrap.
- 71.** Hydrogen can be in both the octahedral and tetrahedral holes for lanthanum. Determine the percentage of the holes that are filled if the formula is $\text{LaH}_{2.76}$.
- 72.** Tin exists in two allotropic forms. Gray tin has a diamond structure and white tin has a close-packed structure. Predict which allotrope is (a) denser, (b) a conductor of electricity. Predict the valence electronic configuration of tin in each allotrope.
- 73.** Find the equilibrium constant at 298 K for the reaction.
- $$\text{[Ag(CN)}_2]^-(aq) + \text{Cu}(s) \rightleftharpoons \text{[Cu(CN)}_2]^-(aq) + \text{Ag}(s)$$
- The K_f for $[\text{Cu(CN)}_2]^- = 1.0 \times 10^{24}$ and the rest of the data needed are in Appendix II.
- 74.** Find the equilibrium constant at 298 K for the reaction.
- $$2 \text{[Cu(NH}_3)_2]^+(aq) \rightleftharpoons \text{[Cu(NH}_3)_4]^{2+}(aq) + \text{Cu}(s)$$
- The K_f for $[\text{Cu(NH}_3)_2]^+ = 6.3 \times 10^{10}$ and the rest of the data needed are in Appendix II.
- 75.** Propose a chemical procedure to extract cobalt from the mineral cobaltite, CoAsS . What are some of the hazards of such a procedure?

Conceptual Problems

76. Why are metals such as Ni and Co economical to mine and use in industrial processes even though they have a very low natural abundance in Earth's crust?
77. Explain why metals such as Au and Ag are found in their elemental states in nature, but metals like Na and Ca are always found in compounds in nature.
78. What allows some pairs of metals to form alloys that have the same structure at any composition, while other pairs of metals form alloys with structures that depend on the relative composition of the two metals?

Answers to Conceptual Connections

Interstitial Alloys

- 23.1** M_4X . Since there are twice as many tetrahedral holes as metal atoms in a closest-packed structure, and since one-eighth of them are occupied by nonmetal atoms, there must be one-quarter as many nonmetal atoms as metal atoms.

24

Transition Metals and Coordination Compounds

“Chemistry must become the astronomy of the molecular world.”

—Alfred Werner (1866–1919)

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IN THIS CHAPTER, WE EXAMINE the chemistry of the transition metals and an important class of their compounds called coordination compounds. We will see that coordination compounds form all of the types of isomers that we have studied so far, as well as some new types. In our examination of the transition metals, we draw on much of what we learned in Chapters 7 and 8 about electronic structure and periodicity. We also briefly revisit valence bond theory to explain bonding in coordination compounds, but we quickly shift to a different theory—called crystal field theory—that better explains many of the properties of these compounds. Transition metals and coordination compounds are important, not only because of their interesting chemistry, but because of their numerous applications. Coordination compounds are the basis for a number of therapeutic drugs, chemical sensors, and coloring agents. In addition, many biological molecules contain transition metals that bond in ways that are similar to coordination compounds. For example, the oxygen-carrying site on hemoglobin is an iron ion bonded partly to an amino acid in the hemoglobin molecule and partly to a flat molecule called a porphyrin. An oxygen molecule reversibly bonds to the iron and is transported throughout the body by blood flow.



The color of ruby is caused by a splitting of the d-orbital energy levels in Cr³⁺ by the host crystal.

24.1 The Colors of Rubies and Emeralds

Rubies are deep red and emeralds are brilliant green, yet the color of both gemstones is caused by the same ion, Cr³⁺. The difference lies in the crystal that hosts the ion. Rubies are crystals of aluminum oxide (Al₂O₃) in which about 1% of the Al³⁺ ions are replaced by Cr³⁺ ions. Emeralds, by contrast, are crystals of beryllium aluminum silicate [Be₃Al₂(SiO₃)₆] in which a similar percentage of the Al³⁺ ions are replaced by Cr³⁺. The imbedded Cr³⁺ ion is red in the aluminum oxide crystal but green in the beryllium aluminum silicate crystal. Why?

The answer to this question lies in the effect that the host crystal has on the energies of the atomic orbitals in Cr³⁺. Atoms in the crystal create a field around the ion—sometimes called the *crystal field*—that splits the five normally degenerate d orbitals into two or more levels. The color of the gemstone is caused by electron transitions between these levels. In rubies, the crystal field is stronger (and the corresponding splitting of the d orbitals greater) than it is in emeralds. Recall from Chapter 7 that the color of a substance depends on the colors *absorbed* by that substance, which in turn depends on the energy differences between the orbitals involved in the absorption. The greater splitting in ruby results in a greater energy difference between the d orbitals of Cr³⁺, and consequently the absorption of a different color of light than in emerald.



▲ **Ruby and Emerald** The red color of ruby and the green color of emerald are both caused by Cr^{3+} .

The colors of several other gemstones are also caused by the splitting of the d orbitals in transition metal ions imbedded within host crystals. For example, the red in garnet, which has $\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3$ as a host crystal, and the yellow-green of peridot, which has Mg_2SiO_4 as a host crystal are both caused by electron transitions between d orbitals in Fe^{2+} . Similarly, the blue in turquoise, which has $[\text{Al}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4 \text{H}_2\text{O}]^{2-}$ as a host crystal, is caused by transitions between the d orbitals in Cu^{2+} .

In this chapter, we examine the properties of the transition metals and their ions more closely. We also examine the properties of coordination compounds in some detail. We first discussed this common type of transition metal compound in Chapter 16 (see Section 16.8). In a coordination compound, bonds to a central metal ion split the d orbitals much as they are split in the crystals of gemstones. The theory that explains these splittings and the corresponding colors is **crystal field theory**, which we also explore in this chapter.



▲ **Garnet, Peridot, and Turquoise** The red in garnet and the yellow-green of peridot are both caused by Fe^{2+} . The blue of turquoise is caused by Cu^{2+} .

24.2 Properties of Transition Metals

Transition metals, the elements in the d block of the periodic table, are a study in similarities and differences. When we compare their properties with the varied properties of the main-group elements, they seem markedly similar. For example, almost all transition metals have moderate to high densities, good electrical conductivity, high melting points, and moderate to extreme hardness. Their similar properties are related to their similar electron configurations: they all have electrons in d orbitals that can be involved in metallic bonding. In spite of their similarities, however, each element is also unique, and they exhibit a wide variety of chemical behavior. Before we examine some of the periodic properties of the transition metals, let's review the electron configurations of these elements, first discussed in Chapter 8.

Electron Configurations

Recall from Section 8.4 that, as we move to the right across a row of transition elements, electrons are added to $(n - 1)d$ orbitals (where n is the row number in the periodic table and also the quantum number of the highest occupied principal level). For example, as we move across the fourth-period transition metals, electrons are added to the $3d$ orbitals, as shown in Table 24.1.

In general, the ground state electron configuration for the first two rows of transition elements is [noble gas] $ns^2(n - 1)d^x$ and for the third and fourth rows is [noble gas] $ns^2(n - 2)f^{14}(n - 1)d^x$, where x ranges from 1 to 10. Recall from Section 8.4, however, that because the ns and $(n - 1)d$ sublevels are close in energy, many exceptions occur. For example, in the first transition series of the d block, the outer configuration is $4s^23d^4$ with two exceptions: Cr is $4s^13d^5$ and Cu is $4s^13d^{10}$. This behavior is related to the closely spaced $3d$ and $4s$ energy levels and the stability associated with a half-filled or completely filled d sublevel.

Recall from Section 8.7 that the transition metals form ions by losing electrons from the ns orbital *before* losing electrons from the $(n - 1)d$ orbitals. For example, Fe^{2+} has an electron configuration of $[\text{Ar}] 3d^6$, because it has lost both of the $4s$ electrons to form the $2+$ charge. Examples 24.1 and 24.2 review the steps in writing electron configurations for transition metals and their ions.

TABLE 24.1 First-Row Transition Metal Orbital Occupancy

	4s	3d				
Sc	↑↓	1				
Ti	↑↓	1	1			
V	↑↓	1	1	1		
Cr	1	1	1	1	1	1
Mn	↑↓	1	1	1	1	1
Fe	↑↓	1	1	1	1	1
Co	↑↓	1	1	1	1	1
Ni	↑↓	1	1	1	1	1
Cu	1	1	1	1	1	1
Zn	↑↓	1	1	1	1	1

PROCEDURE FOR...**Writing Electron Configurations**

Identify the noble gas that precedes the element and write it in square brackets.

Count down the periods to determine the outer principal quantum level—this is the quantum level for the *s* orbital. Subtract one to obtain the quantum level for the *d* orbital. If the element is in the third or fourth transition series, include $(n - 2)f^{14}$ electrons in the configuration.

Count across the row to see how many electrons are in the neutral atom and fill the orbitals accordingly.

For an ion, remove the required number of electrons, first from the *s* and then from the *d* orbitals.

EXAMPLE 24.1**Writing Electron Configurations for Transition Metals**

Write the ground state electron configuration for Zr.

SOLUTION

[Kr]

Zr is in the fifth period so the orbitals used are

[Kr] 5s4d

Zr has four more electrons than Kr.

[Kr] 5s²4d²

EXAMPLE 24.2**Writing Electron Configurations for Transition Metals**

Write the ground state electron configuration for Co³⁺.

SOLUTION

[Ar]

Co is in the fourth period so the orbitals used are

[Ar] 4s3d

Co has nine more electrons than Ar.

[Ar] 4s²3d⁷

FOR PRACTICE 24.1

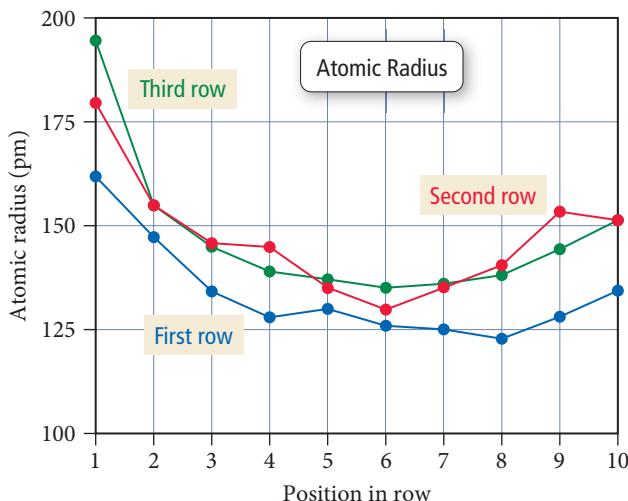
Write the ground state electron configuration for Os.

FOR PRACTICE 24.2

Write the ground state electron configuration for Nb²⁺.

► **FIGURE 24.1 Trends in Atomic Radius**

With the exception of a decrease in radius from the first to the second element, there is only a small variation in atomic radius across a row. There is a small and expected increase in radius from the first to the second transition row but virtually no difference in radius from the second to the third.



Atomic Size

As we discussed in Section 8.6, for main-group elements, the size of atoms decreases across a period and increases down a column. For transition metals, however, there is little variation in size across a row (other than for the first two elements in each transition metal row, such as Sc and Ti in the first row), as shown in Figure 24.1 ▲. The reason for the difference is that, across a row of transition elements, the number of electrons in the outermost principal energy level (highest n value) is nearly constant. As another proton is added to the nucleus with each successive element, another electron is added as well, but the electron goes into an $n - 1$ orbital. The number of outermost electrons thus stays the same, and the electrons experience a roughly constant effective nuclear charge as we move across the row, keeping the radii approximately constant.

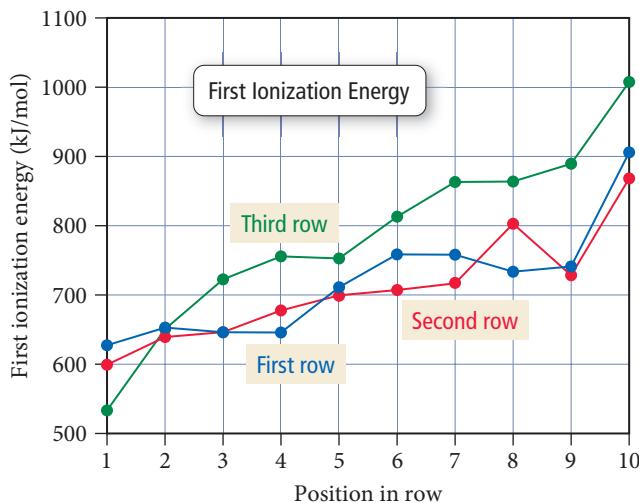
Looking down a group, we see a small but expected increase in size from the first transition metal row to the second, but the size of elements in the third row is about the same as it is for those in the second row. This pattern is also different from that of the main-group elements, especially when we consider that in any given column, the third transition row has 32 more electrons than the second row. The reason that the third transition row elements are not larger is because 14 of the 32 electrons are in a $(n - 2)f$ sub-level, and while electrons in f orbitals are in lower principal quantum levels, they are not very effective at shielding the outer electrons from nuclear charge. Consequently, the outer electrons are held more tightly by the nucleus, offsetting the typical increase in size between the periods—an effect called the **lanthanide contraction**.

Conceptual Connection 24.1 Atomic Size

Which element has the larger atomic radius, Fe or W?

Ionization Energy

The first ionization energies of transition elements follow the expected main-group periodic trend and slowly increase across a row (Figure 24.2 ►), but the increase is smaller than for main-group elements. As we move down a group, we see that the third transition row generally has a higher ionization energy than do the first two rows, a trend counter to that observed in the main-group elements. In the transition elements the charge of the nucleus increases substantially from one row to the next, but there is only a small increase in atomic size between the first and second rows, and no increase in size between the second and third row. The outer electrons are therefore held more tightly in the third transition row than in the first two rows.



◀ FIGURE 24.2 Trends in First Ionization

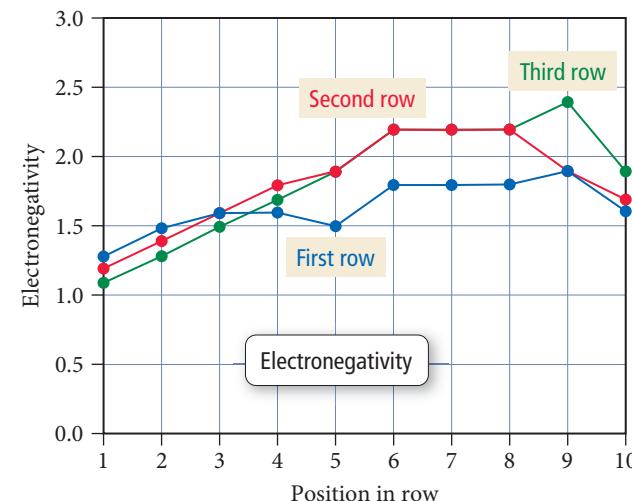
Energy First ionization energy generally increases across a row, following the main-group trend. However, in contrast to the main-group trend, the third transition row has a greater ionization energy than the first and second rows.

Electronegativity

The electronegativity values of the transition metals, like their ionization energies, follow the main-group trend and slowly increase across a row, as shown in Figure 24.3 ▶. The increase is smaller than the increase that occurs in the main-group elements, but we would expect that given the similarity in the sizes of the atoms. The trend in electronegativity values down a group (or column) is another example of the transition metals behaving differently from the main-group elements. The electronegativity values generally increase from the first transition row to the second, but there is no further increase for the third row. In the main-group elements, by contrast, we see a *decrease* in electronegativity down a group. The difference is again caused by the relatively small change in atomic size as we move down a column for the transition elements, accompanied by a large increase in nuclear charge. One of the heaviest metals, gold (Au), is also the most electronegative metal. Its electronegativity value ($\text{EN} = 2.4$) is even higher than that of some nonmetals (EN of P is 2.1), and compounds of an Au^- ion have been observed.

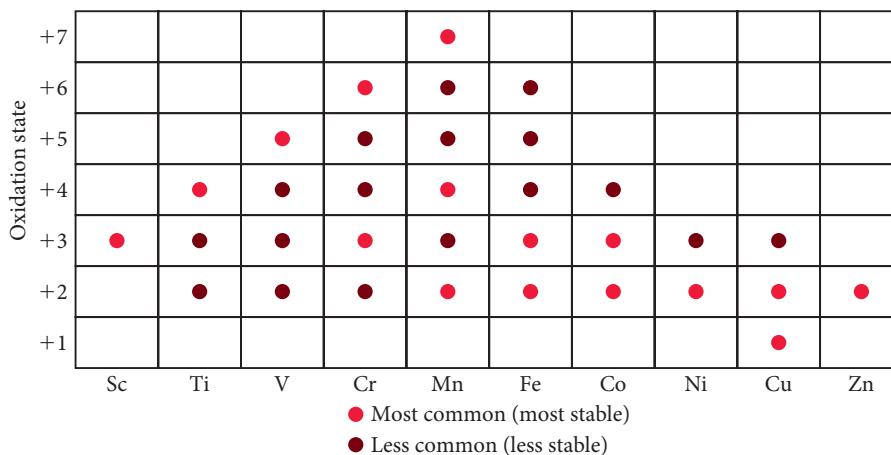
Oxidation States

Unlike main-group metals, which tend to exhibit only one oxidation state, the transition metals often exhibit a variety of oxidation states (Figure 24.4 ▷). The highest oxidation state for a transition metal is +7 for manganese (Mn). The electron configuration of



◀ FIGURE 24.3 Trends in Electronegativity

The electronegativity of the transition elements generally increases across a row, following the main-group trend. However, in contrast to the main-group trend, electronegativity increases from the first transition row to the second. There is little electronegativity difference between the second and third transition rows.



◀ FIGURE 24.4 First-Row Transition

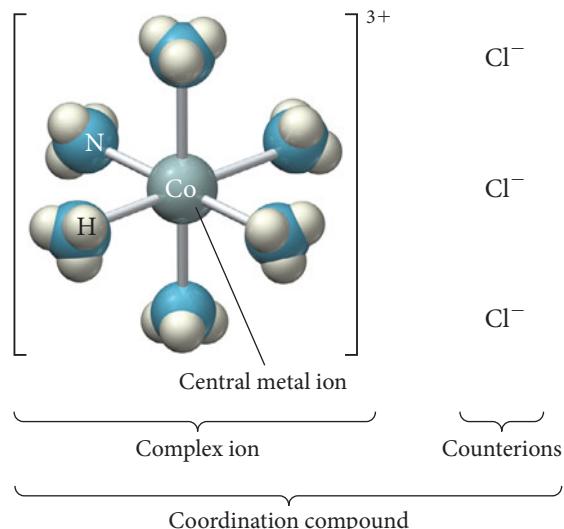
Metal Oxidation States The transition metals exhibit many more oxidation states than the main-group elements. These oxidation states range from +7 to +1.

Metals in high oxidation states, such as +7, exist only when the metal is bound to a highly electronegative element such as oxygen; they do not exist as bare ions.

manganese in this oxidation state corresponds to the loss of all the electrons in the 4s and 3d orbitals, leaving a noble gas electron configuration ([Ar]). This is the same configuration we see for all of the highest oxidation states of the elements to the left of Mn. To the right of manganese, the oxidation states are all lower, mostly +2 or +3. A +2 oxidation state for a transition metal is not surprising, since 4s electrons are readily lost.

24.3 Coordination Compounds

We discussed at the end of Chapter 16 that transition metals tend to form *complex ions*. A **complex ion** contains a central metal ion bound to one or more *ligands*. A **ligand** is a Lewis base (or electron donor) that forms a bond with the metal. When a complex ion combines with one or more *counterions* (ions of opposite charge that are not acting as ligands), the resulting neutral compound is a **coordination compound**.



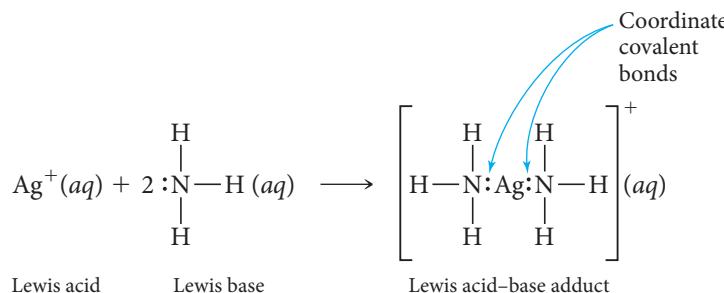
▲ Complex Ion and Coordination

Compound A coordination compound contains a complex ion and corresponding counterions. The complex ion contains a central metal atom coordinated to several ligands. The compound shown here is $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$.

The first coordination compounds were discovered in the early eighteenth century, but their nature was not understood until nearly 200 years later. Swiss chemist Alfred Werner studied coordination compounds extensively—especially a series of cobalt(III) compounds with ammonia, whose formulas were then written as $\text{CoCl}_3 \cdot 6 \text{ NH}_3$, $\text{CoCl}_3 \cdot 5 \text{ NH}_3$ and, $\text{CoCl}_3 \cdot 4 \text{ NH}_3$. In 1893, he proposed that the central metal ion has two types of interactions that he named **primary valence** and **secondary valence**. The primary valence is the oxidation state on the central metal atom, and the secondary valence is the number of molecules or ions directly bound to the metal atom, called the **coordination number**. In $\text{CoCl}_3 \cdot 6 \text{ NH}_3$ the primary valence is +3, and it was discovered that the ammonia molecules are directly bound to the central cobalt, giving a coordination number of 6. Today we write the formula of this compound as $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ to better represent the coordination compound as the combination of a complex ion, $\text{Co}(\text{NH}_3)_6^{3+}$, and three Cl^- counterions.

We write the formulas of the other cobalt(III) compounds studied by Werner as $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$. In these two cases, the complex ions are $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ (with two Cl^- counterions) and $\text{Co}(\text{NH}_3)_4\text{Cl}_2^{+}$ (with one Cl^- counterion), respectively. With this series of compounds, Werner demonstrated that the Cl^- can replace NH_3 in the secondary valence. In other words, Cl^- can act as a counterion, or it can bond directly to the metal as part of the complex ion.

The complex ion itself contains the metal ion in the center and the ligands—which can be neutral molecules or ions—arranged around it. We can think of the metal–ligand complex as a Lewis acid–base adduct (see Section 15.11) because the bond is formed when the ligand donates a pair of electrons to an empty orbital on the metal. For example, consider the reaction between the silver ion and ammonia:



A bond of this type, which we first encountered in Section 10.6, is often referred to as a **coordinate covalent bond**. Ligands are therefore good Lewis bases and have at least one pair of electrons to donate to, and bond with, the central metal ion. Table 24.2 contains a number of common ligands.

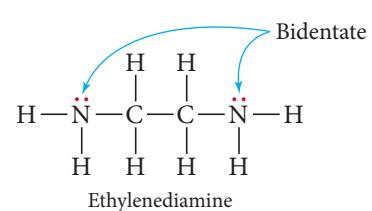
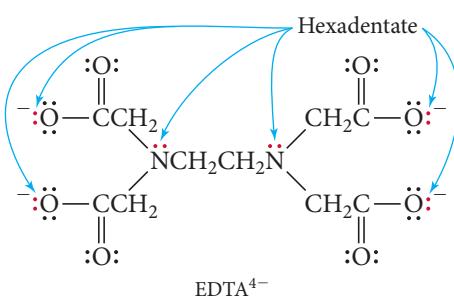
Ligands that donate only one electron pair to the central metal are **monodentate**. Some ligands, however, have the ability to donate two pairs of electrons (from two different atoms) to the metal; these are **bidentate**. Examples of bidentate ligands include

TABLE 24.2 Common Ligands

Name	Lewis diagram
Water	H— $\ddot{\text{O}}$ —H
Ammonia	H— $\ddot{\text{N}}$ —H H
Chloride ion	$[\text{:Cl:}]^-$
Carbon monoxide	:C≡O:
Cyanide ion	$[\text{:C}\equiv\text{N}:]^-$
Thiocyanate ion	$[\text{:S}\equiv\text{C}=\text{N}:]^-$
Oxalate ion (ox)	$\left[\begin{array}{c} \text{:O:} & \text{:O:} \\ \diagup & \diagdown \\ \text{C} & \text{C} \\ \diagdown & \diagup \\ \text{:O:} & \text{:O:} \end{array} \right]^{2-}$
Ethylenediamine (en)	H— $\ddot{\text{N}}$ —C(H) ₂ —C(H) ₂ — $\ddot{\text{N}}$ —H
Ethylenediaminetetraacetate (EDTA)	$\left[\begin{array}{c} \text{:O:} & & \text{:O:} \\ \diagup & & \diagdown \\ -\text{O}-\text{CCH}_2 & \text{NCH}_2\text{CH}_2\text{N} & \text{CH}_2\text{C}-\text{O}:^- \\ \diagdown & & \diagup \\ \text{:O:} & & \text{CH}_2\text{C}-\text{O}:^- \\ \diagup & & \diagdown \\ -\text{O}-\text{CCH}_2 & & \text{CH}_2\text{C}-\text{O}:^- \\ \diagdown & & \diagup \\ \text{:O:} & & \text{CH}_2\text{C}-\text{O}:^- \end{array} \right]^{4-}$

the oxalate ion (abbreviated ox) and the ethylenediamine molecule (abbreviated en) shown here in the right margin. The ethylenediamine ligand bonded to Co^{3+} is shown in Figure 24.5(a) ► (on the next page).

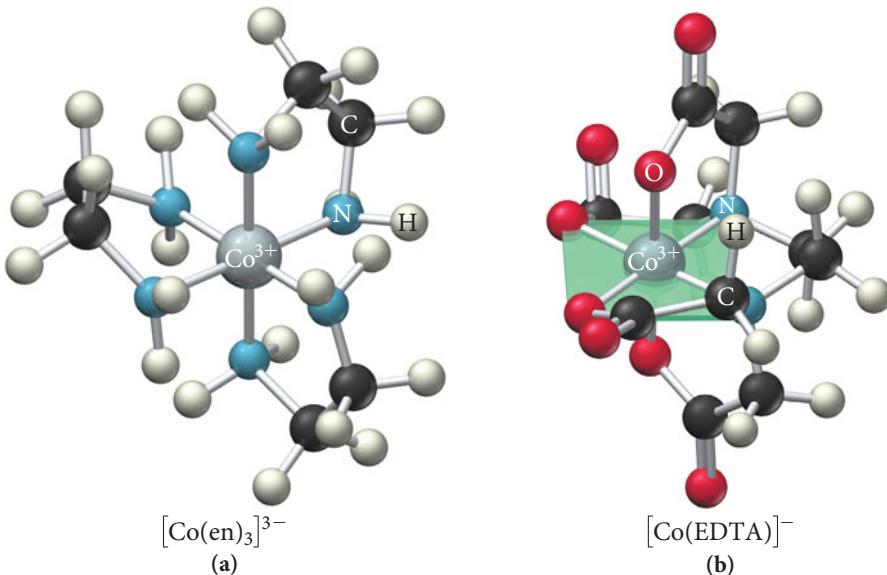
Some ligands, called **polydentate** ligands, can donate even more than two electron pairs (from more than two atoms) to the metal. The most common polydentate ligand is the ethylenediaminetetraacetate ion (EDTA^{4-}) shown below.



Ethylenediamine

► **FIGURE 24.5** Bidentate and Polydentate Ligands Coordinated to Co(III)
(a) Ethylenediamine is a bidentate ligand; **(b)** EDTA is a hexadentate ligand.

Bidentate and Polydentate Ligands Coordinated to Co(III)



The EDTA ligand wraps itself completely around the metal, donating up to six pairs of electrons (Figure 24.5b ▲). A complex ion that contains either a bidentate or polydentate ligand is a **chelate** (pronounced “key-late”), and the coordinating ligand is known as a **chelating agent**.

A survey of many coordination compounds shows that coordination numbers can vary from as low as 2 to as high as 12. The most common coordination numbers are 6, as occurs in $[\text{Co}(\text{NH}_3)_6]^{3+}$, and 4, as occurs in $[\text{PdCl}_4]^{2-}$. Coordination numbers greater than 6 are rarely observed for the first-row transition metals. Typically, only 1+ metal ions have a coordination number as low as 2, as occurs in $[\text{Ag}(\text{NH}_3)_2]^+$. Odd coordination numbers exist, but they are rare.

The common geometries of complex ions, shown in Table 24.3, depend in part on their coordination number. A coordination number of 2 results in a linear geometry, and a coordination number of 6 results in an octahedral geometry. A coordination number of 4

TABLE 24.3 Common Geometries of Complex Ions

Coordination Number	Shape	Model	Example
2	Linear		$[\text{Ag}(\text{NH}_3)_2]^+$
4	Square planar		$[\text{PdCl}_4]^{2-}$
4	Tetrahedral		$[\text{Zn}(\text{NH}_3)_4]^{2+}$
6	Octahedral		$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

can have either a tetrahedral geometry or a square planar geometry, depending on the number of d electrons in the metal ion. Metal ions with a d^8 electron configuration (such as $[\text{PdCl}_4]^{2-}$) exhibit square planar geometry, and metal ions with a d^{10} electron configuration (such as $[\text{Zn}(\text{NH}_3)_4]^{2+}$) exhibit tetrahedral geometry.

Naming Coordination Compounds

To name coordination compounds, you follow a series of general rules based on the system originally proposed by Werner. As with all salts (see Section 3.5), the name of the cation goes before the name of the anion.

Guidelines for Naming Complex Ions	Examples
<p>1. Name the ligands.</p> <ul style="list-style-type: none"> Name neutral ligands as molecules with the following notable exceptions. <p>H₂O (aqua) NH₃ (ammine) CO (carbonyl)</p> <ul style="list-style-type: none"> Name anionic ligands with the name of the ion plus an ending modified as follows: <p>-ide becomes -o -ate becomes -ato -ite becomes -ito</p>	<p>NH₂CH₂CH₂NH₂ is ethylenediamine.</p> <p>H₂O is aqua.</p> <p>Cl⁻ is chloro. SO₄²⁻ is sulfato. SO₃²⁻ is sulfito.</p>

Table 24.4 lists the names of some common ligands.

<p>2. List the names of the ligands in alphabetical order before the name of the metal cation.</p>	<p>Ammine (NH₃) is listed before chloro (Cl⁻), which is listed before nitrito (NO₂⁻).</p>
<p>3. Use a prefix to indicate the number of ligands (when there is more than one of a particular type): <i>di-</i> (2), <i>tri-</i> (3), <i>tetra-</i> (4), <i>penta-</i> (5), or <i>hexa-</i> (6).</p> <p>If the name of the ligand already contains a prefix, such as ethylenediamine, place parentheses around the ligand name and use <i>bis-</i> (2), <i>tris-</i> (3), or <i>tetrakis-</i> (4) to indicate the number.</p> <p>Prefixes do not affect the order in which you list the ligands.</p>	<p>Trichloro indicates three Cl⁻ ligands. Tetraammine indicates four NH₃ ligands.</p> <p>Tris(ethylenediamine) indicates three ethylenediamine ligands.</p>
<p>4. Name the metal.</p> <p>a. When the complex ion is a cation, use the name of the metal followed by the oxidation state written with a Roman numeral.</p> <p>b. If the complex ion is an anion, drop the ending of the metal and add -ate followed by the oxidation state written with a Roman numeral. Some metals use the Latin root with the -ate ending. Table 24.5 lists the names for some common metals in anionic complexes.</p>	<p>In cations:</p> <p>Co³⁺ is cobalt(III). Pt²⁺ is platinum(II). Cu⁺ is copper(I).</p> <p>In anions:</p> <p>Co³⁺ is cobaltate(III). Pt²⁺ is platinate(II). Cu⁺ is cuprate(I).</p>
<p>5. Write the entire name of the complex ion by listing the ligands first followed by the metal.</p>	<p>[Pt(NH₃)₂Cl₄]²⁻ is diamminetetrachloroplatinate(II). [Co(NH₃)₆]³⁺ is hexaamminecobalt(III).</p>

TABLE 24.4 Names and Formulas of Common Ligands

Ligand	Name in Complex Ion
Anions	
Bromide, Br ⁻	Bromo
Chloride, Cl ⁻	Chloro
Hydroxide, OH ⁻	Hydroxo
Cyanide, CN ⁻	Cyano
Nitrite, NO ₂ ⁻	Nitro
Oxalate, C ₂ O ₄ ²⁻ (ox)	Oxalato
Ethylenediaminetetraacetate (EDTA ⁴⁻)	Ethylenediaminetetraacetato
Neutral molecules	
Water, H ₂ O	Aqua
Ammonia, NH ₃	Ammine
Carbon monoxide, CO	Carbonyl
Ethylenediamine (en)	Ethylenediamine

TABLE 24.5 Names of Common Metals when Found in Anionic Complex Ions

Metal	Name in Anionic Complex
Chromium	Chromate
Cobalt	Cobaltate
Copper	Cuprate
Gold	Aurate
Iron	Ferrate
Lead	Plumbate
Manganese	Manganate
Molybdenum	Molybdate
Nickel	Nickelate
Platinum	Platinate
Silver	Argentate
Tin	Stannate
Zinc	Zincate

When you write the *formula* of a complex ion, write the symbol for the metal first, followed by neutral molecules and then anions. If there is more than one anion or neutral molecule acting as a ligand, list them in alphabetical order based on the chemical symbol.

PROCEDURE FOR...

Naming Coordination Compounds

Identify the cation and anion and first name the simple ion (i.e., not the complex one).

Give each ligand a name and list them in alphabetical order.

Name the metal ion.

Name the complex ion by adding prefixes to indicate the number of each ligand followed by the name of each ligand followed by the name of the metal ion.

Name the compound by writing the name of the cation before the anion. The only space is between ion names.

EXAMPLE 24.3

Naming Coordination Compounds

Name the following compound: [Cr(H₂O)₅Cl]Cl₂.

SOLUTION

[Cr(H₂O)₅Cl]²⁺ is a complex cation. Cl⁻ is chloride.

H₂O is aqua.

Cl⁻ is chloro.

Cr³⁺ is chromium(III).

[Cr(H₂O)₅Cl]²⁺ is pentaaquachlorochromium(III).

FOR PRACTICE 24.3

Name the following compound: [Mn(CO)(NH₃)₅]SO₄.

EXAMPLE 24.4

Naming Coordination Compounds

Name the following compound: K₃[Fe(CN)₆].

SOLUTION

K⁺ is potassium.

[Fe(CN)₆]³⁻ is a complex anion.

CN⁻ is cyano.

Fe³⁺ is ferrate(III) because the complex is anionic.

[Fe(CN)₆]³⁻ is hexacyanoferrate(III).

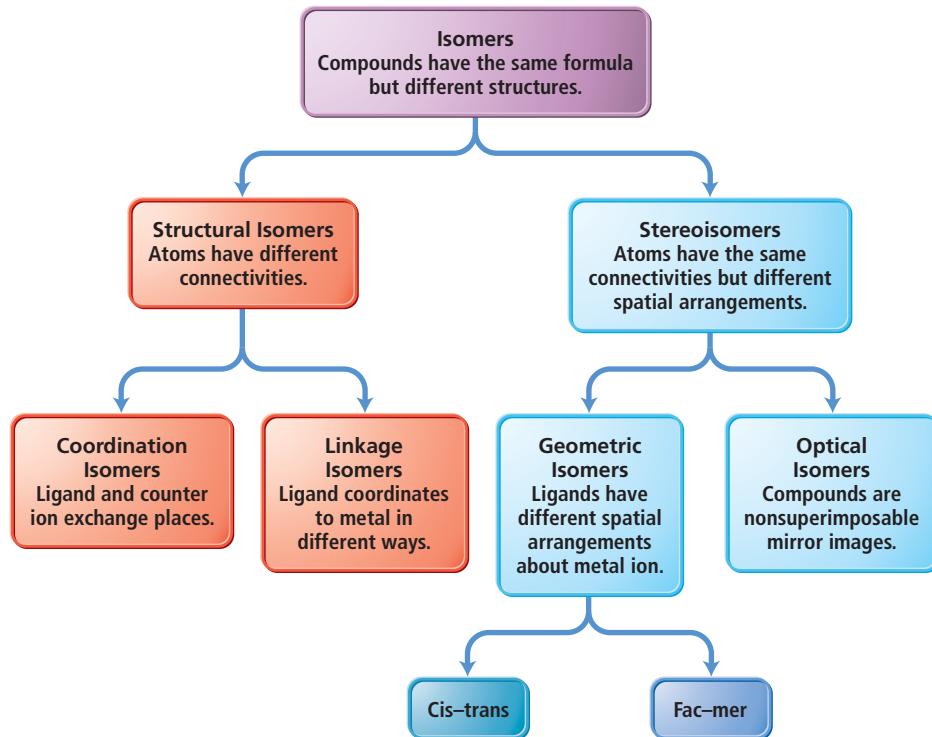
K₃[Fe(CN)₆] is potassium hexacyanoferrate(III).

FOR PRACTICE 24.4

Name the following compound: Na₂[PtCl₄].

24.4 Structure and Isomerization

Isomerism is common in coordination compounds. We broadly divide the isomerism observed in coordination compounds into two categories, each with subcategories, as shown in Figure 24.6 ▶. In **structural isomers**, atoms are connected to one another in different ways, whereas in **stereoisomers**, atoms are connected in the same way but the ligands have a different spatial arrangement about the metal atom.



▲ FIGURE 24.6 Types of Isomers

Structural Isomerism

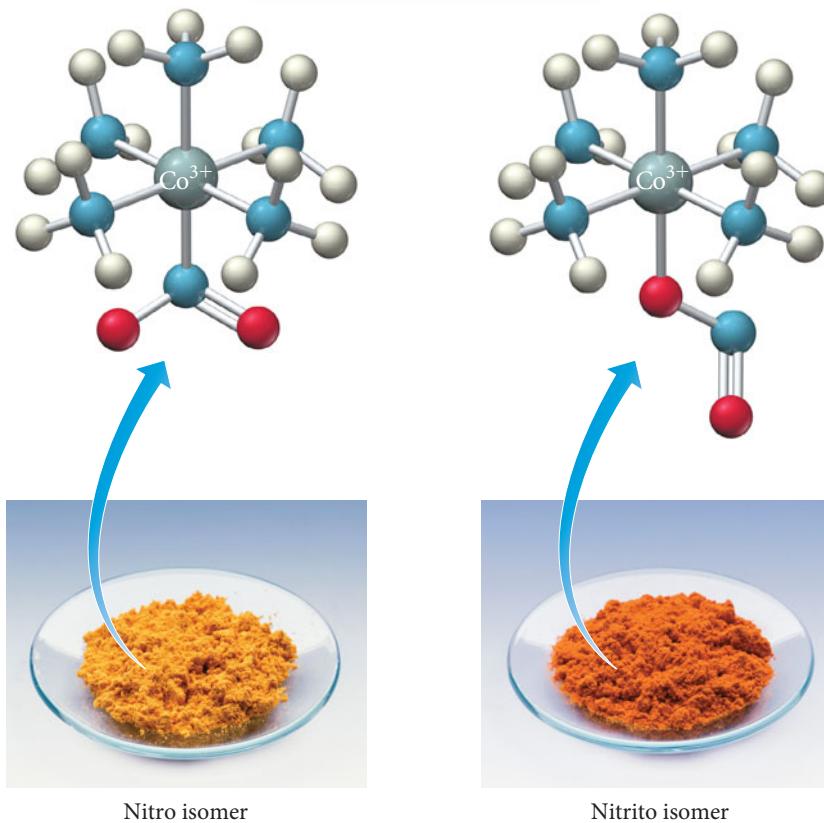
We can subdivide the broad category of structural isomers into two types: coordination isomers and linkage isomers. **Coordination isomers** occur when a coordinated ligand exchanges places with the uncoordinated counterion. For example, two different compounds have the general formula $\text{Co}(\text{NH}_3)_5 \text{BrCl}$. In one of them, the bromine coordinates to the metal and chloride is a counterion, pentaamminebromocobalt(II) chloride, $[\text{Co}(\text{NH}_3)_5 \text{Br}] \text{Cl}$; in the other one, the chlorine coordinates to the metal and bromide is the counterion, pentaamminechlorocobalt(II) bromide, $[\text{Co}(\text{NH}_3)_5 \text{Cl}] \text{Br}$.

Linkage isomers have ligands that can coordinate to the metal in different orientations. For example, the nitrite ion (NO_2^-) has a lone pair on the N atom as well as lone pairs on the O atoms—either of the two atoms can form coordinate covalent bonds with the metal. When the nitrite ion coordinates through the N atom it is a *nitro* ligand and is represented as NO_2^- , but when it coordinates through the O atom, it is a *nitrito* ligand and is usually represented as ONO^- . An example of linkage isomerization can be seen in the yellow-orange complex ion pentaaminenitrocobalt(III), $[\text{Co}(\text{NH}_3)_5 \text{NO}_2]^{2+}$, which contrasts with the red-orange complex ion pentaaminenitritocobalt(III), $[\text{Co}(\text{NH}_3)_5 \text{ONO}]^{2+}$, as shown in Figure 24.7 ►. Other ligands capable of linkage isomerization are listed in Table 24.6.

► **FIGURE 24.7** Linkage Isomers

In $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$, the NO_2^- ligand bonds to the central metal atom through the nitrogen atom. In $[\text{Co}(\text{NH}_3)_5\text{ONO}]^{2+}$, the NO_2^- ligand bonds through the oxygen atoms. The different isomers have different colors.

N-bond and O-bond NO_2^- ligand



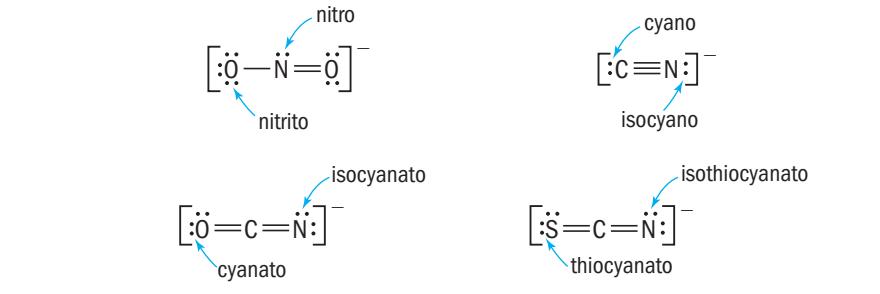
Nitro isomer

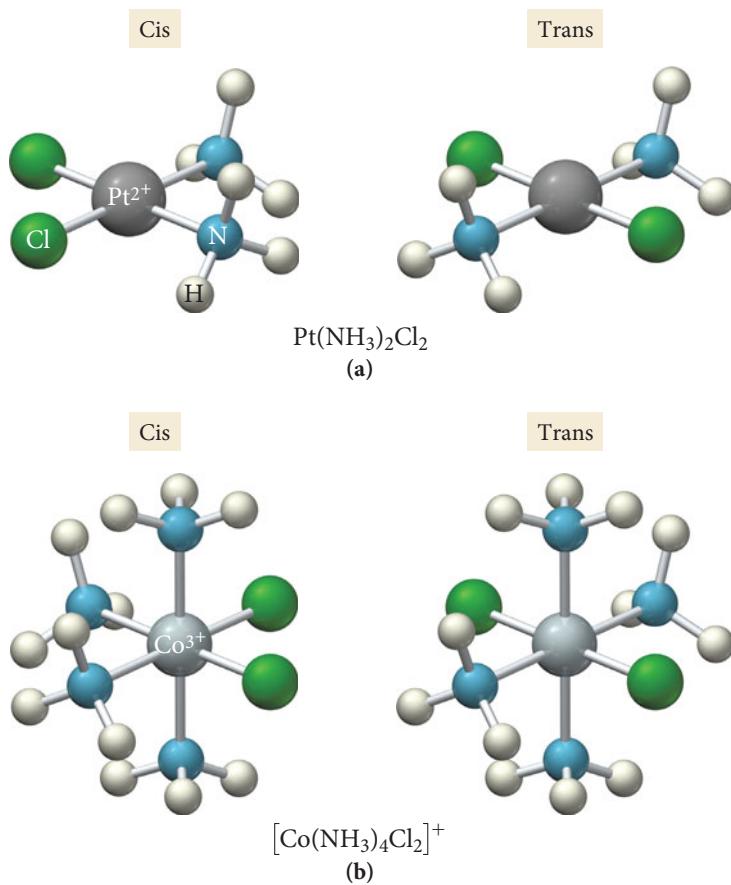
Nitrito isomer

Stereoisomerism

We can also subdivide the broad category of stereoisomers into two types: geometric isomers and optical isomers. **Geometric isomers** result when the ligands bonding to the metal have a different spatial arrangement. One type of geometric isomerism, as we saw in Section 20.5, is cis-trans isomerism, which in complex ions occurs in square planar complexes of the general formula MA_2B_2 or octahedral complexes of the general formula MA_4B_2 . For example, cis-trans isomerism occurs in the square planar complex $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$. Figure 24.8(a) ▶ shows the two distinct ways in which the ligands can be oriented around the metal. In one complex, the Cl^- ligands are next to each other on one side of the molecule—this is the cis isomer. In the other complex, the Cl^- ligands are on opposite sides of the molecule—this is the trans isomer. Geometric isomerism also exists in the octahedral complex ion $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$. As shown in Figure 24.8(b) ▶, the ligands arrange themselves around the metal in two ways, one with the Cl^- ligands on the same

TABLE 24.6 Ligands Capable of Linkage Isomerization

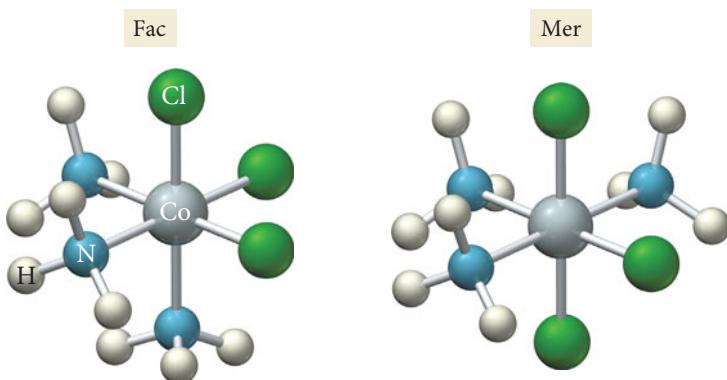




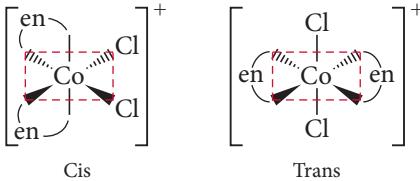
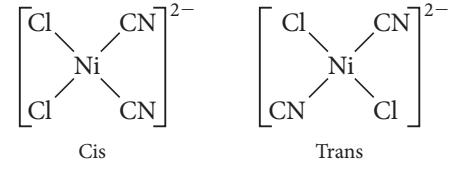
▲ FIGURE 24.8 Cis–trans Isomerism (a) Cis–trans isomerism in square planar $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$. In the cis isomer, the Cl^- ligands are next to each other on one side of the molecule. In the trans isomer, the Cl^- ligands are on opposite sides of the molecule. (b) Cis–trans isomerism in octahedral $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$. In the cis isomer, the Cl^- ligands are on the same side. In the trans isomer, the Cl^- ligands are on opposite sides.

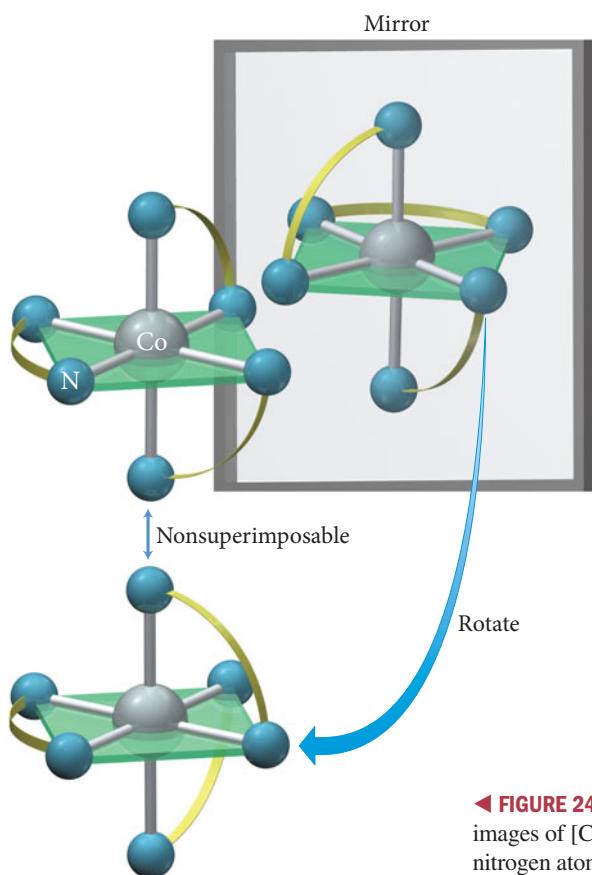
side (the cis isomer) and another with the Cl^- ligands on opposite sides of the metal (the trans isomer). Note that cis–trans isomerism does not occur in tetrahedral complexes because all bond angles around the metal are 109.5° , and each corner of a tetrahedron is considered to be adjacent to all three other corners.

Another type of geometric isomerism is fac–mer isomerism, which occurs in octahedral complexes of the general formula MA_3B_3 . For example, in $\text{Co}(\text{NH}_3)_3\text{Cl}_3$, the ligands arrange themselves around the metal in two ways (Figure 24.9 ▶). In the fac isomer the three Cl^- ligands are all on one side of the molecule and make up one face of the octahedron (fac is short for facial). In the mer isomer the three ligands form an arc around the middle of the octahedron (mer is short for meridian).



◀ FIGURE 24.9 Fac–Mer Isomerism in $\text{CO}(\text{NH}_3)_3\text{Cl}_3$ In the fac isomer, the three Cl^- ligands are all on one side of the molecule and make up one face of the octahedron. In the mer isomer, the three ligands inscribe an arc around the middle (or meridian) of the octahedron.

PROCEDURE FOR... Identifying and Drawing Geometric Isomers	EXAMPLE 24.5 Identifying and Drawing Geometric Isomers Draw the structures and label the type of all the isomers of $[\text{Co}(\text{en})_2\text{Cl}_2]^+$.	EXAMPLE 24.6 Identifying and Drawing Geometric Isomers Draw the structures and label the type for of the isomers of $[\text{Ni}(\text{CN})_2\text{Cl}_2]^{2-}$.
Identify the coordination number and the geometry around the metal.	SOLUTION The ethylenediamine (en) ligand is bidentate so each occupies two coordination sites. Each Cl^- is monodentate, occupying one site. The total coordination number is 6, so this must be an octahedral complex.	SOLUTION All the ligands are monodentate, so the total coordination number is 4. Ni^{2+} is a d^8 electronic configuration, so we expect a square planar complex.
Identify if this is cis-trans or fac-mer isomerism.	With ethylenediamine occupying four sites and Cl^- occupying two sites, it fits the general formula MA_4B_2 , leading to cis-trans isomers.	Square planar complexes can only have cis-trans isomers.
Draw and label the two isomers.		
	FOR PRACTICE 24.5 Draw the structures and label the type of all the isomers of $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3]^+$.	FOR PRACTICE 24.6 Draw the structures and label the type of all the isomers of $[\text{Co}(\text{NH}_3)_2\text{Cl}_2(\text{ox})]^-$.



◀ FIGURE 24.10 Optical Isomerism in $[\text{Co}(\text{en})_3]^{3+}$ The mirror images of $[\text{Co}(\text{en})_3]^{3+}$ are not superimposable. (The connected nitrogen atoms represent the ethylenediamine ligand.)

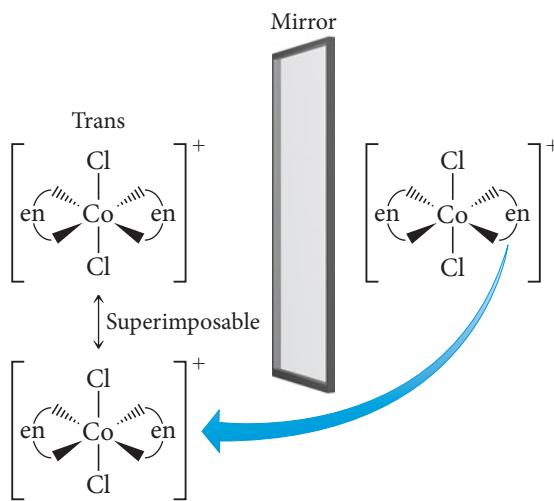
The second category of stereoisomerism is optical isomerism. Recall from Section 20.3 that **optical isomers** are nonsuperimposable mirror images of one another. If you hold your right hand up to a mirror, the image in the mirror looks like your left hand. No matter how you rotate or flip your left hand, you cannot superimpose it on your right hand. Molecules or ions that exhibit this quality are *chiral*. The isomers are *enantiomers*, and they exhibit the property of optical activity (the rotation of polarized light). The complex ion $[\text{Co}(\text{en})_3]^{3+}$ is nonsuperimposable on its mirror image, so it is a chiral complex (Figure 24.10 ◀).

EXAMPLE 24.7 Recognizing and Drawing Optical Isomers

Determine whether the cis or trans isomers in Example 24.5 are optically active (demonstrate optical isomerism).

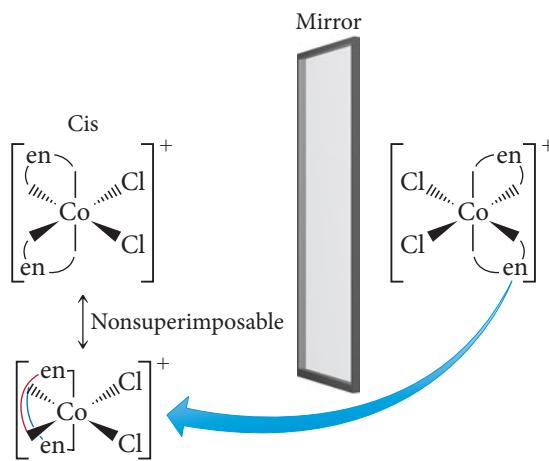
SOLUTION

Draw the trans isomer of $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ and its mirror image. Check to see if they are superimposable by rotating one isomer 180°.



In this case the two are identical, so there is no optical activity.

Draw the cis isomer and its mirror image. Check to see if they are superimposable by rotating one isomer 180°.



In this case the two structures are not superimposable, so the cis isomer does exhibit optical activity.

FOR PRACTICE 24.7

Determine whether the fac or mer isomers of $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3]^+$ are optically active.

The previous examples demonstrate optical isomerism in octahedral complexes. Tetrahedral complexes can also exhibit optical isomerism, but only if all four coordination sites are occupied by different ligands. Square planar complexes do not normally exhibit optical isomerism as they are superimposable on their mirror images.

24.5 Bonding in Coordination Compounds

Valence Bond Theory

The bonding in complex ions, particularly the geometries of the ions, can be described by one of our previous bonding models, valence bond theory. Recall from Section 10.6 that in valence bond theory, a coordinate covalent bond is the overlap between a completely

► **FIGURE 24.11** Common Hybridization Schemes in Complex Ions

The valence bond model hybridization schemes can be deduced from the geometry of the complex ion.

Geometry	Hybridization	Orbitals
Linear	sp	
Tetrahedral	sp^3	
Square planar	dsp^2	
Octahedral	d^2sp^3	

filled atomic orbital and an empty atomic orbital. In complex ions, the filled orbital is on the ligand, and the empty orbital is on the metal ion. The metal ion orbitals are hybridized according to the geometry of the complex ion. The common hybridization schemes are shown in Figure 24.11 ▲. An octahedral complex ion requires six empty orbitals in an octahedral arrangement on the metal ion. A full set of d^2sp^3 hybrid orbitals results in the exact orbitals needed for this geometry. A set of sp^3 hybrid orbitals results in a tetrahedral arrangement of orbitals, a set of dsp^2 hybrid orbitals results in a square planar arrangement, and a set of sp hybrid orbitals results in a linear arrangement of orbitals. In each case, the coordinate covalent bond is formed by the overlap between the orbitals on the ligands and the hybridized orbitals on the metal ion.

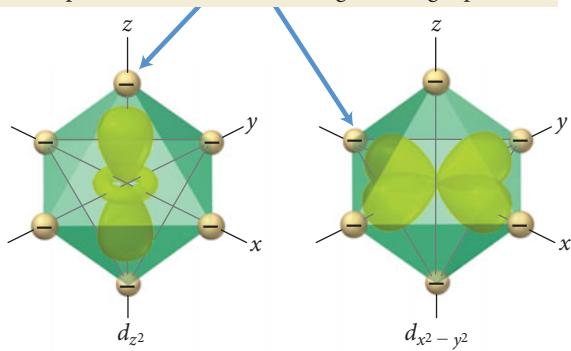
Crystal Field Theory

Valence bond theory, while useful for describing the geometries of the complex ions, cannot explain other properties such as color and magnetism. Crystal field theory (CFT), a bonding model for transition metal complexes, accounts for these properties. To illustrate the basic principles of CFT, we examine the central metal atom's d orbitals in an octahedral complex.

Octahedral Complexes

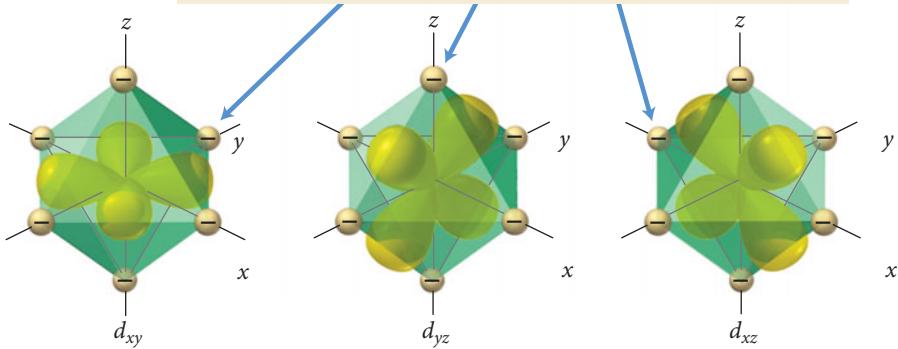
The basic premise of CFT is that complex ions form because of attractions between the electrons on the ligands and the positive charge on the metal ion. However, the electrons on the ligands also repel the electrons in the *unhybridized* metal d orbitals. CFT focuses on these repulsions. Figure 24.12 ► shows how the ligand positions superimpose on the d orbitals in an octahedral complex. Notice that the ligands in an octahedral complex are located in the same space as the lobes of the $d_{x^2-y^2}$ and d_z^2 orbitals. The repulsions *between* electron pairs in the ligands and any potential electrons in the d orbitals result in an increase in the energies of these orbitals. In contrast, the d_{xy} , d_{xz} , and d_{yz} orbitals lie *between* the axes and have nodes directly on the axes, which results in less repulsion and lower energies for these three orbitals. In other words, the d orbitals—which are degenerate in the bare metal ion—are split into higher and lower energy levels because of the spatial arrangement of the ligands (Figure 24.13 ►). The difference in energy between these split d orbitals is known as the crystal field splitting energy (Δ). The magnitude of the splitting depends on the particular complex. In **strong-field complexes**, the splitting is large; and in **weak-field complexes**, the splitting is small.

Ligands overlap with orbital lobes, resulting in strong repulsions.

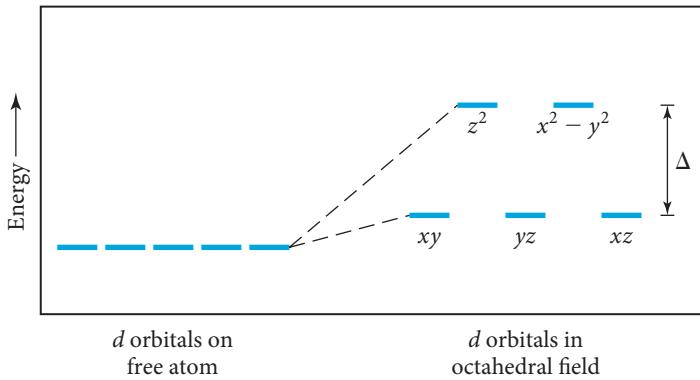


◀ **FIGURE 24.12** Relative Positions of *d* Orbitals and Ligands in an Octahedral Complex The ligands in an octahedral complex (represented here as spheres of negative charge) interact most strongly with the d_{z^2} and $d_{x^2-y^2}$ orbitals.

Ligands come in between orbital lobes, resulting in weak repulsions.

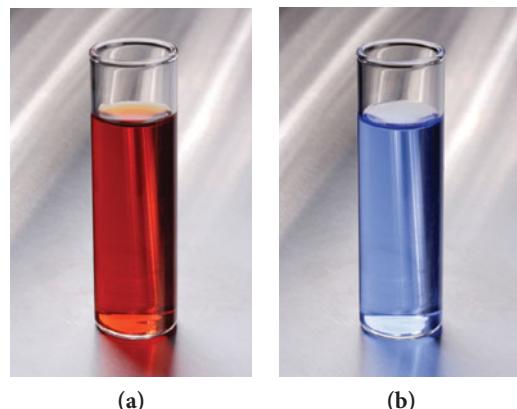


▼ **FIGURE 24.13** *d* Orbital Splitting in an Octahedral Field The otherwise degenerate *d* orbitals are split into two energy levels by the ligands in an octahedral complex ion.

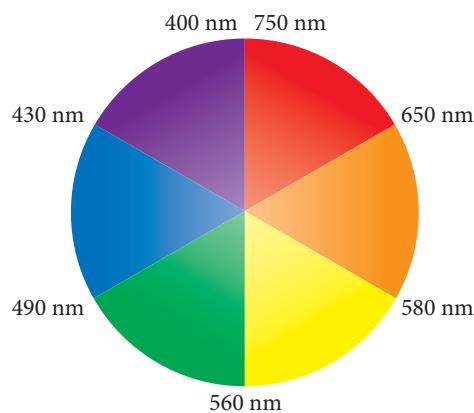


The Color of Complex Ions and Crystal Field Strength

We discussed in the opening section of this chapter that transition metals in host crystals often show brilliant colors because of the crystal field splitting of their *d* orbitals. Solutions of complex ions display brilliant colors because of similar splittings. For example, an $[\text{Fe}(\text{CN})_6]^{3-}$ solution is deep red, and an $[\text{Ni}(\text{NH}_3)_6]^{2+}$ solution is blue (Figure 24.14 ▶). Recall from Chapter 7 that the color of an object is related to the absorption of light energy by its electrons. If a substance absorbs all of the visible wavelengths, it appears black. If it transmits (or reflects) all the wavelengths (absorbs no light), it appears colorless. A substance appears to be a particular color if it absorbs some visible light but also transmits (or reflects) the wavelengths associated with that color. A substance also appears to be a given color if it transmits (or reflects) most wavelengths but absorbs the



▲ **FIGURE 24.14** Colors of Complex Ions (a) The complex ion $[\text{Fe}(\text{CN})_6]^{3-}$ forms a deep red solution, and (b) $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is blue.



▲ FIGURE 24.15 The Color Wheel

Colors across from one another on the color wheel are said to be complementary. A substance that absorbs a color on the wheel will appear to be its complementary color.

complementary color on a color wheel (Figure 24.15 ▲). For example, a substance that absorbs green light (the complement of red) will appear red. A solution of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is purple because it absorbs strongly between 490 and 580 nm, the yellow-green region of the visible spectrum (Figure 24.16a ▼).

The easiest way to measure the energy difference between the d orbitals in a complex ion is to use spectroscopy to determine the wavelength of light absorbed when an electron makes a transition from the lower energy d orbitals to the higher energy ones. With that information we can calculate the crystal field splitting energy, Δ :

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda} = \Delta$$

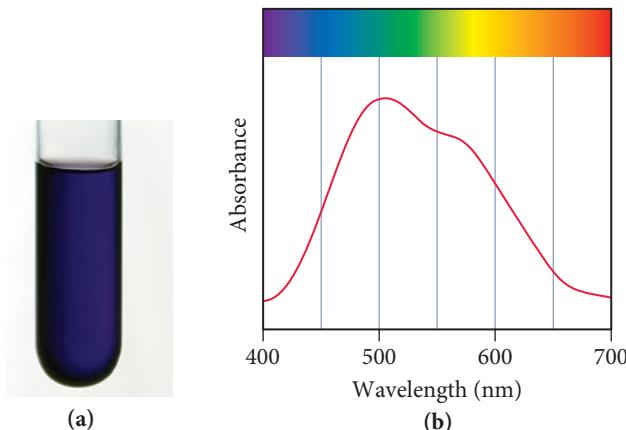
Consider the $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ absorption spectrum shown in Figure 24.16b. The maximum absorbance is at 498 nm. Using this wavelength, we calculate Δ :

$$\Delta = hc/\lambda = (6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})/(498 \text{ nm} \times 1 \times 10^{-9} \text{ m/nm})$$

$$\Delta = 3.99 \times 10^{-19} \text{ J}$$

This energy corresponds to a single $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion. We can convert to kilojoules per mole:

$$\Delta = (3.99 \times 10^{-19} \text{ J/ion})(6.02 \times 10^{23} \text{ ion/mol})(1 \text{ kJ}/1000 \text{ J}) = 240 \text{ kJ/mol}$$



► FIGURE 24.16 The Color and Absorption Spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$
 (a) A solution containing $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is purple. (b) The absorption spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ extends across the green-yellow region of the spectrum.

EXAMPLE 24.8 Crystal Field Splitting Energy

The complex ion $[\text{Cu}(\text{NH}_3)_6]^{2+}$ is blue in aqueous solution. Estimate the crystal field splitting energy (in kJ/mol) for this ion.

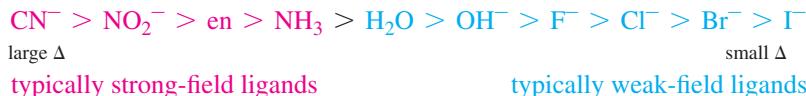
SOLUTION

Begin by consulting the color wheel to determine approximately what wavelength is being absorbed.	Since the solution is blue, you can deduce that orange light is absorbed since orange is the complementary color to blue.
Estimate the absorbed wavelength.	The color orange ranges from 580 to 650 nm, so you can estimate the average wavelength as 615 nm.
Calculate the energy corresponding to this wavelength, using $E = hc/\lambda$. This energy corresponds to Δ .	$E = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{(615 \text{ nm})(1 \times 10^{-9} \text{ m/nm})}$ $E = 3.23 \times 10^{-19} \text{ J} = \Delta$
Convert J/ion into kJ/mol.	$\Delta = \frac{(3.23 \times 10^{-19} \text{ J/ion})(6.02 \times 10^{23} \text{ ion/mol})}{(1000 \text{ J/kJ})}$ $\Delta = 195 \text{ kJ/mol}$

FOR PRACTICE 24.8

The complex ion $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$ is yellow. Estimate the crystal field splitting energy (in kJ/mol) for this ion.

The magnitude of the crystal field splitting in a complex ion—and, therefore whether it is a strong-field or a weak-field complex—depends in large part on the ligands attached to the central metal ion. Spectroscopic studies of various ligands attached to the same metal allow us to arrange different ligands in order of their ability to split the d orbitals. This list is known as the *spectrochemical series* and is arranged from ligands that result in the largest Δ to those that result in the smallest:



Ligands that produce large values of Δ are *strong-field ligands* and those that give small values of Δ are *weak-field ligands*.

The metal ion also has an effect on the magnitude of Δ . If we examine different metal ions with the same ligand, we find that Δ increases as the charge on the metal ion increases. The greater charge on the metal draws the ligands closer, causing greater repulsion with the d orbitals and therefore a larger Δ . An example of this behavior occurs in the complex ions between NH_3 (a ligand in the middle of the spectrochemical series) and the +2 or +3 oxidation states of cobalt. Hexaamminecobalt(II) ion, $[\text{Co}(\text{NH}_3)_6]^{2+}$, has a weak crystal field (small Δ) and hexaamminecobalt(III) ion, $[\text{Co}(\text{NH}_3)_6]^{3+}$, has a strong field (large Δ).

Conceptual Connection 24.2 Weak- and Strong-Field Ligands

Two ligands, A and B, both form complexes with a particular metal ion. When the metal ion complexes with ligand A, the resulting solution is red. When the metal ion complexes with ligand B, the resulting solution is yellow. Which of the two ligands produces the larger Δ ?

Magnetic Properties

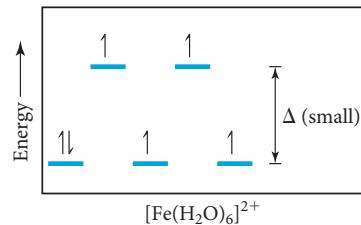
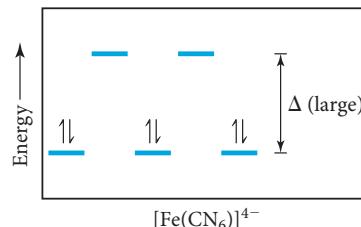
The strength of the crystal field can affect the magnetic properties of a transition metal complex. Recall that, according to Hund's rule, electrons occupy degenerate orbitals singly as long as an empty orbital is available. When the energies of the d orbitals are split by ligands, the lower energy orbitals fill first. Once they are half-filled, the next electron can either (1) pair with an electron in one of the lower energy half-filled orbitals by overcoming the electron–electron repulsion associated with having two electrons in the same orbital or (2) go into an empty orbital of higher energy by overcoming the energy difference between the orbitals—in this case, the crystal field splitting energy, Δ . The magnitude of Δ compared to the electron–electron repulsions determines which of these two actually occurs.

We can compare two iron(II) complexes to see the difference in behavior under strong- and weak-field conditions. $[\text{Fe}(\text{CN})_6]^{4-}$ is known to be diamagnetic and $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ is known to be paramagnetic. Both of these complexes contain Fe^{2+} , which has an electron configuration of $[\text{Ar}] 3d^6$. In the case of $[\text{Fe}(\text{CN})_6]^{4-}$, CN^- is a strong-field ligand that generates a large Δ , so it takes more energy to occupy the higher energy level than it does to pair the electrons in the lower energy level. The result is that all six electrons are paired and the compound is diamagnetic, as shown in the accompanying figure.

In $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, H_2O is a weak-field ligand that generates a small Δ , so the electron pairing energy is greater than Δ . Consequently, the first five electrons occupy the five d orbitals singly and only the sixth pairs up, resulting in a paramagnetic compound with four unpaired electrons, as shown in the accompanying figure.

In general, complexes with strong-field ligands have fewer unpaired electrons relative to the free metal ion and are therefore called **low-spin complexes**. Complexes with weak-field ligands, by contrast, have the same number of unpaired electrons as the free metal ion and are called **high-spin complexes**.

Recall from Section 8.7 that a paramagnetic species contains unpaired electrons and a diamagnetic one does not.

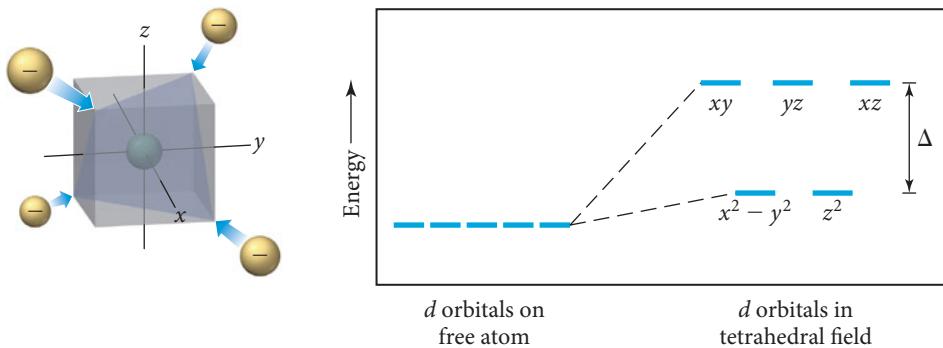


When we examine the orbital diagrams of the d^1 through d^{10} metal ions in octahedral complexes, we find that only d^4 , d^5 , d^6 , and d^7 metal ions have low- and high-spin possibilities. Since there are three lower energy d orbitals, the d^1 , d^2 , and d^3 metal ions always have unpaired electrons, independent of Δ . In the d^8 , d^9 , and d^{10} metal ions, the three lower energy orbitals are completely filled, so the remaining electrons fill the two higher orbitals (as expected according to Hund's rule), also independent of Δ .

PROCEDURE FOR...	EXAMPLE 24.9	EXAMPLE 24.10
Determining the Number of Unpaired Electrons in Octahedral Complexes	High- and Low-Spin Octahedral Complexes How many unpaired electrons are there in the complex ion $[\text{CoF}_6]^{3-}$?	High- and Low-Spin Octahedral Complexes How many unpaired electrons are there in the complex ion $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$?
Begin by determining the charge and number of d electrons on the metal.	SOLUTION The metal is Co^{3+} and has a d^6 electronic configuration.	SOLUTION The metal is Co^{3+} and has a d^6 electronic configuration.
Look at the spectrochemical series to determine whether the ligand is a strong-field or a weak-field ligand.	F^- is a weak-field ligand, so Δ is relatively small.	NH_3 and NO_2^- are both strong-field ligands, so Δ is relatively large.
Decide if the complex is high- or low-spin and draw the electron configuration. 	Weak-field ligands yield high-spin configurations.	Strong-field ligands yield low-spin configurations.
Count the unpaired electrons.	This configuration has four unpaired electrons.	This configuration has no unpaired electrons.
	FOR PRACTICE 24.9 How many unpaired electrons are there in the complex ion $[\text{FeCl}_6]^{3-}$?	FOR PRACTICE 24.10 How many unpaired electrons are there in the complex ion $[\text{Co}(\text{CN})_6]^{4-}$?

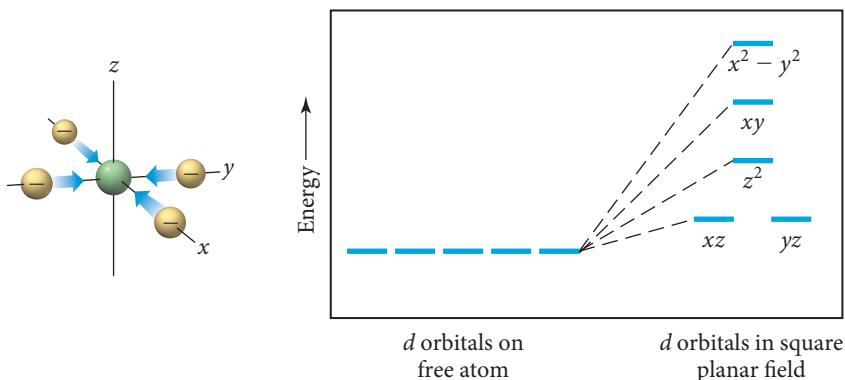
Tetrahedral and Square Planar Complexes

So far, we have examined the d orbital energy changes only for octahedral complexes, but transition metal complexes can have other geometries, such as tetrahedral and square planar. We use crystal field theory to determine the d orbital splitting pattern for these geometries as well. For a tetrahedral complex, the d orbital splitting pattern is the opposite of the octahedral splitting pattern: three d orbitals (d_{xy} , d_{xz} , and d_{yz}) are higher in energy, and two d orbitals ($d_{x^2-y^2}$ and d_{z^2}) are lower in energy (Figure 24.17 ▶). Almost all tetrahedral complexes are high-spin because of reduced ligand–metal interactions. The d orbitals in a tetrahedral complex interact with only four ligands, as opposed to six in the octahedral complex, so the value of Δ is generally smaller.



◀ FIGURE 24.17 Splitting of *d* Orbitals by a Tetrahedral Ligand Geometry In tetrahedral complexes, the splitting of the *d* orbitals has a pattern that is the opposite of the octahedral splitting pattern. The d_{xy} , d_{yz} , and d_{xz} orbitals are higher in energy than the d_{z^2} and $d_{x^2-y^2}$ orbitals.

A square planar complex gives us the most complex splitting pattern of the three geometries (Figure 24.18 ▶). As we discussed previously, square planar complexes occur in d^8 metal ions, such as Pt^{2+} , Pd^{2+} , Ir^+ , or Au^{3+} , and in nearly all cases they are low-spin.



◀ FIGURE 24.18 Splitting of *d* Orbitals by a Square Planar Ligand Geometry Square planar complexes produce the *d* orbital energy pattern shown here.

24.6 Applications of Coordination Compounds

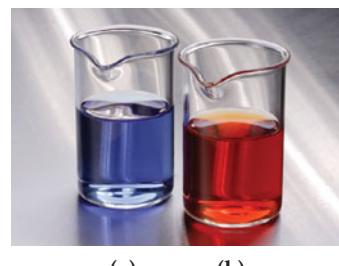
Coordination compounds are found in living systems, in industry, and even in household products. Recall from Chapter 23 how both silver and gold metals are extracted from their respective ores using cyanide complexes and how nickel metal is extracted by forming the gaseous carbonyl complex, $\text{Ni}(\text{CO})_4$. In this section we describe a few additional applications of coordination compounds.

Chelating Agents

In Section 24.3, we introduced the chelating agent ethylenediaminetetraacetate ion (EDTA^{4-}). This ligand has lone pairs on six different donor atoms that can interact with a metal ion to form very stable metal complexes. EDTA is used to treat the victims of heavy metal poisoning such as lead poisoning. The patient is given $[\text{Ca}(\text{EDTA})]^{2-}$ and since the lead complex ($K_f = 2 \times 10^{18}$) is more stable than the calcium complex ($K_f = 4 \times 10^{10}$), the lead displaces the calcium. The body excretes the lead complex and leaves behind the calcium, which is nontoxic (and is in fact a nutrient).

Chemical Analysis

Some ligands are selective in their binding, preferring specific metal ions; these ligands can be used in chemical analysis. For example, dimethylglyoxime (dmg) is used to chemically analyze a sample for Ni^{2+} or Pd^{2+} . In the presence of Ni^{2+} , an insoluble red precipitate forms, and in the presence of Pd^{2+} , an insoluble yellow precipitate forms. Similarly, the SCN^- ligand is used to test for Co^{2+} or Fe^{3+} . In the presence of Co^{2+} a blue solution forms, and in the presence of Fe^{3+} a deep red solution forms (Figure 24.19 ▶).



◀ FIGURE 24.19 Chemical Analysis with SCN^- (a) Blue indicates Co^{2+} . (b) Red indicates Fe^{3+} .

Coloring Agents

Because of the wide variety of colors found in coordination complexes, they are often used as coloring agents. For example, a commercially available agent, iron blue, is a mixture of the hexacyano complexes of iron(II) and iron(III). Iron blue is used in ink, paint, cosmetics (eye shadow), and blueprints.

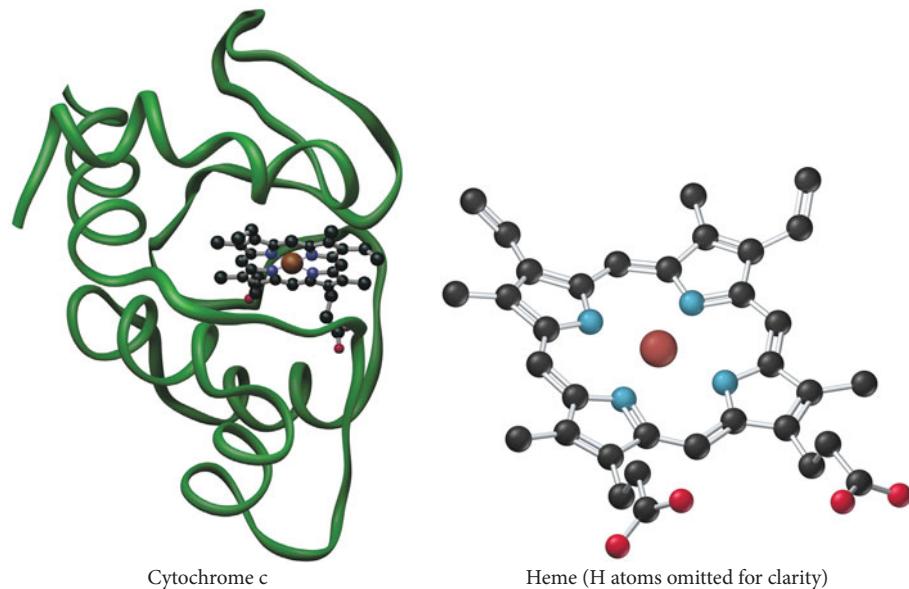
Biomolecules

Living systems contain many molecules based on metal complexes. Hemoglobin (involved in oxygen transport), cytochrome c (involved in electron transport), carbonic anhydrase (involved in respiration), and chlorophyll (involved in photosynthesis) all have coordinated metal ions that are critical to their structure and function. Table 24.7 summarizes the biological significance of many of the other first-row transition metals.

TABLE 24.7 Transition Metals and Some of Their Functions in the Human Body

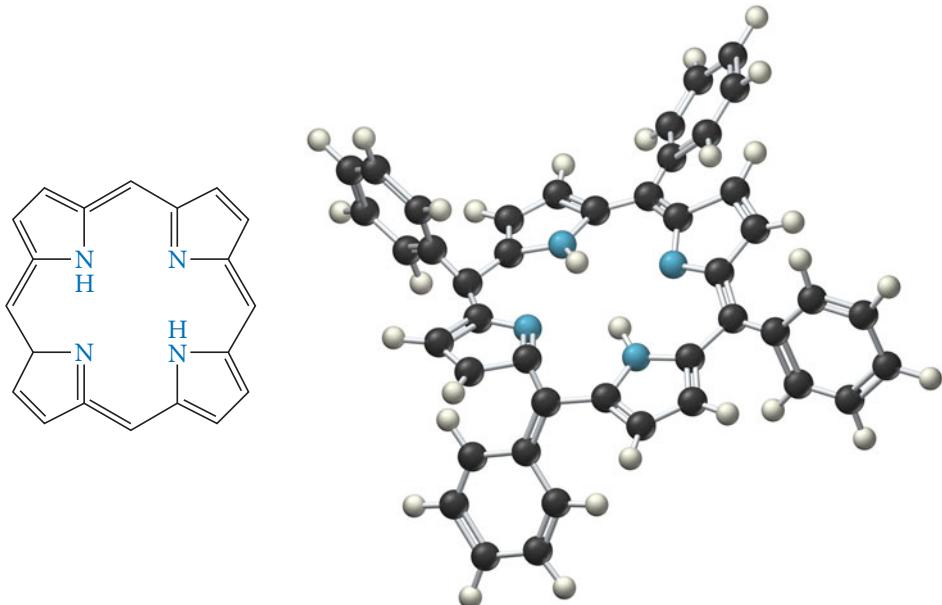
Transition Metal	Biological Function
Chromium	Works with insulin to control utilization of glucose
Manganese	Fat and carbohydrate synthesis
Molybdenum	Involved in hemoglobin synthesis
Iron	Oxygen transport
Copper	Involved in hemoglobin synthesis
Zinc	Involved in cell reproduction and tissue growth; part of more than 70 enzymes; assists in the utilization of carbohydrate, protein, and fat

Hemoglobin and Cytochrome C In hemoglobin and in cytochrome c, an iron complex called a heme is connected to a protein, as shown in the figure below. A heme is an iron ion coordinated to a flat, polydentate ligand called a porphyrin (Figure 24.20 ►). The porphyrin ligand has a planar ring structure with four nitrogen atoms that can coordinate to the metal ion. Different porphyrins have different substituent groups connected around the outside of the ring.

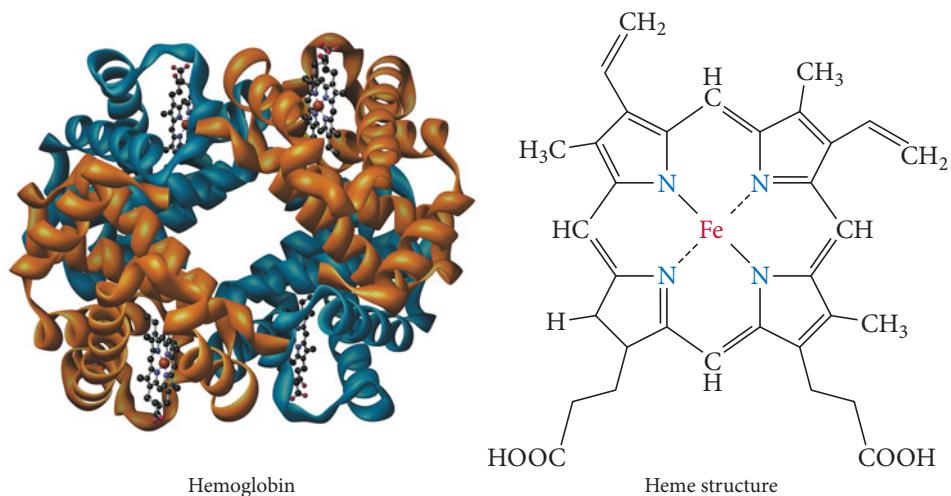


Hemoglobin is discussed in Sections 1.1 and 14.1.

In hemoglobin, the iron complex is octahedral, with the four nitrogen atoms of the porphyrin in a square planar arrangement around the metal. A nitrogen atom from a nearby amino acid of the protein occupies the fifth coordination site, and either O₂ or H₂O occupies the last coordination site (Figure 24.21 ►). In the lungs, where the oxygen content is high, the hemoglobin coordinates to an O₂ molecule. The oxygen-rich



◀ FIGURE 24.20 Porphyrin A porphyrin has four nitrogen atoms that can coordinate to a central metal atom.

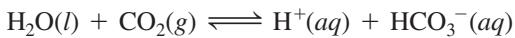


◀ FIGURE 24.21 Hemoglobin In hemoglobin, the iron complex is octahedral, with the four nitrogen atoms of the porphyrin in a square planar arrangement around the metal. A nitrogen atom from a nearby amino acid of the protein occupies the fifth coordination site, and either O₂ or H₂O occupies the last coordination site.

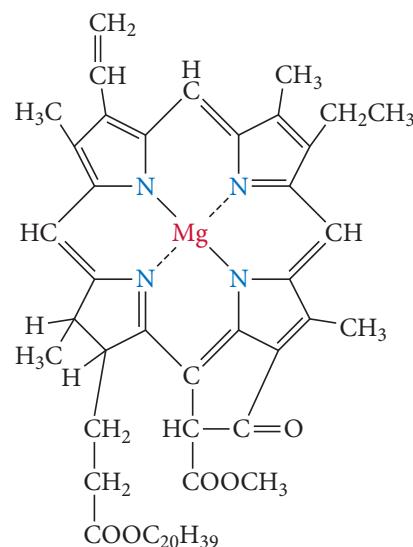
hemoglobin is carried by the bloodstream to areas throughout the body that are depleted in oxygen, where oxygen is released and replaced by a water molecule. The hemoglobin then travels back to the lungs to repeat the cycle.

Chlorophyll Chlorophyll, shown in Figure 24.22 ▶, is another porphyrin-based biomolecule, but in chlorophyll the porphyrin is not surrounded by a protein, and the coordinated metal is magnesium (which is not a transition metal). Chlorophyll is essential for photosynthesis process performed by plants, in which light energy from the sun is converted to chemical energy to fuel the plant's growth.

Carbonic Anhydrase In carbonic anhydrase, the zinc ion is bound in a tetrahedral complex, with three of the coordination sites occupied by nitrogen atoms from surrounding amino acids and the fourth site available to bind a water molecule (Figure 24.23 ▶). Carbonic anhydrase catalyzes the reaction between water and CO₂ in respiration.



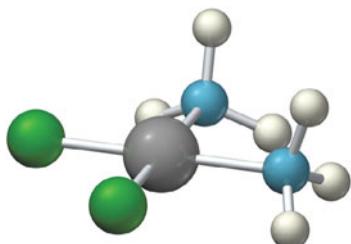
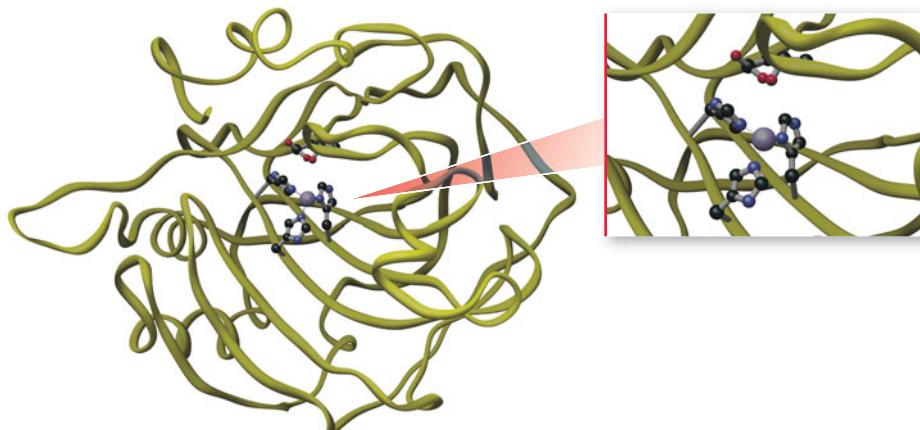
A water molecule alone is not acidic enough to react with a CO₂ molecule at a sufficient rate. When the water molecule is bound to the zinc ion in carbonic anhydrase, the positive charge on the metal draws electron density from the O—H bond and the H₂O becomes more acidic—sufficiently so to readily lose a proton. The resulting bound OH⁻ easily reacts with a CO₂ molecule, and the reaction is much faster than the uncatalyzed version.



◀ FIGURE 24.22 Chlorophyll Chlorophyll, involved in photosynthesis in plants, contains magnesium coordinated to a porphyrin.

► FIGURE 24.23 Carbonic Anhydrase

Carbonic anhydrase contains a zinc ion that is bound in a tetrahedral complex, with three of the coordination sites occupied by nitrogen atoms from surrounding amino acids. The fourth site is available to bind a water molecule.



▲ FIGURE 24.24 Cisplatin Cisplatin is an effective anticancer agent.

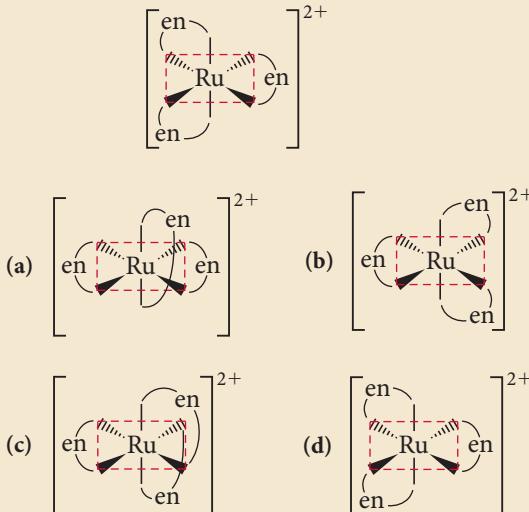
Drugs and Therapeutic Agents In the mid-1960s researchers found that the platinum(II) complex *cis*-[Pt(NH₃)₂Cl₂], known as cisplatin, is an effective anticancer agent (Figure 24.24). Interestingly, the closely related geometric isomer *trans*-[Pt(NH₃)₂Cl₂] has little or no effect on cancer tumors. Cisplatin is believed to function by attaching itself to the cancer cell's DNA and replacing the Cl⁻ ligands with donor atoms from the DNA strands. The *cis* arrangement of the Cl⁻ ligands corresponds to the geometry required to bind to the DNA strands. The *trans* isomer, although closely related, cannot bind properly due to the arrangement of the Cl⁻ ligands and is therefore not an effective agent. Cisplatin and other closely related platinum(II) complexes are still used today in chemotherapy for certain types of cancer and are among the most effective anticancer agents available for these cases.

CHAPTER IN REVIEW

Self Assessment Quiz

- Q1.** What is the electron configuration of the Cu⁺ ion?
 a) [Ar]4s²3d⁹ b) [Ar]4s²3d⁸
 c) [Ar]4s¹3d⁹ d) [Ar]4s⁰3d¹⁰
- Q2.** Which metal has the highest first ionization energy?
 a) Ti b) Mn
 c) Ru d) Au
- Q3.** What is the name of the compound [CoCl(NH₃)₅]Cl₂?
 a) pentaaminetrichlorocobalt(III) chloride
 b) pentaaminechlorocobalt(III) chloride
 c) pentaaminechlorocobalt(II) chloride
 d) pentaaminetrichlorocobalt(II) chloride
- Q4.** What is the formula of hexaaquamanganese(II) sulfate?
 a) [Mn(OH)₆]SO₄ b) [Mn(H₂O)₆]SO₄
 c) [Mn(H₂O)₆]₂SO₄ d) [Mn₂(H₂O)₆]SO₄
- Q5.** Which complex ion can exhibit geometric isomerism?
 Assume that M is the metal ion, A and B are ligands, and the geometry is octahedral.
 a) [MA₆]²⁺ b) [MA₅B]²⁺
 c) [MA₄B₂]²⁺ d) [MA₃B₃]²⁺

- Q6.** Pick the optical isomer of the complex ion represented here:



- Q7.** According to valence bond theory, what is the hybridization of the central metal ion in an octahedral complex ion?
- sp
 - sp^3
 - dsp^2
 - d^2sp^3
- Q8.** Estimate the crystal field splitting energy (in kJ/mol) for a complex ion that is red in solution.
- 228 kJ/mol
 - 171 kJ/mol
 - 2.84×10^{-19} kJ/mol
 - 3.79×10^{-19} kJ/mol

- Q9.** Use crystal field theory to determine the number of unpaired electrons in the complex ion $[Fe(CN)_6]^{4-}$.
- 0
 - 2
 - 3
 - 4

- Q10.** Which complex ion is diamagnetic?
- $[Cr(H_2O)_4Cl_2]^+$
 - $[Fe(H_2O)_6]^{2+}$
 - $[Co(NH_3)_6]^{3+}$
 - $[CoCl_6]^{3-}$

Answers: 1. (d) 2. (d) 3. (b) 4. (b) 5. (c) 6. (q) 7. (d) 8. (a) 9. (a) 10. (c)

Key Terms

Section 24.1

crystal field theory (1100)

Section 24.2

lanthanide contraction (1102)

Section 24.3

complex ion (1104)

ligand (1104)

coordination compound (1104)

primary valence (1104)
secondary valence (1104)
coordination number (1104)
coordinate covalent bond (1104)
monodentate (1104)
bidentate (1104)
polydentate (1105)
chelate (1106)

chelating agent (1106)

Section 24.4

structural isomers (1109)
stereoisomers (1109)
coordination isomers (1109)
linkage isomers (1109)
geometric isomers (1110)
optical isomers (1112)

Section 24.5

strong-field complex (1114)
weak-field complex (1114)
low-spin complex (1117)
high-spin complex (1117)

Key Concepts

Electron Configurations (24.2)

- As we move across a row of transition elements, we add electrons to the $(n - 1)d$ orbitals, resulting in a general electron configuration for first- and second-row transition elements of [noble gas] $ns^2(n - 1)d^x$ and for the third and fourth rows of [noble gas] $ns^2(n - 2)f^{14}(n - 1)d^x$, where x ranges from 1 to 10.
- A transition element forms a cation by losing electrons from the ns orbitals before losing electrons from the $(n - 1)d$ orbitals.

Periodic Trends (24.2)

- The variations in atomic size, ionization energy, and electronegativity across a row in the periodic table are similar to those of main-group elements (although the trends are less pronounced and less regular). As we move down a group, however, atomic size increases from the first row to the second but stays roughly constant from the second row to the third because of the lanthanide contraction. This contraction results in ionization energy and electronegativity trends as we move down a column that are opposite of the main group elements.

Composition and Naming of Coordination Compounds (24.3)

- A coordination compound is composed of a complex ion and a counterion.
- A complex ion contains a central metal ion bound to one or more ligands. The number of ligands directly bound to the metal ion is called the coordination number.
- The ligand forms a coordinate covalent bond to the metal ion by donating a pair of electrons to an empty orbital on the metal.

- Ligands that donate a single pair of electrons are monodentate. A ligand that donates two pairs of electrons is bidentate, and a ligand that donates more than two pairs is polydentate.
- In naming coordination compounds, we use the name of the cation followed by the name of the anion. To name a complex ion we use the guidelines outlined in Section 24.3.

Types of Isomers (24.4)

- We broadly divide the isomerism observed in coordination compounds into two categories: structural isomers, in which atoms are connected differently to one another, and stereoisomers, in which atoms are connected in the same way but the ligands have a different spatial arrangement about the metal atom.
- Structural isomers are either coordination isomers (a coordinated ligand exchanges places with an uncoordinated counterion) or linkage isomers (a particular ligand has the ability to coordinate to the metal in different ways).
- Stereoisomers are either geometric isomers (the ligands bonded to the metal have a different spatial arrangement relative to each other, leading to cis-trans or fac-mer isomers) or optical isomers (nonsuperimposable mirror images of one another).

Crystal Field Theory (24.5)

- Crystal field theory is a bonding model for transition metal complex ions. The model describes how the degeneracy of the d orbitals is broken by the repulsive forces between the electrons on the ligands around the metal ion and the d orbitals in the metal ion.

- The energy difference between the split d orbitals is the crystal field splitting energy (Δ). The magnitude of Δ depends in large part on the ligands bound to the metal.
- Octahedral complexes with a d^4 , d^5 , d^6 , or d^7 metal ion can have two possible electronic configurations with different numbers of

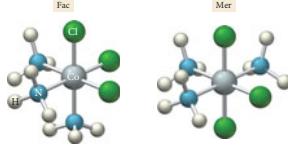
unpaired electrons. The first, called high-spin, has the same number of unpaired electrons as the free metal ion and is usually the result of a weak crystal field. The second, called low-spin, has fewer unpaired electrons than the free metal ion and is usually the result of a strong crystal field.

Key Equations and Relationships

Crystal Field Splitting Energy (24.5)

$$\Delta = hc/\lambda \text{ (where } \lambda \text{ is the wavelength of maximum absorption)}$$

Key Learning Outcomes

Chapter Objectives	Assessment
Writing Electronic Configurations for Transition Metals and Their Ions (24.2)	Examples 24.1, 24.2 For Practice 24.1, 24.2 Exercises 19–20, 57, 58
Naming Coordination Compounds (24.3)	Examples 24.3, 24.4 For Practice 24.3, 24.4 Exercises 23–28
Recognizing and Drawing Geometric Isomers (24.4)	Examples 24.5, 24.6 For Practice 24.5, 24.6 Exercises 5–40, 61–62
 Fac: A ball-and-stick model of a fac octahedral complex. It shows a central grey sphere (metal) bonded to three green spheres (chloride ligands) in a horizontal row, and three blue spheres (ammonia ligands) above and below the row. A label "Fac" is above the model. Mer: A ball-and-stick model of a mer octahedral complex. It shows a central grey sphere (metal) bonded to one green sphere (chloride ligand) at the top, and one blue sphere (ammonia ligand) and one white sphere (water ligand) to its left and right respectively. A label "Mer" is above the model.	
Recognizing and Drawing Optical Isomers (24.4)	Example 24.7 For Practice 24.7 Exercises 39–40, 61–62
Calculating Crystal Field Splitting Energy (24.5)	Example 24.8 For Practice 24.8 Exercises 43–46
 (a) A test tube containing a red liquid. (b) A test tube containing a blue liquid.	
Recognizing and Predicting High-Spin and Low-Spin Octahedral Complex Ions (24.5)	Examples 24.9, 24.10 For Practice 24.9, 24.10 Exercises 49–52, 65

EXERCISES

Review Questions

- When a transition metal atom forms an ion, which electrons are lost first?
- Explain why transition metals exhibit multiple oxidation states instead of a single oxidation state (like most of the main-group metals).
- Why is the +2 oxidation state so common for transition metals?
- Explain why atomic radii of elements in the third row of the transition metals are no larger than those of elements in the second row.
- Gold is the most electronegative transition metal. Explain.
- Briefly define each term.
 - coordination number
 - ligand
 - bidentate and polydentate
 - complex ion
 - chelating agent

7. Using the Lewis acid-base definition, how would you categorize a ligand? How would you categorize a transition metal ion?
8. Explain the differences between each pair of isomer types.
 - a. structural isomer and stereoisomer
 - b. linkage isomer and coordination isomer
 - c. geometric isomer and optical isomer
9. Which complex ion geometry has the potential to exhibit cis-trans isomerism: linear, tetrahedral, square planar, octahedral?
10. How can you tell whether a complex ion is optically active?
11. Explain the differences between weak-field and strong-field metal complexes.
12. Explain why compounds of Sc^{3+} are colorless, but compounds of Ti^{3+} are colored.
13. Explain why compounds of Zn^{2+} are white, but compounds of Cu^{2+} are often blue or green.
14. Explain the differences between high-spin and low-spin metal complexes.
15. Why are almost all tetrahedral complexes high-spin?
16. Many transition metal compounds are colored. How does crystal field theory account for this?

Problems by Topic

Properties of Transition Metals

17. Write the ground state electron configuration for each atom and ion pair.
 - a. Ni, Ni^{2+}
 - b. Mn, Mn^{4+}
 - c. Y, Y^+
 - d. Ta, Ta^{2+}
18. Write the ground state electron configuration for each atom and ion pair.
 - a. Zr, Zr^{2+}
 - b. Co, Co^{2+}
 - c. Tc, Tc^{3+}
 - d. Os, Os^{4+}
19. Determine the highest possible oxidation state for each element.
 - a. V
 - b. Re
 - c. Pd
20. Which first-row transition metal(s) has the following highest possible oxidation state?
 - a. +3
 - b. +7
 - c. +4

Coordination Compounds

21. Determine the oxidation state and coordination number of the metal ion in each complex ion.
 - a. $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
 - b. $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]^-$
 - c. $[\text{Cu}(\text{CN})_4]^{2-}$
 - d. $[\text{Ag}(\text{NH}_3)_2]^+$
22. Determine the oxidation state and coordination number of the metal ion in each complex ion.
 - a. $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$
 - b. $[\text{Fe}(\text{CN})_6]^{4-}$
 - c. $[\text{Co}(\text{ox})_3]^{4-}$
 - d. $[\text{PdCl}_4]^{2-}$
23. Name each complex ion or coordination compound.
 - a. $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
 - b. $[\text{Cu}(\text{CN})_4]^{2-}$
 - c. $[\text{Fe}(\text{NH}_3)_5\text{Br}]\text{SO}_4$
 - d. $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)(\text{OH})]\text{Cl}_2$

24. Name each complex ion or coordination compound.

- a. $[\text{Cu}(\text{en})_2]^{2+}$
- b. $[\text{Mn}(\text{CO})_3(\text{NO}_2)_3]^{2+}$
- c. $\text{Na}[\text{Cr}(\text{H}_2\text{O})_2(\text{ox})_2]$
- d. $[\text{Co}(\text{en})_3][\text{Fe}(\text{CN})_6]$

25. Write the formula for each complex ion or coordination compound.

- a. hexaaamminechromium(III)
- b. potassium hexacyanoferrate(III)
- c. ethylenediaminedithiocyanatocupper(II)
- d. tetraaquaplatinum(II) hexachloroplatinate(IV)

26. Write the formula for each complex ion or coordination compound.

- a. hexaaquanickel(II) chloride
- b. pentacarbonylchloromanganese(I)
- c. ammonium diaquatetrabromovanadate(III)
- d. tris(ethylenediamine)cobalt(III) trioxalatoferrate(III)

27. Write the formula and the name of each complex ion.

- a. a complex ion with Co^{3+} as the central ion and three NH_3 molecules and three CN^- ions as ligands
- b. a complex ion with Cr^{3+} as the central ion and a coordination number of 6 with ethylenediamine ligands

28. Write the formula and the name of each complex ion or coordination compound.

- a. a complex ion with four water molecules and two ONO^- ions connected to an Fe(III) ion
- b. a coordination compound made of two complex ions: one a complex of V(III) with two ethylenediamine molecules and two Cl^- ions as ligands and the other a complex of Ni(II) having a coordination number of 4 with Cl^- ions as ligands

Structure and Isomerism

29. Draw two linkage isomers of $[\text{Mn}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$.
30. Draw two linkage isomers of $[\text{PtCl}_3(\text{SCN})]^{2-}$.
31. Write the formulas and names for the coordination isomers of $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_2$.
32. Write the formulas and names for the coordination isomers of $[\text{Co}(\text{en})_3][\text{Cr}(\text{ox})_3]$.
33. Which complexes exhibit geometric isomerism?

a. $[\text{Cr}(\text{NH}_3)_5(\text{OH})]^{2+}$	b. $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$
c. $[\text{Cr}(\text{H}_2\text{O})(\text{NH}_3)_3\text{Cl}_2]^{+}$	d. $[\text{Pt}(\text{NH}_3)\text{Cl}_3]^-$
e. $[\text{Pt}(\text{H}_2\text{O})_2(\text{CN})_2]$	

34. Which complexes exhibit geometric isomerism?
- $[\text{Co}(\text{H}_2\text{O})_2(\text{ox})_2]^-$
 - $[\text{Co}(\text{en})_3]^{3+}$
 - $[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_2(\text{ox})]^+$
 - $[\text{Ni}(\text{NH}_3)_2(\text{en})]^{2+}$
 - $[\text{Ni}(\text{CO})_2\text{Cl}_2]$
35. If W, X, Y, and Z are different monodentate ligands, how many geometric isomers are there for each ion?
- square planar $[\text{NiWXYZ}]^{2+}$
 - tetrahedral $[\text{ZnWXYZ}]^{2+}$
36. How many geometric isomers are there for each species?
- $[\text{Fe}(\text{CO})_3\text{Cl}_3]$
 - $[\text{Mn}(\text{CO})_2\text{Cl}_2\text{Br}_2]^{+}$
37. Draw the structures and label the type for all the isomers of each ion.
- $[\text{Cr}(\text{CO})_3(\text{NH}_3)_3]^{3+}$
 - $[\text{Pd}(\text{CO})_2(\text{H}_2\text{O})\text{Cl}]^+$
38. Draw the structures and label the type for all the isomers of each species.
- $[\text{Fe}(\text{CO})_4\text{Cl}_2]^{+}$
 - $[\text{Pt}(\text{en})\text{Cl}_2]$
39. Determine if either isomer of $[\text{Cr}(\text{NH}_3)_2(\text{ox})_2]^-$ is optically active.
40. Determine if either isomer of $[\text{Fe}(\text{CO})_3\text{Cl}_3]$ is optically active.
41. Draw the octahedral crystal field splitting diagram for each metal ion.
- Zn^{2+}
 - Fe^{3+} (high- and low-spin)
 - V^{3+}
 - Co^{2+} (high-spin)
42. Draw the octahedral crystal field splitting diagram for each metal ion.
- Cr^{3+}
 - Cu^{2+}
 - Mn^{3+} (high- and low-spin)
 - Fe^{2+} (low-spin)
43. The $[\text{CrCl}_6]^{3-}$ ion has a maximum in its absorption spectrum at 735 nm. Calculate the crystal field splitting energy (in kJ/mol) for this ion.
44. The absorption spectrum of the complex ion $[\text{Rh}(\text{NH}_3)_6]^{3+}$ has maximum absorbance at 295 nm. Calculate the crystal field splitting energy (in kJ/mol) for this ion.
45. Three complex ions of cobalt(III), $[\text{Co}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, and $[\text{CoF}_6]^{3-}$, absorb light at wavelengths of (in no particular order) 290 nm, 440 nm, and 770 nm. Match each complex ion to the appropriate wavelength absorbed. What color would you expect each solution to be?
46. Three bottles of aqueous solutions are discovered in an abandoned lab. The solutions are green, yellow, and purple. It is known that three complex ions of chromium(III) were commonly used in that lab: $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Cr}(\text{NH}_3)_6]^{3+}$, and $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^{+}$. Determine the likely identity of each of the colored solutions.
47. The $[\text{Mn}(\text{NH}_3)_6]^{2+}$ ion is paramagnetic with five unpaired electrons. The NH_3 ligand is usually a strong field ligand. Is NH_3 acting as a strong field ligand in this case?
48. The complex $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ is paramagnetic. Is the H_2O ligand inducing a strong or weak field?
49. How many unpaired electrons would you expect for each complex ion?
- $[\text{RhCl}_6]^{3-}$
 - $[\text{Co}(\text{OH})_6]^{4-}$
 - cis*- $[\text{Fe}(\text{en})_2(\text{NO}_2)_2]^{+}$
50. How many unpaired electrons would you expect for each complex ion?
- $[\text{Cr}(\text{CN})_6]^{4-}$
 - $[\text{MnF}_6]^{4-}$
 - $[\text{Ru}(\text{en})_3]^{2+}$
51. How many unpaired electrons would you expect for the complex ion $[\text{CoCl}_4]^{2-}$ if it is a tetrahedral shape?
52. The complex ion $[\text{PdCl}_4]^{2-}$ is known to be diamagnetic. Use this information to determine if it is a tetrahedral or square planar structure.

Bonding in Coordination Compounds

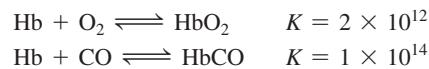
41. Draw the octahedral crystal field splitting diagram for each metal ion.
- Zn^{2+}
 - Fe^{3+} (high- and low-spin)
 - V^{3+}
 - Co^{2+} (high-spin)
42. Draw the octahedral crystal field splitting diagram for each metal ion.
- Cr^{3+}
 - Cu^{2+}
 - Mn^{3+} (high- and low-spin)
 - Fe^{2+} (low-spin)
43. The $[\text{CrCl}_6]^{3-}$ ion has a maximum in its absorption spectrum at 735 nm. Calculate the crystal field splitting energy (in kJ/mol) for this ion.
44. The absorption spectrum of the complex ion $[\text{Rh}(\text{NH}_3)_6]^{3+}$ has maximum absorbance at 295 nm. Calculate the crystal field splitting energy (in kJ/mol) for this ion.
45. Three complex ions of cobalt(III), $[\text{Co}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, and $[\text{CoF}_6]^{3-}$, absorb light at wavelengths of (in no particular order) 290 nm, 440 nm, and 770 nm. Match each complex ion to the appropriate wavelength absorbed. What color would you expect each solution to be?

Cumulative Problems

57. Recall from Chapter 8 that Cr and Cu are exceptions to the normal orbital filling, resulting in a $[\text{Ar}]4s^13d^x$ configuration. Write the ground state electron configuration for each species.
- $\text{Cr}, \text{Cr}^+, \text{Cr}^{2+}, \text{Cr}^{3+}$
 - $\text{Cu}, \text{Cu}^+, \text{Cu}^{2+}$
58. Most of the second row transition metals do not follow the normal orbital filling pattern. Five of them—Nb, Mo, Ru, Rh, and Ag—have a $[\text{Kr}]5s^14d^x$ configuration and Pd has a $[\text{Kr}]4d^{10}$ configuration. Write the ground state electron configuration for each species.
- $\text{Mo}, \text{Mo}^+, \text{Ag}, \text{Ag}^+$
 - $\text{Ru}, \text{Ru}^{3+}$
 - $\text{Rh}, \text{Rh}^{2+}$
 - $\text{Pd}, \text{Pd}^+, \text{Pd}^{2+}$

Applications of Coordination Compounds

53. What structural feature do hemoglobin, cytochrome c, and chlorophyll have in common?
54. Identify the central metal atom in each complex.
- hemoglobin
 - carbonic anhydrase
 - chlorophyll
 - iron blue
55. Hemoglobin exists in two predominant forms in our bodies. One form, known as oxyhemoglobin, has O_2 bound to the iron and the other, known as deoxyhemoglobin, has a water molecule bound instead. Oxyhemoglobin is a low-spin complex that gives arterial blood its red color, and deoxyhemoglobin is a high-spin complex that gives venous blood its darker color. Explain these observations in terms of crystal field splitting. Would you categorize O_2 as a strong- or weak-field ligand?
56. Carbon monoxide and the cyanide ion are both toxic because they bind more strongly than oxygen to the iron in hemoglobin (Hb).



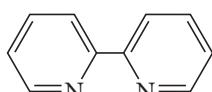
Calculate the equilibrium constant value for this reaction:



Does the equilibrium favor reactants or products?

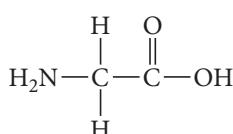
59. Draw the Lewis diagrams for each ligand. Indicate the lone pair(s) that may be donated to the metal. Indicate any you expect to be bidentate or polydentate.
- NH_3
 - SCN^-
 - H_2O

60. Draw the Lewis diagrams for each ligand. Indicate the lone pair(s) that may be donated to the metal. Indicate any you expect to be bidentate or polydentate.
- CN^-
 - bipyridyl (bipy), which has the following structure:



61. List all the different formulas for an octahedral complex made from a metal (M) and three different ligands (A, B, and C). Describe any isomers for each complex.

62. Amino acids, such as glycine (gly), form complexes with the trace metal ions found in the bloodstream. Glycine, whose structure is shown here, acts as a bidentate ligand coordinating with the nitrogen atom and one of the oxygen atoms.



Challenge Problems

69. When a solution of PtCl_2 reacts with the ligand trimethylphosphine, $\text{P}(\text{CH}_3)_3$, two compounds are produced. The compounds share the same elemental analysis: 46.7% Pt; 17.0% Cl; 14.8% P; 17.2% C; 4.34% H. Determine the formula, draw the structure, and give the systematic name for each compound.

70. Draw a crystal field splitting diagram for a trigonal planar complex ion. Assume the plane of the molecule is perpendicular to the z axis.

71. Draw a crystal field splitting diagram for a trigonal bipyramidal complex ion. Assume the axial positions are on the z axis.

72. Explain why $[\text{Ni}(\text{NH}_3)_4]^{2+}$ is paramagnetic, while $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic.

73. Sulfide (S^{2-}) salts are notoriously insoluble in aqueous solution.

- Calculate the molar solubility of nickel(II) sulfide in water. $K_{\text{sp}}(\text{NiS}) = 3 \times 10^{-16}$
- Nickel(II) ions form a complex ion in the presence of ammonia with a formation constant (K_f) of 2.0×10^8 : $\text{Ni}^{2+} + 6 \text{NH}_3 \rightleftharpoons [\text{Ni}(\text{NH}_3)_6]^{2+}$. Calculate the molar solubility of NiS in 3.0 M NH_3 .
- Explain any differences between the answers to parts a and b.

Conceptual Problems

78. Two ligands, A and B, both form complexes with a particular metal ion. When the metal ion complexes with ligand A, the solution is green. When the metal ion complexes with ligand B, the solution is violet. Which of the two ligands results in the largest Δ ?
79. Which element has the higher ionization energy, Cu or Au?

Draw all the possible isomers of:

- square planar $[\text{Ni}(\text{gly})_2]$
- tetrahedral $[\text{Zn}(\text{gly})_2]$
- octahedral $[\text{Fe}(\text{gly})_3]$

63. Oxalic acid solutions remove rust stains. Draw a complex ion that is likely responsible for this effect. Does it have any isomers?

64. W, X, Y, and Z are different monodentate ligands.
- Is the square planar $[\text{NiWXYZ}]^{2+}$ optically active?
 - Is the tetrahedral $[\text{ZnWXYZ}]^{2+}$ optically active?

65. Hexacyanomanganese(III) ion is a low-spin complex. Draw the crystal field splitting diagram with electrons filled in appropriately. Is this complex paramagnetic or diamagnetic?

66. Determine the color and approximate wavelength absorbed most strongly by each solution.

- blue solution
- red solution
- yellow solution

67. Draw the structures of all the geometric isomers of $[\text{Ru}(\text{H}_2\text{O})_2(\text{NH}_3)_2\text{Cl}_2]^+$. Draw the mirror images of any that are chiral.

68. A 0.32 mol amount of NH_3 is dissolved in 0.47 L of a 0.38 M silver nitrate solution. Calculate the equilibrium concentrations of all species in the solution.

74. Calculate the solubility of $\text{Zn}(\text{OH})_2(s)$ in 2.0 M NaOH solution. (Hint: you must take into account the formation of $\text{Zn}(\text{OH})_4^{2-}$, which has a $K_f = 2 \times 10^{15}$.)

75. Halide complexes of metal M of the form $[\text{MX}_6]^{3-}$ are found to be stable in aqueous solution. But it is possible that they undergo rapid ligand exchange with water (or other ligands) that is not detectable because the complexes are less stable. This property is referred to as their *lability*. Suggest an experiment to measure the lability of these complexes that does not employ radioactive labels.

76. The K_f for $[\text{Cu}(\text{en})_2]^{2+}$ is much larger than the one for $[\text{Cu}(\text{NH}_3)_4]^{2+}$. This difference is primarily an entropy effect. Explain why and calculate the difference between the ΔS° values at 298 K for the complete dissociation of the two complex ions. (Hint: the value of ΔH is about the same for both systems.)

77. When solid $\text{Cd}(\text{OH})_2$ is added to a solution of 0.10 M NaI some of it dissolves. Calculate the pH of the solution at equilibrium.

80. The complexes of Fe^{3+} have magnetic properties that depend on whether the ligands are strong or weak field. Explain why this observation supports the idea that electrons are lost from the 4s orbital before the 3d orbitals in the transition metals.

Answers to Conceptual Connections

Atomic Size

24.1 The element W has the larger radius because it is in the third transition row and Fe is in the first. Atomic radii increase from the first to the second transition row and stay roughly constant from the second to the third.

Weak- and Strong-Field Ligands

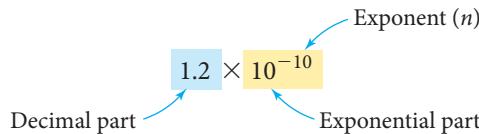
24.2 Ligand B forms a yellow solution, which means that the complex absorbs in the violet region. Ligand A forms a red solution, which means that the complex absorbs in the green. Since the violet region of the electromagnetic spectrum is of shorter wavelength (higher energy) than the green region, ligand B produces a higher Δ .

Appendix I:

Common Mathematical Operations in Chemistry

A. Scientific Notation

A number written in scientific notation consists of a **decimal part**, a number that is usually between 1 and 10, and an **exponential part**, 10 raised to an **exponent**, n .



Each of the following numbers is written in both scientific and decimal notation:

$$1.0 \times 10^5 = 100,000 \quad 1.0 \times 10^{-5} = 0.000001$$

$$6.7 \times 10^3 = 6700 \quad 6.7 \times 10^{-3} = 0.0067$$

A positive exponent means 1 multiplied by 10 n times.

$$10^0 = 1$$

$$10^1 = 1 \times 10$$

$$10^2 = 1 \times 10 \times 10 = 100$$

$$10^3 = 1 \times 10 \times 10 \times 10 = 1000$$

A negative exponent ($-n$) means 1 divided by 10 n times.

$$10^{-1} = \frac{1}{10} = 0.1$$

$$10^{-2} = \frac{1}{10 \times 10} = 0.01$$

$$10^{-3} = \frac{1}{10 \times 10 \times 10} = 0.001$$

To convert a number to scientific notation, we move the decimal point to obtain a number between 1 and 10 and then multiply by 10 raised to the appropriate power. For example, to write 5983 in scientific notation, we move the decimal point to the left three places to get 5.983 (a number between 1 and 10) and then multiply by 1000 to make up for moving the decimal point.

$$5983 = 5.983 \times 1000$$

Since 1000 is 10^3 , we write:

$$5983 = 5.983 \times 10^3$$

We can do this in one step by counting how many places we move the decimal point to obtain a number between 1 and 10 and then writing the decimal part multiplied by 10 raised to the number of places we moved the decimal point.

$$5983 = 5.983 \times 10^3$$

If the decimal point is moved to the left, as in the previous example, the exponent is positive. If the decimal is moved to the right, the exponent is negative.

$$0.00034 = 3.4 \times 10^{-4}$$

To express a number in scientific notation:

1. Move the decimal point to obtain a number between 1 and 10.
2. Write the result from step 1 multiplied by 10 raised to the number of places you moved the decimal point.
 - The exponent is positive if you moved the decimal point to the left.
 - The exponent is negative if you moved the decimal point to the right.

Consider the following additional examples:

$$290,809,000 = 2.90809 \times 10^8$$

$$0.00000000070 \text{ m} = 7.0 \times 10^{-11} \text{ m}$$

Multiplication and Division

To multiply numbers expressed in scientific notation, multiply the decimal parts and add the exponents.

$$(A \times 10^m)(B \times 10^n) = (A \times B) \times 10^{m+n}$$

To divide numbers expressed in scientific notation, divide the decimal parts and subtract the exponent in the denominator from the exponent in the numerator.

$$\frac{(A \times 10^m)}{(B \times 10^n)} = \left(\frac{A}{B}\right) \times 10^{m-n}$$

Consider the following example involving multiplication:

$$\begin{aligned}(3.5 \times 10^4)(1.8 \times 10^6) &= (3.5 \times 1.8) \times 10^{4+6} \\ &= 6.3 \times 10^{10}\end{aligned}$$

Consider the following example involving division:

$$\begin{aligned}\frac{(5.6 \times 10^7)}{(1.4 \times 10^3)} &= \left(\frac{5.6}{1.4}\right) \times 10^{7-3} \\ &= 4.0 \times 10^4\end{aligned}$$

Addition and Subtraction

To add or subtract numbers expressed in scientific notation, rewrite all the numbers so that they have the same exponent, then add or subtract the decimal parts of the numbers. The exponents remained unchanged.

$$\begin{array}{r} A \times 10^n \\ \pm B \times 10^n \\ \hline (A \pm B) \times 10^n \end{array}$$

Notice that the numbers *must have* the same exponent. Consider the following example involving addition:

$$\begin{array}{r} 4.82 \times 10^7 \\ + 3.4 \times 10^6 \\ \hline \end{array}$$

First, express both numbers with the same exponent. In this case, we rewrite the lower number and perform the addition as follows:

$$\begin{array}{r} 4.82 \times 10^7 \\ + 0.34 \times 10^7 \\ \hline 5.16 \times 10^7 \end{array}$$

Consider the following example involving subtraction:

$$\begin{array}{r} 7.33 \times 10^5 \\ - 1.9 \times 10^4 \\ \hline \end{array}$$

First, express both numbers with the same exponent. In this case, we rewrite the lower number and perform the subtraction as follows:

$$\begin{array}{r} 7.33 \times 10^5 \\ - 0.19 \times 10^5 \\ \hline 7.14 \times 10^5 \end{array}$$

Powers and Roots

To raise a number written in scientific notation to a power, raise the decimal part to the power and multiply the exponent by the power:

$$\begin{aligned} (4.0 \times 10^6)^2 &= 4.0^2 \times 10^{6 \times 2} \\ &= 16 \times 10^{12} \\ &= 1.6 \times 10^{13} \end{aligned}$$

To take the n^{th} root of a number written in scientific notation, take the n^{th} root of the decimal part and divide the exponent by the root:

$$\begin{aligned} (4.0 \times 10^6)^{1/3} &= 4.0^{1/3} \times 10^{6/3} \\ &= 1.6 \times 10^2 \end{aligned}$$

B. Logarithms

Common (or Base 10) Logarithms

The common or base 10 logarithm (abbreviated log) of a number is the exponent to which 10 must be raised to obtain

that number. For example, the log of 100 is 2 because 10 must be raised to the second power to get 100. Similarly, the log of 1000 is 3 because 10 must be raised to the third power to get 1000. The logs of several multiples of 10 are shown below:

$$\begin{aligned} \log 10 &= 1 \\ \log 100 &= 2 \\ \log 1000 &= 3 \\ \log 10,000 &= 4 \end{aligned}$$

Because $10^0 = 1$ by definition, $\log 1 = 0$.

The log of a number smaller than one is negative because 10 must be raised to a negative exponent to get a number smaller than one. For example, the log of 0.01 is -2 because 10 must be raised to -2 to get 0.01. Similarly, the log of 0.001 is -3 because 10 must be raised to -3 to get 0.001. The logs of several fractional numbers are shown below:

$$\begin{aligned} \log 0.1 &= -1 \\ \log 0.01 &= -2 \\ \log 0.001 &= -3 \\ \log 0.0001 &= -4 \end{aligned}$$

The logs of numbers that are not multiples of 10 can be computed on your calculator. See your calculator manual for specific instructions.

Inverse Logarithms

The inverse logarithm or invlog function is exactly the opposite of the log function. For example, the log of 100 is 2 and the inverse log of 2 is 100. The log function and the invlog function undo one another.

$$\begin{aligned} \log 100 &= 2 \\ \text{invlog } 2 &= 100 \\ \text{invlog}(\log 100) &= 100 \end{aligned}$$

The inverse log of a number is 10 raised to that number.

$$\begin{aligned} \text{invlog } x &= 10^x \\ \text{invlog } 3 &= 10^3 = 1000 \end{aligned}$$

The inverse logs of numbers can be computed on your calculator. See your calculator manual for specific instructions.

Natural (or Base e) Logarithms

The natural (or base e) logarithm (abbreviated ln) of a number is the exponent to which e (which has the value of 2.71828...) must be raised to obtain that number. For example, the ln of 100 is 4.605 because e must be raised to 4.605 to get 100. Similarly, the ln of 10.0 is 2.303 because e must be raised to 2.303 to get 10.0.

The inverse natural logarithm or invln function is exactly the opposite of the ln function. For example, the ln of 100 is

4.605 and the inverse \ln of 4.605 is 100. The inverse \ln of a number is simply e raised to that number.

$$\text{invln } x = e^x$$

$$\text{invln } 3 = e^3 = 20.1$$

The invln of a number can be computed on your calculator. See your calculator manual for specific instructions.

Mathematical Operations Using Logarithms

Because logarithms are exponents, mathematical operations involving logarithms are similar to those involving exponents as follows:

$$\log(a \times b) = \log a + \log b \quad \ln(a \times b) = \ln a + \ln b$$

$$\log \frac{a}{b} = \log a - \log b \quad \ln \frac{a}{b} = \ln a - \ln b$$

$$\log a^n = n \log a \quad \ln a^n = n \ln a$$

C. Quadratic Equations

A quadratic equation contains at least one term in which the variable x is raised to the second power (and no terms in which x is raised to a higher power). A quadratic equation has the following general form:

$$ax^2 + bx + c = 0$$

A quadratic equation can be solved for x using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Quadratic equations are often encountered when solving equilibrium problems. Below we show how to use the quadratic formula to solve a quadratic equation for x .

$$3x^2 - 5x + 1 = 0 \quad (\text{quadratic equation})$$

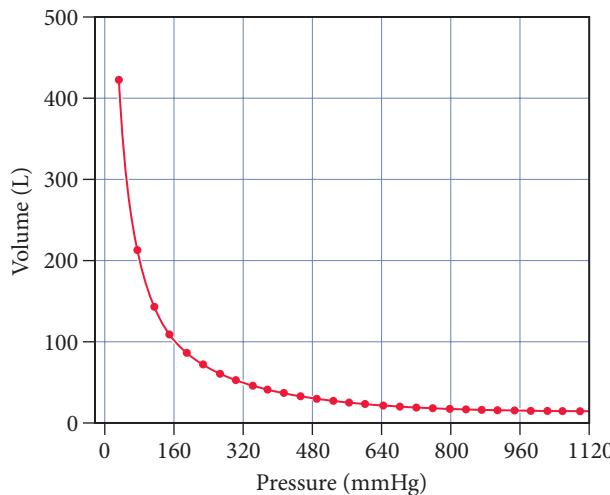
$$\begin{aligned} x &= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \\ &= \frac{-(-5) \pm \sqrt{(-5)^2 - 4(3)(1)}}{2(3)} \\ &= \frac{5 \pm 3.6}{6} \\ x &= 1.43 \quad \text{or} \quad x = 0.233 \end{aligned}$$

As you can see, the solution to a quadratic equation usually has two values. In any real chemical system, one of the values can be eliminated because it has no physical significance. (For example, it may correspond to a negative concentration, which does not exist.)

D. Graphs

Graphs are often used to visually show the relationship between two variables. For example, in Chapter 5 we show

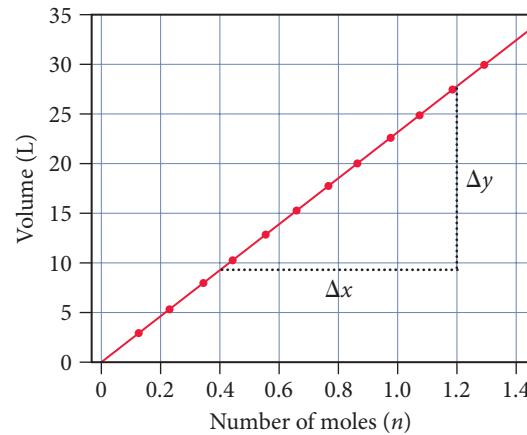
the following relationship between the volume of a gas and its pressure:



▲ **Volume versus Pressure** A plot of the volume of a gas sample—as measured in a J-tube—versus pressure. The plot shows that volume and pressure are inversely related.

The horizontal axis is the x -axis and is normally used to show the independent variable. The vertical axis is the y -axis and is normally used to show how the other variable (called the dependent variable) varies with a change in the independent variable. In this case, the graph shows that as the pressure of a gas sample increases, its volume decreases.

Many relationships in chemistry are *linear*, which means that if you change one variable by a factor of n the other variable will also change by a factor of n . For example, the volume of a gas is linearly related to the number of moles of gas. When two quantities are linearly related, a graph of one versus the other produces a straight line. For example, the graph below shows how the volume of an ideal gas sample depends on the number of moles of gas in the sample:



▲ **Volume versus Number of Moles** The volume of a gas sample increases linearly with the number of moles of gas in the sample.

A linear relationship between any two variables x and y can be expressed by the following equation:

$$y = mx + b$$

where m is the slope of the line and b is the y -intercept. The slope is the change in y divided by the change in x .

$$m = \frac{\Delta y}{\Delta x}$$

For the graph above, we can estimate the slope by simply estimating the changes in y and x for a given interval. For example, between $x = 0.4$ mol and 1.2 mol, $\Delta x = 0.80$ mol and we can estimate that $\Delta y = 18$ L. Therefore the slope is

$$m = \frac{\Delta y}{\Delta x} = \frac{18 \text{ L}}{0.80 \text{ mol}} = 23 \text{ mol/L}$$

In several places in this book, logarithmic relationships between variables can be plotted in order to obtain a linear relationship. For example, the variables $[A]_t$ and t in the following equation are not linearly related, but the natural logarithm of $[A]_t$ and t are linearly related.

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

$$y = mx + b$$

A plot of $\ln[A]_t$ versus t will therefore produce a straight line with slope $= -k$ and y -intercept $= \ln[A]_0$.

Appendix II:

Useful Data

A. Atomic Colors

Atomic number:	1	4	5	6	7	8	9
Atomic symbol:	H	Be	B	C	N	O	F
Atomic number:	11	12	14	15	16	17	19
Atomic symbol:	Na	Mg	Si	P	S	Cl	K
Atomic number:	20	29	30	35	53	54	
Atomic symbol:	Ca	Cu	Zn	Br	I	Xe	

B. Standard Thermodynamic Quantities for Selected Substances at 25 °C

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol · K)
Aluminum			
Al(s)	0	0	28.32
Al(g)	330.0	289.4	164.6
Al ³⁺ (aq)	-538.4	-483	-325
AlCl ₃ (s)	-704.2	-628.8	109.3
Al ₂ O ₃ (s)	-1675.7	-1582.3	50.9
Barium			
Ba(s)	0	0	62.5
Ba(g)	180.0	146.0	170.2
Ba ²⁺ (aq)	-537.6	-560.8	9.6
BaCO ₃ (s)	-1213.0	-1134.4	112.1
BaCl ₂ (s)	-855.0	-806.7	123.7
BaO(s)	-548.0	-520.3	72.1
Ba(OH) ₂ (s)	-944.7		
BaSO ₄ (s)	-1473.2	-1362.2	132.2

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol · K)
Beryllium			
Be(s)	0	0	9.5
BeO(s)	-609.4	-580.1	13.8
Be(OH) ₂ (s)	-902.5	-815.0	45.5
Bismuth			
Bi(s)	0	0	56.7
BiCl ₃ (s)	-379.1	-315.0	177.0
Bi ₂ O ₃ (s)	-573.9	-493.7	151.5
Bi ₂ S ₃ (s)	-143.1	-140.6	200.4
Boron			
B(s)	0	0	5.9
B(g)	565.0	521.0	153.4
BCl ₃ (g)	-403.8	-388.7	290.1
BF ₃ (g)	-1136.0	-1119.4	254.4
B ₂ H ₆ (g)	36.4	87.6	232.1

(continued on the next page)

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol · K)
$\text{B}_2\text{O}_3(s)$	-1273.5	-1194.3	54.0
$\text{H}_3\text{BO}_3(s)$	-1094.3	-968.9	90.0
Bromine			
$\text{Br}(g)$	111.9	82.4	175.0
$\text{Br}_2(l)$	0	0	152.2
$\text{Br}_2(g)$	30.9	3.1	245.5
$\text{Br}^-(aq)$	-121.4	-102.8	80.71
$\text{HBr}(g)$	-36.3	-53.4	198.7
Cadmium			
$\text{Cd}(s)$	0	0	51.8
$\text{Cd}(g)$	111.8	77.3	167.7
$\text{Cd}^{2+}(aq)$	-75.9	-77.6	-73.2
$\text{CdCl}_2(s)$	-391.5	-343.9	115.3
$\text{CdO}(s)$	-258.4	-228.7	54.8
$\text{CdS}(s)$	-161.9	-156.5	64.9
$\text{CdSO}_4(s)$	-933.3	-822.7	123.0
Calcium			
$\text{Ca}(s)$	0	0	41.6
$\text{Ca}(g)$	177.8	144.0	154.9
$\text{Ca}^{2+}(aq)$	-542.8	-553.6	-53.1
$\text{CaC}_2(s)$	-59.8	-64.9	70.0
$\text{CaCO}_3(s)$	-1207.6	-1129.1	91.7
$\text{CaCl}_2(s)$	-795.4	-748.8	108.4
$\text{CaF}_2(s)$	-1228.0	-1175.6	68.5
$\text{CaH}_2(s)$	-181.5	-142.5	41.4
$\text{Ca}(\text{NO}_3)_2(s)$	-938.2	-742.8	193.2
$\text{CaO}(s)$	-634.9	-603.3	38.1
$\text{Ca}(\text{OH})_2(s)$	-985.2	-897.5	83.4
$\text{CaSO}_4(s)$	-1434.5	-1322.0	106.5
$\text{Ca}_3(\text{PO}_4)_2(s)$	-4120.8	-3884.7	236.0
Carbon			
$\text{C}(s, \text{graphite})$	0	0	5.7
$\text{C}(s, \text{diamond})$	1.88	2.9	2.4
$\text{C}(g)$	716.7	671.3	158.1
$\text{CH}_4(g)$	-74.6	-50.5	186.3
$\text{CH}_3\text{Cl}(g)$	-81.9	-60.2	234.6
$\text{CH}_2\text{Cl}_2(g)$	-95.4		270.2
$\text{CH}_2\text{Cl}_2(l)$	-124.2	-63.2	177.8
$\text{CHCl}_3(l)$	-134.1	-73.7	201.7
$\text{CCl}_4(g)$	-95.7	-62.3	309.7
$\text{CCl}_4(l)$	-128.2	-66.4	216.4
$\text{CH}_2\text{O}(g)$	-108.6	-102.5	218.8
$\text{CH}_2\text{O}_2(l, \text{formic acid})$	-425.0	-361.4	129.0
$\text{CH}_3\text{NH}_2(g, \text{methylamine})$	-22.5	32.7	242.9
$\text{CH}_3\text{OH}(l)$	-238.6	-166.6	126.8
$\text{CH}_3\text{OH}(g)$	-201.0	-162.3	239.9

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol · K)
$\text{C}_2\text{H}_2(g)$	227.4	209.9	200.9
$\text{C}_2\text{H}_4(g)$	52.4	68.4	219.3
$\text{C}_2\text{H}_6(g)$	-84.68	-32.0	229.2
$\text{C}_2\text{H}_5\text{OH}(l)$	-277.6	-174.8	160.7
$\text{C}_2\text{H}_5\text{OH}(g)$	-234.8	-167.9	281.6
$\text{C}_2\text{H}_3\text{Cl}$ (g, vinyl chloride)	37.2	53.6	264.0
$\text{C}_2\text{H}_4\text{Cl}_2$ (l, dichloroethane)	-166.8	-79.6	208.5
$\text{C}_2\text{H}_4\text{O}$ (g, acetaldehyde)	-166.2	-133.0	263.8
$\text{C}_2\text{H}_4\text{O}_2$ (l, acetic acid)	-484.3	-389.9	159.8
$\text{C}_3\text{H}_8(g)$	-103.85	-23.4	270.3
$\text{C}_3\text{H}_6\text{O}$ (l, acetone)	-248.4	-155.6	199.8
$\text{C}_3\text{H}_7\text{OH}$ (l, isopropanol)	-318.1		181.1
$\text{C}_4\text{H}_{10}(l)$	-147.3	-15.0	231.0
$\text{C}_4\text{H}_{10}(g)$	-125.7	-15.71	310.0
$\text{C}_6\text{H}_6(l)$	49.1	124.5	173.4
$\text{C}_6\text{H}_5\text{NH}_2$ (l, aniline)	31.6	149.2	191.9
$\text{C}_6\text{H}_5\text{OH}$ (s, phenol)	-165.1	-50.4	144.0
$\text{C}_6\text{H}_{12}\text{O}_6$ (s, glucose)	-1273.3	-910.4	212.1
C_{10}H_8 (s, naphthalene)	78.5	201.6	167.4
$\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (s, sucrose)	-2226.1	-1544.3	360.24
$\text{CO}(g)$	-110.5	-137.2	197.7
$\text{CO}_2(g)$	-393.5	-394.4	213.8
$\text{CO}_2(aq)$	-413.8	-386.0	117.6
$\text{CO}_3^{2-}(aq)$	-677.1	-527.8	-56.9
$\text{HCO}_3^-(aq)$	-692.0	-586.8	91.2
$\text{H}_2\text{CO}_3(aq)$	-699.7	-623.2	187.4
$\text{CN}^-(aq)$	151	166	118
$\text{HCN}(l)$	108.9	125.0	112.8
$\text{HCN}(g)$	135.1	124.7	201.8
$\text{CS}_2(l)$	89.0	64.6	151.3
$\text{CS}_2(g)$	116.7	67.1	237.8
$\text{COCl}_2(g)$	-219.1	-204.9	283.5
$\text{C}_{60}(s)$	2327.0	2302.0	426.0
Cesium			
$\text{Cs}(s)$	0	0	85.2
$\text{Cs}(g)$	76.5	49.6	175.6
$\text{Cs}^+(aq)$	-258.0	-292.0	132.1
$\text{CsBr}(s)$	-400	-387	117
$\text{CsCl}(s)$	-438	-414	101.2

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol · K)
CsF(s)	-553.5	-525.5	92.8
CsI(s)	-342	-337	127
Chlorine			
Cl(g)	121.3	105.3	165.2
Cl ₂ (g)	0	0	223.1
Cl ⁻ (aq)	-167.1	-131.2	56.6
HCl(g)	-92.3	-95.3	186.9
HCl(aq)	-167.2	-131.2	56.5
ClO ₂ (g)	102.5	120.5	256.8
Cl ₂ O(g)	80.3	97.9	266.2
Chromium			
Cr(s)	0	0	23.8
Cr(g)	396.6	351.8	174.5
Cr ³⁺ (aq)	-1971		
CrO ₄ ²⁻ (aq)	-872.2	-717.1	44
Cr ₂ O ₃ (s)	-1139.7	-1058.1	81.2
Cr ₂ O ₇ ²⁻ (aq)	-1476	-1279	238
Cobalt			
Co(s)	0	0	30.0
Co(g)	424.7	380.3	179.5
CoO(s)	-237.9	-214.2	53.0
Co(OH) ₂ (s)	-539.7	-454.3	79.0
Copper			
Cu(s)	0	0	33.2
Cu(g)	337.4	297.7	166.4
Cu ⁺ (aq)	51.9	50.2	-26
Cu ²⁺ (aq)	64.9	65.5	-98
CuCl(s)	-137.2	-119.9	86.2
CuCl ₂ (s)	-220.1	-175.7	108.1
CuO(s)	-157.3	-129.7	42.6
CuS(s)	-53.1	-53.6	66.5
CuSO ₄ (s)	-771.4	-662.2	109.2
Cu ₂ O(s)	-168.6	-146.0	93.1
Cu ₂ S(s)	-79.5	-86.2	120.9
Fluorine			
F(g)	79.38	62.3	158.75
F ₂ (g)	0	0	202.79
F ⁻ (aq)	-335.35	-278.8	-13.8
HF(g)	-273.3	-275.4	173.8
Gold			
Au(s)	0	0	47.4
Au(g)	366.1	326.3	180.5
Helium			
He(g)	0	0	126.2
Hydrogen			
H(g)	218.0	203.3	114.7
H ⁺ (aq)	0	0	0

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol · K)
H ⁺ (g)	1536.3	1517.1	108.9
H ₂ (g)	0	0	130.7
Iodine			
I(g)	106.76	70.2	180.79
I ₂ (s)	0	0	116.14
I ₂ (g)	62.42	19.3	260.69
I ⁻ (aq)	-56.78	-51.57	106.45
HI(g)	26.5	1.7	206.6
Iron			
Fe(s)	0	0	27.3
Fe(g)	416.3	370.7	180.5
Fe ²⁺ (aq)	-87.9	-84.94	113.4
Fe ³⁺ (aq)	-47.69	-10.54	293.3
FeCO ₃ (s)	-740.6	-666.7	92.9
FeCl ₂ (s)	-341.8	-302.3	118.0
FeCl ₃ (s)	-399.5	-334.0	142.3
FeO(s)	-272.0	-255.2	60.75
Fe(OH) ₃ (s)	-823.0	-696.5	106.7
FeS ₂ (s)	-178.2	-166.9	52.9
Fe ₂ O ₃ (s)	-824.2	-742.2	87.4
Fe ₃ O ₄ (s)	-1118.4	-1015.4	146.4
Lead			
Pb(s)	0	0	64.8
Pb(g)	195.2	162.2	175.4
Pb ²⁺ (aq)	0.92	-24.4	18.5
PbBr ₂ (s)	-278.7	-261.9	161.5
PbCO ₃ (s)	-699.1	-625.5	131.0
PbCl ₂ (s)	-359.4	-314.1	136.0
PbI ₂ (s)	-175.5	-173.6	174.9
Pb(NO ₃) ₂ (s)	-451.9		
PbO(s)	-217.3	-187.9	68.7
PbO ₂ (s)	-277.4	-217.3	68.6
PbS(s)	-100.4	-98.7	91.2
PbSO ₄ (s)	-920.0	-813.0	148.5
Lithium			
Li(s)	0	0	29.1
Li(g)	159.3	126.6	138.8
Li ⁺ (aq)	-278.47	-293.3	12.24
LiBr(s)	-351.2	-342.0	74.3
LiCl(s)	-408.6	-384.4	59.3
LiF(s)	-616.0	-587.7	35.7
LiI(s)	-270.4	-270.3	86.8
LiNO ₃ (s)	-483.1	-381.1	90.0
LiOH(s)	-487.5	-441.5	42.8
Li ₂ O(s)	-597.9	-561.2	37.6

(continued on the next page)

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol · K)
Magnesium			
Mg(s)	0	0	32.7
Mg(g)	147.1	112.5	148.6
Mg ²⁺ (aq)	-467.0	-455.4	-137
MgCl ₂ (s)	-641.3	-591.8	89.6
MgCO ₃ (s)	-1095.8	-1012.1	65.7
MgF ₂ (s)	-1124.2	-1071.1	57.2
MgO(s)	-601.6	-569.3	27.0
Mg(OH) ₂ (s)	-924.5	-833.5	63.2
MgSO ₄ (s)	-1284.9	-1170.6	91.6
Mg ₃ N ₂ (s)	-461	-401	88
Manganese			
Mn(s)	0	0	32.0
Mn(g)	280.7	238.5	173.7
Mn ²⁺ (aq)	-219.4	-225.6	-78.8
MnO(s)	-385.2	-362.9	59.7
MnO ₂ (s)	-520.0	-465.1	53.1
MnO ₄ ⁻ (aq)	-529.9	-436.2	190.6
Mercury			
Hg(l)	0	0	75.9
Hg(g)	61.4	31.8	175.0
Hg ²⁺ (aq)	170.21	164.4	-36.19
Hg ₂ ²⁺ (aq)	166.87	153.5	65.74
HgCl ₂ (s)	-224.3	-178.6	146.0
HgO(s)	-90.8	-58.5	70.3
HgS(s)	-58.2	-50.6	82.4
Hg ₂ Cl ₂ (s)	-265.4	-210.7	191.6
Nickel			
Ni(s)	0	0	29.9
Ni(g)	429.7	384.5	182.2
NiCl ₂ (s)	-305.3	-259.0	97.7
NiO(s)	-239.7	-211.7	37.99
NiS(s)	-82.0	-79.5	53.0
Nitrogen			
N(g)	472.7	455.5	153.3
N ₂ (g)	0	0	191.6
NF ₃ (g)	-132.1	-90.6	260.8
NH ₃ (g)	-45.9	-16.4	192.8
NH ₃ (aq)	-80.29	-26.50	111.3
NH ₄ ⁺ (aq)	-133.26	-79.31	111.17
NH ₄ Br(s)	-270.8	-175.2	113.0
NH ₄ Cl(s)	-314.4	-202.9	94.6
NH ₄ CN(s)	0.4		
NH ₄ F(s)	-464.0	-348.7	72.0
NH ₄ HCO ₃ (s)	-849.4	-665.9	120.9
NH ₄ I(s)	-201.4	-112.5	117.0
NH ₄ NO ₃ (s)	-365.6	-183.9	151.1
NH ₄ NO ₃ (aq)	-339.9	-190.6	259.8

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol · K)
HNO ₃ (g)	-133.9	-73.5	266.9
HNO ₃ (aq)	-207	-110.9	146
NO(g)	91.3	87.6	210.8
NO ₂ (g)	33.2	51.3	240.1
NO ₃ ⁻ (aq)	-206.85	-110.2	146.70
NOBr(g)	82.2	82.4	273.7
NOCl(g)	51.7	66.1	261.7
N ₂ H ₄ (l)	50.6	149.3	121.2
N ₂ H ₄ (g)	95.4	159.4	238.5
N ₂ O(g)	81.6	103.7	220.0
N ₂ O ₄ (l)	-19.5	97.5	209.2
N ₂ O ₄ (g)	9.16	99.8	304.4
N ₂ O ₅ (s)	-43.1	113.9	178.2
N ₂ O ₅ (g)	13.3	117.1	355.7
Oxygen			
O(g)	249.2	231.7	161.1
O ₂ (g)	0	0	205.2
O ₃ (g)	142.7	163.2	238.9
OH ⁻ (aq)	-230.02	-157.3	-10.90
H ₂ O(l)	-285.8	-237.1	70.0
H ₂ O(g)	-241.8	-228.6	188.8
H ₂ O ₂ (l)	-187.8	-120.4	109.6
H ₂ O ₂ (g)	-136.3	-105.6	232.7
Phosphorus			
P(s, white)	0	0	41.1
P(s, red)	-17.6	-12.1	22.8
P(g)	316.5	280.1	163.2
P ₂ (g)	144.0	103.5	218.1
P ₄ (g)	58.9	24.4	280.0
PCl ₃ (l)	-319.7	-272.3	217.1
PCl ₃ (g)	-287.0	-267.8	311.8
PCl ₅ (s)	-443.5		
PCl ₅ (g)	-374.9	-305.0	364.6
PF ₅ (g)	-1594.4	-1520.7	300.8
PH ₃ (g)	5.4	13.5	210.2
POCl ₃ (l)	-597.1	-520.8	222.5
POCl ₃ (g)	-558.5	-512.9	325.5
PO ₄ ³⁻ (aq)	-1277.4	-1018.7	-220.5
HPO ₄ ²⁻ (aq)	-1292.1	-1089.2	-33.5
H ₂ PO ₄ ⁻ (aq)	-1296.3	-1130.2	90.4
H ₃ PO ₄ (s)	-1284.4	-1124.3	110.5
H ₃ PO ₄ (aq)	-1288.3	-1142.6	158.2
P ₄ O ₆ (s)	-1640.1		
P ₄ O ₁₀ (s)	-2984	-2698	228.9
Platinum			
Pt(s)	0	0	41.6
Pt(g)	565.3	520.5	192.4

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol · K)
Potassium			
K(s)	0	0	64.7
K(g)	89.0	60.5	160.3
K ⁺ (aq)	-252.14	-283.3	101.2
KBr(s)	-393.8	-380.7	95.9
KCN(s)	-113.0	-101.9	128.5
KCl(s)	-436.5	-408.5	82.6
KClO ₃ (s)	-397.7	-296.3	143.1
KClO ₄ (s)	-432.8	-303.1	151.0
KF(s)	-567.3	-537.8	66.6
KI(s)	-327.9	-324.9	106.3
KNO ₃ (s)	-494.6	-394.9	133.1
KOH(s)	-424.6	-379.4	81.2
KOH(aq)	-482.4	-440.5	91.6
KO ₂ (s)	-284.9	-239.4	116.7
K ₂ CO ₃ (s)	-1151.0	-1063.5	155.5
K ₂ O(s)	-361.5	-322.1	94.14
K ₂ O ₂ (s)	-494.1	-425.1	102.1
K ₂ SO ₄ (s)	-1437.8	-1321.4	175.6
Rubidium			
Rb(s)	0	0	76.8
Rb(g)	80.9	53.1	170.1
Rb ⁺ (aq)	-251.12	-283.1	121.75
RbBr(s)	-394.6	-381.8	110.0
RbCl(s)	-435.4	-407.8	95.9
RbClO ₃ (s)	-392.4	-292.0	152
RbF(s)	-557.7		
RbI(s)	-333.8	-328.9	118.4
Scandium			
Sc(s)	0	0	34.6
Sc(g)	377.8	336.0	174.8
Selenium			
Se(s, gray)	0	0	42.4
Se(g)	227.1	187.0	176.7
H ₂ Se(g)	29.7	15.9	219.0
Silicon			
Si(s)	0	0	18.8
Si(g)	450.0	405.5	168.0
SiCl ₄ (l)	-687.0	-619.8	239.7
SiF ₄ (g)	-1615.0	-1572.8	282.8
SiH ₄ (g)	34.3	56.9	204.6
SiO ₂ (s, quartz)	-910.7	-856.3	41.5
Si ₂ H ₆ (g)	80.3	127.3	272.7
Silver			
Ag(s)	0	0	42.6
Ag(g)	284.9	246.0	173.0
Ag ⁺ (aq)	105.79	77.11	73.45

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol · K)
AgBr(s)	-100.4	-96.9	107.1
AgCl(s)	-127.0	-109.8	96.3
AgF(s)	-204.6	-185	84
AgI(s)	-61.8	-66.2	115.5
AgNO ₃ (s)	-124.4	-33.4	140.9
Ag ₂ O(s)	-31.1	-11.2	121.3
Ag ₂ S(s)	-32.6	-40.7	144.0
Ag ₂ SO ₄ (s)	-715.9	-618.4	200.4
Sodium			
Na(s)	0	0	51.3
Na(g)	107.5	77.0	153.7
Na ⁺ (aq)	-240.34	-261.9	58.45
NaBr(s)	-361.1	-349.0	86.8
NaCl(s)	-411.2	-384.1	72.1
NaCl(aq)	-407.2	-393.1	115.5
NaClO ₃ (s)	-365.8	-262.3	123.4
NaF(s)	-576.6	-546.3	51.1
NaHCO ₃ (s)	-950.8	-851.0	101.7
NaHSO ₄ (s)	-1125.5	-992.8	113.0
Nal(s)	-287.8	-286.1	98.5
NaNO ₃ (s)	-467.9	-367.0	116.5
NaNO ₃ (aq)	-447.5	-373.2	205.4
NaOH(s)	-425.8	-379.7	64.4
NaOH(aq)	-470.1	-419.2	48.2
NaO ₂ (s)	-260.2	-218.4	115.9
Na ₂ CO ₃ (s)	-1130.7	-1044.4	135.0
Na ₂ O(s)	-414.2	-375.5	75.1
Na ₂ O ₂ (s)	-510.9	-447.7	95.0
Na ₂ SO ₄ (s)	-1387.1	-1270.2	149.6
Na ₃ PO ₄ (s)	-1917	-1789	173.8
Strontium			
Sr(s)	0	0	55.0
Sr(g)	164.4	130.9	164.6
Sr ²⁺ (aq)	-545.51	-557.3	-39
SrCl ₂ (s)	-828.9	-781.1	114.9
SrCO ₃ (s)	-1220.1	-1140.1	97.1
SrO(s)	-592.0	-561.9	54.4
SrSO ₄ (s)	-1453.1	-1340.9	117.0
Sulfur			
S(s, rhombic)	0	0	32.1
S(s, monoclinic)	0.3	0.096	32.6
S(g)	277.2	236.7	167.8
S ₂ (g)	128.6	79.7	228.2
S ₈ (g)	102.3	49.7	430.9
S ²⁻ (aq)	41.8	83.7	22
SF ₆ (g)	-1220.5	-1116.5	291.5
HS ⁻ (aq)	-17.7	12.4	62.0

(continued on the next page)

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol · K)
$\text{H}_2\text{S}(g)$	-20.6	-33.4	205.8
$\text{H}_2\text{S}(aq)$	-39.4	-27.7	122
$\text{SOCl}_2(l)$	-245.6		
$\text{SO}_2(g)$	-296.8	-300.1	248.2
$\text{SO}_3(g)$	-395.7	-371.1	256.8
$\text{SO}_4^{2-}(aq)$	-909.3	-744.6	18.5
$\text{HSO}_4^-(aq)$	-886.5	-754.4	129.5
$\text{H}_2\text{SO}_4(l)$	-814.0	-690.0	156.9
$\text{H}_2\text{SO}_4(aq)$	-909.3	-744.6	18.5
$\text{S}_2\text{O}_3^{2-}(aq)$	-648.5	-522.5	67
Tin			
$\text{Sn}(s, \text{white})$	0	0	51.2
$\text{Sn}(s, \text{gray})$	-2.1	0.1	44.1
$\text{Sn}(g)$	301.2	266.2	168.5
$\text{SnCl}_4(l)$	-511.3	-440.1	258.6
$\text{SnCl}_4(g)$	-471.5	-432.2	365.8
$\text{SnO}(s)$	-280.7	-251.9	57.2
$\text{SnO}_2(s)$	-577.6	-515.8	49.0
Titanium			
$\text{Ti}(s)$	0	0	30.7
$\text{Ti}(g)$	473.0	428.4	180.3
$\text{TiCl}_4(l)$	-804.2	-737.2	252.3
$\text{TiCl}_4(g)$	-763.2	-726.3	353.2

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol · K)
$\text{TiO}_2(s)$	-944.0	-888.8	50.6
Tungsten			
$\text{W}(s)$	0	0	32.6
$\text{W}(g)$	849.4	807.1	174.0
$\text{WO}_3(s)$	-842.9	-764.0	75.9
Uranium			
$\text{U}(s)$	0	0	50.2
$\text{U}(g)$	533.0	488.4	199.8
$\text{UF}_6(s)$	-2197.0	-2068.5	227.6
$\text{UF}_6(g)$	-2147.4	-2063.7	377.9
$\text{UO}_2(s)$	-1085.0	-1031.8	77.0
Vanadium			
$\text{V}(s)$	0	0	28.9
$\text{V}(g)$	514.2	754.4	182.3
Zinc			
$\text{Zn}(s)$	0	0	41.6
$\text{Zn}(g)$	130.4	94.8	161.0
$\text{Zn}^{2+}(aq)$	-153.39	-147.1	-109.8
$\text{ZnCl}_2(s)$	-415.1	-369.4	111.5
$\text{ZnO}(s)$	-350.5	-320.5	43.7
ZnS (s, zinc blende)	-206.0	-201.3	57.7
$\text{ZnSO}_4(s)$	-982.8	-871.5	110.5

C. Aqueous Equilibrium Constants

1. Dissociation Constants for Acids at 25 °C

Name	Formula	K_{a_1}	K_{a_2}	K_{a_3}
Acetic	$\text{HC}_2\text{H}_3\text{O}_2$	1.8×10^{-5}		
Acetylsalicylic	$\text{HC}_9\text{H}_7\text{O}_4$	3.3×10^{-4}		
Adipic	$\text{H}_2\text{C}_6\text{H}_8\text{O}_4$	3.9×10^{-5}	3.9×10^{-6}	
Arsenic	H_3AsO_4	5.5×10^{-3}	1.7×10^{-7}	5.1×10^{-12}
Arsenous	H_3AsO_3	5.1×10^{-10}		
Ascorbic	$\text{H}_2\text{C}_6\text{H}_6\text{O}_6$	8.0×10^{-5}	1.6×10^{-12}	
Benzoic	$\text{HC}_7\text{H}_5\text{O}_2$	6.5×10^{-5}		
Boric	H_3BO_3	5.4×10^{-10}		
Butanoic	$\text{HC}_4\text{H}_7\text{O}_2$	1.5×10^{-5}		
Carbonic	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Chloroacetic	$\text{HC}_2\text{H}_2\text{O}_2\text{Cl}$	1.4×10^{-3}		
Chlorous	HClO_2	1.1×10^{-2}		
Citric	$\text{H}_3\text{C}_6\text{H}_5\text{O}_7$	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Cyanic	HCNO	2×10^{-4}		
Formic	HCHO_2	1.8×10^{-4}		
Hydrazoic	HN_3	2.5×10^{-5}		

Name	Formula	K_{a_1}	K_{a_2}	K_{a_3}
Hydrocyanic	HCN	4.9×10^{-10}		
Hydrofluoric	HF	3.5×10^{-4}		
Hydrogen chromate ion	HCrO_4^-		3.0×10^{-7}	
Hydrogen peroxide	H_2O_2		2.4×10^{-12}	
Hydrogen selenate ion	HSeO_4^-		2.2×10^{-2}	
Hydrosulfuric	H_2S	8.9×10^{-8}	1×10^{-19}	
Hydrotelluric	H_2Te	2.3×10^{23}	1.6×10^{-11}	
Hypobromous	HBrO	2.8×10^{-9}		
Hypochlorous	HClO	2.9×10^{-8}		
Hypoiodous	HIO	2.3×10^{-11}		
Iodic	HIO_3	1.7×10^{-1}		
Lactic	$\text{HC}_3\text{H}_5\text{O}_3$	1.4×10^{-4}		
Maleic	$\text{H}_2\text{C}_4\text{H}_2\text{O}_4$	1.2×10^{-2}	5.9×10^{-7}	
Malonic	$\text{H}_2\text{C}_3\text{H}_2\text{O}_4$	1.5×10^{-3}	2.0×10^{-6}	

Name	Formula	K_{a_1}	K_{a_2}	K_{a_3}
Nitrous	HNO ₂	4.6×10^{-4}		
Oxalic	H ₂ C ₂ O ₄	6.0×10^{-2}	6.1×10^{-5}	
Paraperiodic	H ₅ IO ₆	2.8×10^{-2}	5.3×10^{-9}	
Phenol	HC ₆ H ₅ O	1.3×10^{-10}		
Phosphoric	H ₃ PO ₄	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Phosphorous	H ₃ PO ₃	5×10^{-2}	2.0×10^{-7}	
Propanoic	HC ₃ H ₅ O ₂	1.3×10^{-5}		
Pyruvic	HC ₃ H ₃ O ₃	4.1×10^{-3}		
Pyrophosphoric	H ₄ P ₂ O ₇	1.2×10^{-1}	7.9×10^{-3}	2.0×10^{-7}

Name	Formula	K_{a_1}	K_{a_2}	K_{a_3}
Selenous	H ₂ SeO ₃	2.4×10^{-3}	4.8×10^{-9}	
Succinic	H ₂ C ₄ H ₄ O ₄	6.2×10^{-5}	2.3×10^{-6}	
Sulfuric	H ₂ SO ₄	Strong acid	1.2×10^{-2}	
Sulfurous	H ₂ SO ₃	1.6×10^{-2}	6.4×10^{-8}	
Tartaric	H ₂ C ₄ H ₄ O ₆	1.0×10^{-3}	4.6×10^{-5}	
Trichloroacetic	HC ₂ Cl ₃ O ₂	2.2×10^{-1}		
Trifluoroacetic acid	HC ₂ F ₃ O ₂	3.0×10^{-1}		

2. Dissociation Constants for Hydrated Metal Ions at 25 °C

Cation	Hydrated Ion	K_a
Al ³⁺	Al(H ₂ O) ₆ ³⁺	1.4×10^{-5}
Be ²⁺	Be(H ₂ O) ₆ ²⁺	3×10^{-7}
Co ²⁺	Co(H ₂ O) ₆ ²⁺	1.3×10^{-9}
Cr ³⁺	Cr(H ₂ O) ₆ ³⁺	1.6×10^{-4}
Cu ²⁺	Cu(H ₂ O) ₆ ²⁺	3×10^{-8}
Fe ²⁺	Fe(H ₂ O) ₆ ²⁺	3.2×10^{-10}

Cation	Hydrated Ion	K_a
Fe ³⁺	Fe(H ₂ O) ₆ ³⁺	6.3×10^{-3}
Ni ²⁺	Ni(H ₂ O) ₆ ²⁺	2.5×10^{-11}
Pb ²⁺	Pb(H ₂ O) ₆ ²⁺	3×10^{-8}
Sn ²⁺	Sn(H ₂ O) ₆ ²⁺	4×10^{-4}
Zn ²⁺	Zn(H ₂ O) ₆ ²⁺	2.5×10^{-10}

3. Dissociation Constants for Bases at 25 °C

Name	Formula	K_b
Ammonia	NH ₃	1.76×10^{-5}
Aniline	C ₆ H ₅ NH ₂	3.9×10^{-10}
Bicarbonate ion	HCO ₃ ⁻	2.3×10^{-8}
Carbonate ion	CO ₃ ²⁻	1.8×10^{-4}
Codeine	C ₁₈ H ₂₁ NO ₃	1.6×10^{-6}
Diethylamine	(C ₂ H ₅) ₂ NH	6.9×10^{-4}
Dimethylamine	(CH ₃) ₂ NH	5.4×10^{-4}
Ethylamine	C ₂ H ₅ NH ₂	5.6×10^{-4}
Ethylenediamine	C ₂ H ₈ N ₂	8.3×10^{-5}
Hydrazine	H ₂ NNH ₂	1.3×10^{-6}
Hydroxylamine	HONH ₂	1.1×10^{-8}

Name	Formula	K_b
Ketamine	C ₁₃ H ₁₆ CINO	3×10^{-7}
Methylamine	CH ₃ NH ₂	4.4×10^{-4}
Morphine	C ₁₇ H ₁₉ NO ₃	1.6×10^{-6}
Nicotine	C ₁₀ H ₁₄ N ₂	1.0×10^{-6}
Piperidine	C ₅ H ₁₀ NH	1.33×10^{-3}
Propylamine	C ₃ H ₇ NH ₂	3.5×10^{-4}
Pyridine	C ₅ H ₅ N	1.7×10^{-9}
Strychnine	C ₂₁ H ₂₂ N ₂ O ₂	1.8×10^{-6}
Triethylamine	(C ₂ H ₅) ₃ N	5.6×10^{-4}
Trimethylamine	(CH ₃) ₃ N	6.4×10^{-5}

4. Solubility Product Constants for Compounds at 25 °C

Compound	Formula	K_{sp}
Aluminum hydroxide	Al(OH) ₃	1.3×10^{-33}
Aluminum phosphate	AlPO ₄	9.84×10^{-21}
Barium carbonate	BaCO ₃	2.58×10^{-9}
Barium chromate	BaCrO ₄	1.17×10^{-10}
Barium fluoride	BaF ₂	2.45×10^{-5}
Barium hydroxide	Ba(OH) ₂	5.0×10^{-3}
Barium oxalate	BaC ₂ O ₄	1.6×10^{-6}
Barium phosphate	Ba ₃ (PO ₄) ₂	6×10^{-39}
Barium sulfate	BaSO ₄	1.07×10^{-10}

Compound	Formula	K_{sp}
Cadmium carbonate	CdCO ₃	1.0×10^{-12}
Cadmium hydroxide	Cd(OH) ₂	7.2×10^{-15}
Cadmium sulfide	CdS	8×10^{-28}
Calcium carbonate	CaCO ₃	4.96×10^{-9}
Calcium chromate	CaCrO ₄	7.1×10^{-4}
Calcium fluoride	CaF ₂	1.46×10^{-10}
Calcium hydroxide	Ca(OH) ₂	4.68×10^{-6}
Calcium hydrogen phosphate	CaHPO ₄	1×10^{-7}

(continued on the next page)

Compound	Formula	K_{sp}
Calcium oxalate	CaC_2O_4	2.32×10^{-9}
Calcium phosphate	$\text{Ca}_3(\text{PO}_4)_2$	2.07×10^{-33}
Calcium sulfate	CaSO_4	7.10×10^{-5}
Chromium(III) hydroxide	$\text{Cr}(\text{OH})_3$	6.3×10^{-31}
Cobalt(II) carbonate	CoCO_3	1.0×10^{-10}
Cobalt(II) hydroxide	$\text{Co}(\text{OH})_2$	5.92×10^{-15}
Cobalt(II) sulfide	CoS	5×10^{-22}
Copper(I) bromide	CuBr	6.27×10^{-9}
Copper(I) chloride	CuCl	1.72×10^{-7}
Copper(I) cyanide	CuCN	3.47×10^{-20}
Copper(II) carbonate	CuCO_3	2.4×10^{-10}
Copper(II) hydroxide	$\text{Cu}(\text{OH})_2$	2.2×10^{-20}
Copper(II) phosphate	$\text{Cu}_3(\text{PO}_4)_2$	1.40×10^{-37}
Copper(II) sulfide	CuS	1.27×10^{-36}
Iron(II) carbonate	FeCO_3	3.07×10^{-11}
Iron(II) hydroxide	$\text{Fe}(\text{OH})_2$	4.87×10^{-17}
Iron(II) sulfide	FeS	3.72×10^{-19}
Iron(III) hydroxide	$\text{Fe}(\text{OH})_3$	2.79×10^{-39}
Lanthanum fluoride	LaF_3	2×10^{-19}
Lanthanum iodate	$\text{La}(\text{IO}_3)_3$	7.50×10^{-12}
Lead(II) bromide	PbBr_2	4.67×10^{-6}
Lead(II) carbonate	PbCO_3	7.40×10^{-14}
Lead(II) chloride	PbCl_2	1.17×10^{-5}
Lead(II) chromate	PbCrO_4	2.8×10^{-13}
Lead(II) fluoride	PbF_2	3.3×10^{-8}
Lead(II) hydroxide	$\text{Pb}(\text{OH})_2$	1.43×10^{-20}
Lead(II) iodide	PbI_2	9.8×10^{-9}
Lead(II) phosphate	$\text{Pb}_3(\text{PO}_4)_2$	1×10^{-54}
Lead(II) sulfate	PbSO_4	1.82×10^{-8}
Lead(II) sulfide	PbS	9.04×10^{-29}
Magnesium carbonate	MgCO_3	6.82×10^{-6}
Magnesium fluoride	MgF_2	5.16×10^{-11}
Magnesium hydroxide	$\text{Mg}(\text{OH})_2$	2.06×10^{-13}
Magnesium oxalate	MgC_2O_4	4.83×10^{-6}

Compound	Formula	K_{sp}
Manganese(II) carbonate	MnCO_3	2.24×10^{-11}
Manganese(II) hydroxide	$\text{Mn}(\text{OH})_2$	1.6×10^{-13}
Manganese(II) sulfide	MnS	2.3×10^{-13}
Mercury(I) bromide	Hg_2Br_2	6.40×10^{-23}
Mercury(I) carbonate	Hg_2CO_3	3.6×10^{-17}
Mercury(I) chloride	Hg_2Cl_2	1.43×10^{-18}
Mercury(I) chromate	Hg_2CrO_4	2×10^{-9}
Mercury(I) cyanide	$\text{Hg}_2(\text{CN})_2$	5×10^{-40}
Mercury(I) iodide	Hg_2I_2	5.2×10^{-29}
Mercury(II) hydroxide	$\text{Hg}(\text{OH})_2$	3.1×10^{-26}
Mercury(II) sulfide	HgS	1.6×10^{-54}
Nickel(II) carbonate	NiCO_3	1.42×10^{-7}
Nickel(II) hydroxide	$\text{Ni}(\text{OH})_2$	5.48×10^{-16}
Nickel(II) sulfide	NiS	3×10^{-20}
Silver bromate	AgBrO_3	5.38×10^{-5}
Silver bromide	AgBr	5.35×10^{-13}
Silver carbonate	Ag_2CO_3	8.46×10^{-12}
Silver chloride	AgCl	1.77×10^{-10}
Silver chromate	Ag_2CrO_4	1.12×10^{-12}
Silver cyanide	AgCN	5.97×10^{-17}
Silver iodide	AgI	8.51×10^{-17}
Silver phosphate	Ag_3PO_4	8.89×10^{-17}
Silver sulfate	Ag_2SO_4	1.20×10^{-5}
Silver sulfide	Ag_2S	6×10^{-51}
Strontium carbonate	SrCO_3	5.60×10^{-10}
Strontium chromate	SrCrO_4	3.6×10^{-5}
Strontium phosphate	$\text{Sr}_3(\text{PO}_4)_2$	1×10^{-31}
Strontium sulfate	SrSO_4	3.44×10^{-7}
Tin(II) hydroxide	$\text{Sn}(\text{OH})_2$	5.45×10^{-27}
Tin(II) sulfide	SnS	1×10^{-26}
Zinc carbonate	ZnCO_3	1.46×10^{-10}
Zinc hydroxide	$\text{Zn}(\text{OH})_2$	3×10^{-17}
Zinc oxalate	ZnC_2O_4	2.7×10^{-8}
Zinc sulfide	ZnS	2×10^{-25}

5. Complex Ion Formation Constants in Water at 25 °C

Complex Ion	K_f
$[\text{Ag}(\text{CN})_2]^-$	1×10^{21}
$[\text{Ag}(\text{EDTA})]^{3-}$	2.1×10^7
$[\text{Ag}(\text{en})_2]^+$	5.0×10^7
$[\text{Ag}(\text{NH}_3)_2]^+$	1.7×10^7
$[\text{Ag}(\text{SCN})_4]^{3-}$	1.2×10^{10}
$[\text{Ag}(\text{S}_2\text{O}_3)_2]^-$	2.8×10^{13}
$[\text{Al}(\text{EDTA})]^-$	1.3×10^{16}
$[\text{AlF}_6]^{3-}$	7×10^{19}

Complex Ion	K_f
$[\text{Al}(\text{OH})_4]^-$	3×10^{33}
$[\text{Al}(\text{ox})_3]^{3-}$	2×10^{16}
$[\text{CdBr}_4]^{2-}$	5.5×10^3
$[\text{Cd}(\text{CN})_4]^{2-}$	3×10^{18}
$[\text{CdCl}_4]^{2-}$	6.3×10^2
$[\text{Cd}(\text{en})_3]^{2+}$	1.2×10^{12}
$[\text{CdI}_4]^{2-}$	2×10^6
$[\text{Co}(\text{EDTA})]^{2-}$	2.0×10^{16}

Complex Ion	K_f
$[\text{Co}(\text{EDTA})]^-$	1×10^{36}
$[\text{Co}(\text{en})_3]^{2+}$	8.7×10^{13}
$[\text{Co}(\text{en})_3]^{3+}$	4.9×10^{48}
$[\text{Co}(\text{NH}_3)_6]^{2+}$	1.3×10^5
$[\text{Co}(\text{NH}_3)_6]^{3+}$	2.3×10^{33}
$[\text{Co}(\text{OH})_4]^{2-}$	5×10^9
$[\text{Co}(\text{ox})_3]^{4-}$	5×10^9
$[\text{Co}(\text{ox})_3]^{3-}$	1×10^{20}
$[\text{Co}(\text{SCN})_4]^{2-}$	1×10^3
$[\text{Cr}(\text{EDTA})]^-$	1×10^{23}
$[\text{Cr}(\text{OH})_4]^-$	8.0×10^{29}
$[\text{CuCl}_3]^{2-}$	5×10^5
$[\text{Cu}(\text{CN})_4]^{2-}$	1.0×10^{25}
$[\text{Cu}(\text{EDTA})]^{2-}$	5×10^{18}
$[\text{Cu}(\text{en})_2]^{2+}$	1×10^{20}
$[\text{Cu}(\text{NH}_3)_4]^{2+}$	1.7×10^{13}
$[\text{Cu}(\text{ox})_2]^{2-}$	3×10^8
$[\text{Fe}(\text{CN})_6]^{4-}$	1.5×10^{35}
$[\text{Fe}(\text{CN})_6]^{3-}$	2×10^{43}
$[\text{Fe}(\text{EDTA})]^{2-}$	2.1×10^{14}
$[\text{Fe}(\text{EDTA})]^-$	1.7×10^{24}
$[\text{Fe}(\text{en})_3]^{2+}$	5.0×10^9
$[\text{Fe}(\text{ox})_3]^{4-}$	1.7×10^5
$[\text{Fe}(\text{ox})_3]^{3-}$	2×10^{20}
$[\text{Fe}(\text{SCN})]^{2+}$	8.9×10^2
$[\text{Hg}(\text{CN})_4]^{2-}$	1.8×10^{41}

Complex Ion	K_f
$[\text{HgCl}_4]^{2-}$	1.1×10^{16}
$[\text{Hg}(\text{EDTA})]^{2-}$	6.3×10^{21}
$[\text{Hg}(\text{en})_2]^{2+}$	2×10^{23}
$[\text{HgI}_4]^{2-}$	2×10^{30}
$[\text{Hg}(\text{ox})_2]^{2-}$	9.5×10^6
$[\text{Ni}(\text{CN})_4]^{2-}$	2×10^{31}
$[\text{Ni}(\text{EDTA})]^{2-}$	3.6×10^{18}
$[\text{Ni}(\text{en})_3]^{2+}$	2.1×10^{18}
$[\text{Ni}(\text{NH}_3)_6]^{2+}$	2.0×10^8
$[\text{Ni}(\text{ox})_3]^{4-}$	3×10^8
$[\text{PbCl}_3]^-$	2.4×10^1
$[\text{Pb}(\text{EDTA})]^{2-}$	2×10^{18}
$[\text{PbI}_4]^{2-}$	3.0×10^4
$[\text{Pb}(\text{OH})_3]^-$	8×10^{13}
$[\text{Pb}(\text{ox})_2]^{2-}$	3.5×10^6
$[\text{Pb}(\text{S}_2\text{O}_3)_3]^{4-}$	2.2×10^6
$[\text{PtCl}_4]^{2-}$	1×10^{16}
$[\text{Pt}(\text{NH}_3)_6]^{2+}$	2×10^{35}
$[\text{Sn}(\text{OH})_3]^-$	3×10^{25}
$[\text{Zn}(\text{CN})_4]^{2-}$	2.1×10^{19}
$[\text{Zn}(\text{EDTA})]^{2-}$	3×10^{16}
$[\text{Zn}(\text{en})_3]^{2+}$	1.3×10^{14}
$[\text{Zn}(\text{NH}_3)_4]^{2+}$	2.8×10^9
$[\text{Zn}(\text{OH})_4]^{2-}$	2×10^{15}
$[\text{Zn}(\text{ox})_3]^{4-}$	1.4×10^8

D. Standard Electrode Potentials at 25 °C

Half-Reaction	$E^\circ(\text{V})$
$\text{F}_2(g) + 2 \text{e}^- \longrightarrow 2 \text{F}^-(aq)$	2.87
$\text{O}_3(g) + 2 \text{H}^+(aq) + 2 \text{e}^- \longrightarrow \text{O}_2(g) + \text{H}_2(l)$	2.08
$\text{Ag}^{2+}(aq) + \text{e}^- \longrightarrow \text{Ag}^+(aq)$	1.98
$\text{Co}^{3+}(aq) + \text{e}^- \longrightarrow \text{Co}^{2+}(aq)$	1.82
$\text{H}_2\text{O}_2(aq) + 2 \text{H}^+(aq) + 2 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(l)$	1.78
$\text{PbO}_2(s) + 4 \text{H}^+(aq) + \text{SO}_4^{2-}(aq) + 2 \text{e}^- \longrightarrow \text{PbSO}_4(s) + 2 \text{H}_2\text{O}(l)$	1.69
$\text{MnO}_4^-(aq) + 4 \text{H}^+(aq) + 3 \text{e}^- \longrightarrow \text{MnO}_2(s) + 2 \text{H}_2\text{O}(l)$	1.68
$2 \text{HClO}(aq) + 2 \text{H}^+(aq) + 2 \text{e}^- \longrightarrow \text{Cl}_2(g) + 2 \text{H}_2\text{O}(l)$	1.61
$\text{MnO}_4^-(aq) + 8 \text{H}^+(aq) + 5 \text{e}^- \longrightarrow \text{Mn}^{2+}(aq) + 4 \text{H}_2\text{O}(l)$	1.51
$\text{Au}^{3+}(aq) + 3 \text{e}^- \longrightarrow \text{Au}(s)$	1.50
$2 \text{BrO}_3^-(aq) + 12 \text{H}^+(aq) + 10 \text{e}^- \longrightarrow \text{Br}_2(l) + 6 \text{H}_2\text{O}(l)$	1.48
$\text{PbO}_2(s) + 4 \text{H}^+(aq) + 2 \text{e}^- \longrightarrow \text{Pb}^{2+}(aq) + 2 \text{H}_2\text{O}(l)$	1.46

Half-Reaction	$E^\circ(\text{V})$
$\text{Cl}_2(g) + 2 \text{e}^- \longrightarrow 2 \text{Cl}^-(aq)$	1.36
$\text{Cr}_2\text{O}_7^{2-}(aq) + 14 \text{H}^+(aq) + 6 \text{e}^- \longrightarrow 2 \text{Cr}^{3+}(aq) + 7 \text{H}_2\text{O}(l)$	1.33
$\text{O}_2(g) + 4 \text{H}^+(aq) + 4 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(l)$	1.23
$\text{MnO}_2(s) + 4 \text{H}^+(aq) + 2 \text{e}^- \longrightarrow \text{Mn}^{2+}(aq) + 2 \text{H}_2\text{O}(l)$	1.21
$\text{IO}_3^-(aq) + 6 \text{H}^+(aq) + 5 \text{e}^- \longrightarrow \frac{1}{2} \text{I}_2(aq) + 3 \text{H}_2\text{O}(l)$	1.20
$\text{Br}_2(l) + 2 \text{e}^- \longrightarrow 2 \text{Br}^-(aq)$	1.09
$\text{AuCl}_4^-(aq) + 3 \text{e}^- \longrightarrow \text{Au}(s) + 4 \text{Cl}^-(aq)$	1.00
$\text{VO}_2^+(aq) + 2 \text{H}^+(aq) + \text{e}^- \longrightarrow \text{VO}^{2+}(aq) + \text{H}_2\text{O}(l)$	1.00
$\text{HNO}_2(aq) + \text{H}^+(aq) + \text{e}^- \longrightarrow \text{NO}(g) + 2 \text{H}_2\text{O}(l)$	0.98
$\text{NO}_3^-(aq) + 4 \text{H}^+(aq) + 3 \text{e}^- \longrightarrow \text{NO}(g) + 2 \text{H}_2\text{O}(l)$	0.96
$\text{ClO}_2(g) + \text{e}^- \longrightarrow \text{ClO}_2^-(aq)$	0.95
$2 \text{Hg}^{2+}(aq) + 2 \text{e}^- \longrightarrow 2 \text{Hg}_2^{2+}(aq)$	0.92

(continued on the next page)

Half-Reaction	$E^\circ(V)$	Half-Reaction	$E^\circ(V)$
$\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag(s)}$	0.80	$\text{AgI(s)} + \text{e}^- \longrightarrow \text{Ag(s)} + \text{I}^-(\text{aq})$	-0.15
$\text{Hg}_2^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow 2 \text{Hg(l)}$	0.80	$\text{N}_2(\text{g}) + 5 \text{H}^+(\text{aq}) + 4 \text{e}^- \longrightarrow \text{N}_2\text{H}_5^+(\text{aq})$	-0.23
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$	0.77	$\text{Ni}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Ni(s)}$	-0.23
$\text{PtCl}_4^{2-}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Pt(s)} + 4 \text{Cl}^-(\text{aq})$	0.76	$\text{Co}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Co(s)}$	-0.28
$\text{O}_2(\text{g}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2\text{O}_2(\text{aq})$	0.70	$\text{PbSO}_4(\text{s}) + 2 \text{e}^- \longrightarrow \text{Pb(s)} + \text{SO}_4^{2-}(\text{aq})$	-0.36
$\text{MnO}_4^-(\text{aq}) + \text{e}^- \longrightarrow \text{MnO}_4^{2-}(\text{aq})$	0.56	$\text{Cd}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Cd(s)}$	-0.40
$\text{I}_2(\text{s}) + 2 \text{e}^- \longrightarrow 2 \text{I}^-(\text{aq})$	0.54	$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Fe(s)}$	-0.45
$\text{Cu}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Cu(s)}$	0.52	$2 \text{CO}_2(\text{g}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2\text{C}_2\text{O}_4(\text{aq})$	-0.49
$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O(l)} + 4 \text{e}^- \longrightarrow 4 \text{OH}^-(\text{aq})$	0.40	$\text{Cr}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Cr}^{2+}(\text{aq})$	-0.50
$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Cu(s)}$	0.34	$\text{Cr}^{3+}(\text{aq}) + 3 \text{e}^- \longrightarrow \text{Cr(s)}$	-0.73
$\text{BiO}^+(\text{aq}) + 2 \text{H}^+(\text{aq}) + 3 \text{e}^- \longrightarrow \text{Bi(s)} + \text{H}_2\text{O(l)}$	0.32	$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Zn(s)}$	-0.76
$\text{Hg}_2\text{Cl}_2(\text{s}) + 2 \text{e}^- \longrightarrow 2 \text{Hg(l)} + 2 \text{Cl}^-(\text{aq})$	0.27	$2 \text{H}_2\text{O(l)} + 2 \text{e}^- \longrightarrow \text{H}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$	-0.83
$\text{AgCl(s)} + \text{e}^- \longrightarrow \text{Ag(s)} + \text{Cl}^-(\text{aq})$	0.22	$\text{Mn}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Mn(s)}$	-1.18
$\text{SO}_4^{2-}(\text{aq}) + 4 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2\text{SO}_3(\text{aq}) + \text{H}_2\text{O(l)}$	0.20	$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \longrightarrow \text{Al(s)}$	-1.66
$\text{Cu}^{2+}(\text{aq}) + \text{e}^- \longrightarrow \text{Cu}^+(\text{aq})$	0.16	$\text{H}_2(\text{g}) + 2 \text{e}^- \longrightarrow 2 \text{H}^-(\text{aq})$	-2.23
$\text{Sn}^{4+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Sn}^{2+}(\text{aq})$	0.15	$\text{Mg}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Mg(s)}$	-2.37
$\text{S(s)} + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2\text{S(g)}$	0.14	$\text{La}^{3+}(\text{aq}) + 3 \text{e}^- \longrightarrow \text{La(s)}$	-2.38
$\text{AgBr(s)} + \text{e}^- \longrightarrow \text{Ag(s)} + \text{Br}^-(\text{aq})$	0.071	$\text{Na}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Na(s)}$	-2.71
$2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2(\text{g})$	0.00	$\text{Ca}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Ca(s)}$	-2.76
$\text{Fe}^{3+}(\text{aq}) + 3 \text{e}^- \longrightarrow \text{Fe(s)}$	-0.036	$\text{Ba}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Ba(s)}$	-2.90
$\text{Pb}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Pb(s)}$	-0.13	$\text{K}^+(\text{aq}) + \text{e}^- \longrightarrow \text{K(s)}$	-2.92
$\text{Sn}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Sn(s)}$	-0.14	$\text{Li}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Li(s)}$	-3.04

E. Vapor Pressure of Water at Various Temperatures

T (°C)	P (torr)						
0	4.58	21	18.65	35	42.2	92	567.0
5	6.54	22	19.83	40	55.3	94	610.9
10	9.21	23	21.07	45	71.9	96	657.6
12	10.52	24	22.38	50	92.5	98	707.3
14	11.99	25	23.76	55	118.0	100	760.0
16	13.63	26	25.21	60	149.4	102	815.9
17	14.53	27	26.74	65	187.5	104	875.1
18	15.48	28	28.35	70	233.7	106	937.9
19	16.48	29	30.04	80	355.1	108	1004.4
20	17.54	30	31.82	90	525.8	110	1074.6

Appendix III:

Answers to Selected Exercises

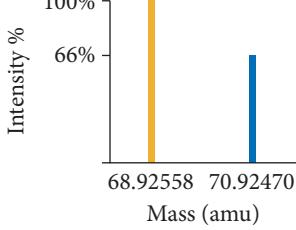
Chapter 1

33. a. theory b. observation
c. law d. observation
35. Several answers possible.
37. a. mixture, homogeneous
b. pure substance, compound
c. pure substance, element
d. mixture, heterogeneous
- | 39. Substance | Pure or Mixture | Type |
|-------------------|-----------------|---------------|
| Aluminum | Pure | Element |
| Apple juice | Mixture | Homogeneous |
| Hydrogen peroxide | Pure | Compound |
| Chicken soup | Mixture | Heterogeneous |
41. a. pure substance, compound
b. mixture, heterogeneous
c. mixture, homogeneous
d. pure substance, element
43. physical, chemical, physical, physical, physical
45. a. chemical b. physical
c. physical d. chemical
47. a. chemical b. physical
c. chemical d. chemical
49. a. physical b. chemical c. physical
51. a. 0°C b. -321°F
c. -78.3°F d. 310.2 K
53. -62.2°C , 210.9 K
55. a. 1.2 nm b. 22 fs
c. 1.5 Gg d. 3.5 ML
57. a. $4.5 \times 10^{-9}\text{ s}$ b. $1.8 \times 10^{-14}\text{ s}$
c. $1.28 \times 10^{-10}\text{ m}$ d. $3.5 \times 10^{-5}\text{ m}$
- | | | |
|----------------------|---------------------------------|-------------------------------|
| 59. 1245 kg | $1.245 \times 10^6\text{ g}$ | $1.245 \times 10^9\text{ mg}$ |
| 515 km | $5.15 \times 10^6\text{ dm}$ | $5.15 \times 10^7\text{ cm}$ |
| 122.355 s | $1.22355 \times 10^5\text{ ms}$ | 0.122355 ks |
| 3.345 kJ | $3.345 \times 10^3\text{ J}$ | $3.345 \times 10^6\text{ mJ}$ |
61. a. 254.998 km b. $2.54998 \times 10^{-1}\text{ Mm}$
c. $254998 \times 10^3\text{ mm}$ d. $254998 \times 10^2\text{ cm}$
63. 10,000 1 cm squares
65. no
67. 1.26 g/cm^3
69. a. 463 g b. 3.7 L
71. $201. \times 10^3\text{ g}$
73. a. 73.7 mL b. 88.3°C c. 647 mL
75. a. 1,050,501 b. 0.0020
c. 0.00000000000002 d. 0.001090
77. a. 3 b. ambiguous, without more information assume three significant figures
c. 3 d. 5
e. ambiguous, without more information assume one significant figure

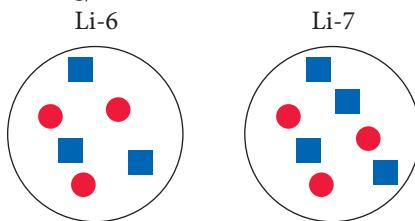
79. a. not exact b. exact
c. not exact d. exact
81. a. 156.9 b. 156.8
c. 156.8 d. 156.9
83. a. 1.84 b. 0.033
c. 0.500 d. 34
85. a. 41.4 b. 133.5
c. 73.0 d. 0.42
87. a. 391.3 b. 1.1×10^4
c. 5.96 d. 5.93×10^4
89. a. $2.78 \times 10^4\text{ cm}^3$ b. $1.898 \times 10^{-3}\text{ kg}$
c. $1.98 \times 10^7\text{ cm}$
91. a. 60.6 in b. $3.14 \times 10^3\text{ g}$
c. 3.7 qt d. 4.29 in
93. $5.0 \times 10^1\text{ min}$
95. $4.0 \times 10^1\text{ mi/gal}$
97. a. $1.95 \times 10^{-4}\text{ km}^2$ b. $1.95 \times 10^4\text{ dm}^2$
c. $1.95 \times 10^6\text{ cm}^2$
99. 0.680 mi^2
101. 0.95 mL
103. $3.1557 \times 10^7\text{ s/solar year}$
105. a. extensive b. intensive
c. intensive d. intensive
e. extensive
107. -34°F
109. $F = \text{kg}(\text{m/s}^2) = \text{N}$ (for newton), kN , pN
111. a. 2.2×10^{-6}
b. 0.0159
c. 6.9×10^4
113. a. mass of can of gold = $1.9 \times 10^4\text{ g}$
mass of can of sand = $3.0 \times 10^3\text{ g}$
b. Yes, the thief sets off the trap because the can of sand is lighter than the gold cylinder.
115. 22 in^3
117. 7.6 g/cm^3
119. $3.11 \times 10^5\text{ lb}$
121. $3.3 \times 10^2\text{ km}$
123. 6.8×10^{-15}
125. $2.4 \times 10^{19}\text{ km}$
127. 488 grams
129. $0.661\text{ }\Omega$
131. 0.492
133. 18.2 atm
135. $1\text{ J} = 1\text{ kg m}^2/\text{s}^2$
 $m = \text{kg}$, $v^2 = (\text{m/s})^2$ $mv = \text{kg m}^2/\text{s}^2$
 $P = \text{N/m}^2 = \text{kg m/s}^2/\text{m}^2 = \text{kg/m s}^2$
 $V = \text{m}^3 PV = \text{kg m}^3/\text{m s}^2 = \text{kg m}^2/\text{s}^2$
137. $9.0 \times 10^1\text{ mg CO}$
139. 13% increase

- 141.** No. Since the container is sealed the atoms and molecules can move around, but they cannot leave. If no atoms or molecules can leave, the mass must be constant.
- 143.** 343 1 cm cubes
- 145.** **a.** the dark block **b.** the light-colored block
c. cannot tell
- 147.** **a.** law **b.** theory
c. observation

Chapter 2

- 29.** 13.5 g
- 31.** These results are not consistent with the law of definite proportions because sample 1 is composed of 11.5 parts Cl to 1 part C and sample 2 is composed of 9.05 parts Cl to 1 part C. The law of definite proportions states that a given compound always contains exactly the same proportion of elements by mass.
- 33.** 23.8 g
- 35.** For the law of multiple proportions to hold, the ratio of the masses of O combining with 1 g of O's in the compound should be a small whole number.
 $0.3369/0.168 = 2.00$
- 37.** Sample 1: 1.00 g O₂/1.00 g S;
 Sample 2: 1.50 g O₂/1.00 g S
 $\text{Sample 2}/\text{sample 1} = 1.50/1.00 = 1.50$
 $3 \text{ O atoms}/2 \text{ O atoms} = 1.5$
- 39.** **a.** not consistent
b. consistent: Dalton's atomic theory states that the atoms of a given element are identical.
c. consistent: Dalton's atomic theory states that atoms combine in simple whole-number ratios to form compounds.
d. not consistent
- 41.** **a.** consistent: Rutherford's nuclear model states that the atom is largely empty space.
b. consistent: Rutherford's nuclear model states that most of the atom's mass is concentrated in a tiny region called the nucleus.
c. not consistent **d.** not consistent
- 43.** -2.3×10^{-19} C
- 45.** 9.4×10^{13} excess electrons, 8.5×10^{-17} kg
- 47.** **a, b, c**
- 49.** 1.83×10^3 e⁻
- 51.** **a.** Ag-107 **b.** Ag-109
c. U-238 **d.** H-2
- 53.** **a.** 7 ${}_1^1$ p and 7 ${}_0^1$ n
c. 86 ${}_1^1$ p and 136 ${}_0^1$ n **b.** 11 ${}_1^1$ p and 12 ${}_0^1$ n
d. 82 ${}_1^1$ p and 126 ${}_0^1$ n
- 55.** 6 ${}_1^1$ p and 8 ${}_0^1$ n, ${}_{14}^6$ C
- 57.** **a.** 28 ${}_1^1$ p and 26 e⁻
c. 35 ${}_1^1$ p and 36 e⁻ **b.** 16 ${}_1^1$ p and 18 e⁻
d. 24 ${}_1^1$ p and 21 e⁻
- 59.** **a.** 2-
c. 3+ **b.** 1+
d. 1+
- 61.**
- | Symbol | Ion Formed | Number of Electrons in Ion | Number of Protons in Ion |
|--------|------------------|----------------------------|--------------------------|
| Ca | Ca ²⁺ | 18 | 20 |
| Be | Be ²⁺ | 2 | 4 |
| Se | Se ²⁻ | 36 | 34 |
| In | In ³⁺ | 46 | 49 |
- 63.** **a.** potassium, metal **b.** barium, metal
c. iodine, nonmetal **d.** oxygen, nonmetal
e. antimony, metalloid
- 65.** **a** and **b** are main group elements.
- 67.** **a.** alkali metal **b.** halogen
c. alkaline earth metal **d.** alkaline earth metal
e. noble gas
- 69.** Cl and F because they are in the same group or family. Elements in the same group or family have similar chemical properties.
- 71.** 
- 73.** The fluorine-19 isotope must have a large percent abundance, which would make fluorine produce a large peak at this mass. Chlorine has two isotopes (Cl-35 and Cl-37). The atomic mass is simply the weighted average of these two, which means that there is no chlorine isotope with a mass of 35.45 amu.
- 75.** 121.8 amu, Sb
- 77.** Br-79 78.92, amu 50.96%
- 79.** 152 amu
- 81.** 3.32×10^{24} atoms
- 83.** **a.** 0.295 mol Ar **b.** 0.0543 mol Zn
c. 0.144 mol Ta **d.** 0.0304 mol Li
- 85.** 2.11×10^{22} atoms
- 87.** **a.** 1.01×10^{23} atoms **b.** 6.78×10^{21} atoms
c. 5.39×10^{21} atoms **d.** 5.6×10^{20} atoms
- 89.** **a.** 36 grams **b.** 0.187 grams
c. 62 grams **d.** 3.1 grams
- 91.** 2.6×10^{21} atoms
- 93.** 3.239×10^{-22} g
- 95.** 1.50 g
- 97.** C₂O₃
- 99.** 4.82241×10^7 C/kg
- 101.** 207 amu
- 103.** ²³⁷Pa, ²³⁸U, ²³⁹Np, ²⁴⁰Pu, ²³⁵Ac, ²³⁴Ra, etc.
- 105.**
- | Symbol | Z | A | #p | #e ⁻ | #n | Charge |
|------------------|----|----|----|-----------------|----|--------|
| 0 | 8 | 16 | 8 | 10 | 8 | 2- |
| Ca ²⁺ | 20 | 40 | 20 | 18 | 20 | 2+ |
| Mg ²⁺ | 12 | 25 | 12 | 10 | 13 | 2+ |
| N ³⁻ | 7 | 14 | 7 | 10 | 7 | 3- |

107. $V_n = 8.2 \times 10^{-8} \text{ pm}^3$, $V_a = 1.4 \times 10^6 \text{ pm}^3$, $5.9 \times 10^{-12}\%$
 109. 6.022×10^{21} dollars total, 9.3×10^{11} dollars per person, billionaires
 111. 15.985 amu
 113. 4.76×10^{24} atoms
 115. Li-6 = 7.494%, Li-7 = 92.506%
 117. 75.0% gold
 119. 106.91 amu
 121. 1.66×10^{22} gold atoms
 123. 1×10^{78} atoms/universe
 125. 0.423
 127. 63.67 g/mol
 129. 25.06 g/mol
 131. Li-6



133. If the amu and mole were not based on the same isotope, the numerical values obtained for an atom of material and a mole of material would not be the same. If, for example, the mole was based on the number of particles in C-12 but the amu was changed to a fraction of the mass of an atom of Ne-20, the number of particles and the number of amu that make up one mole of material would no longer be the same. We would no longer have the relationship in which the mass of an atom in amu is numerically equal to the mass of a mole of those atoms in grams.
 135. The different isotopes of the same element have the same number of protons and electrons, so the attractive forces between the nucleus and the electrons are constant and there is no difference in the radii of the isotopes. Ions, on the other hand, have a different number of electrons than the parent atom from which they are derived. Cations have fewer electrons than the parent atom. The attractive forces are greater because there is a larger positive charge in the nucleus than the negative charge in the electron cloud. So, cations are smaller than the atom they are derived from. Anions have more electrons than the parent. The electron cloud has a greater negative charge than the nucleus, so the anions have larger radii than the parent.

Chapter 3

23. a. 3 Mg, 2 P, 8 O b. 1 Ba, 2 Cl
 c. 1 Fe, 2 N, 4 O d. 1 Ca, 2 O, 2 H
 25. a. NH₃ b. C₂H₆ c. SO₃
 27. a. atomic b. molecular
 c. atomic d. molecular
 29. a. molecular b. ionic
 c. ionic d. molecular
 31. a. molecular element b. molecular compound
 c. atomic element

33. a. CaO b. ZnS
 c. RbBr d. Al₂O₃
 35. a. Ca(OH)₂ b. CaCrO₄
 c. Ca₃(PO₄)₂ d. Ca(CN)₂
 37. a. magnesium nitride b. potassium fluoride
 c. sodium oxide d. lithium sulfide
 e. cesium fluoride f. potassium iodide
 39. a. tin(II) oxide b. chromium(III) sulfide
 c. rubidium iodide d. barium bromide
 41. a. copper(I) nitrite b. magnesium acetate
 c. barium nitrate d. lead(II) acetate
 43. a. NaHSO₃ b. LiMnO₄
 c. AgNO₃ d. K₂SO₄
 e. RbHSO₄ f. KHCO₃
 45. a. cobalt(II) sulfate heptahydrate b. IrBr₃ · 4 H₂O
 c. Magnesium bromate hexahydrate d. K₂CO₃ · 2 H₂O
 47. a. carbon monoxide b. nitrogen triiodide
 c. silicon tetrachloride d. tetranitrogen tetraselenide
 49. a. PCl₃ b. ClO
 c. S₂F₄ d. PF₅
 51. a. hydroiodic acid b. nitric acid
 c. carbonic acid d. acetic acid
 53. a. HF b. HBr c. H₂SO₃
 55. a. strontium chloride b. tin(IV) oxide
 c. diphosphorus pentasulfide d. acetic acid
 57. a. potassium chlorate b. diiodine pentoxide
 c. lead(II) sulfate d. 58.12 amu
 59. a. 46.01 amu b. 238.03 amu
 c. 180.16 amu d. 0.0362 mol
 61. a. 0.471 mol b. 0.279 mol
 c. 968 mol d. 28.4 mol
 63. a. 0.554 mol b. 1093 mol
 c. 0.378 mol d. 2.992 × 10⁻²² g
 65. a. 2.2 × 10²³ molecules b. 7.06 × 10²³ molecules
 c. 4.16 × 10²³ molecules d. 1.09 × 10²³ molecules
 67. a. 0.0790 g b. 0.84 g c. 0.10 mg
 69. a. 74.87% C b. 79.88% C
 c. 92.24% C d. 37.23% C
 73. NH₃: 82.27% N
 CO(NH₂)₂: 46.65% N
 NH₄NO₃: 35.00% N
 (NH₄)₂SO₄: 21.20% N
 NH₃ has the highest N content
 75. 20.8 g F
 77. 196 μg KI
 79. a. 2 : 1 b. 4 : 1 c. 6 : 2 : 1
 81. a. 0.885 mol H b. 5.2 mol H
 c. 29 mol H d. 33.7 mol H
 83. a. 3.3 g Na b. 3.6 g Na
 c. 1.4 g Na d. 1.7 g Na
 85. a. Ag₂O b. Co₃As₂O₈ c. SeBr₄

87. a. C_5H_7N b. $C_4H_5N_2O$

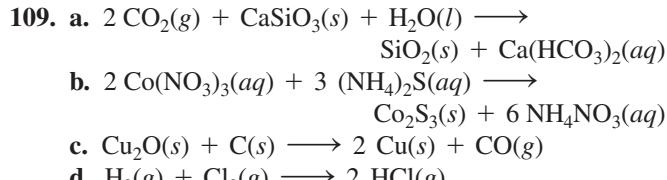
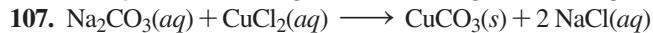
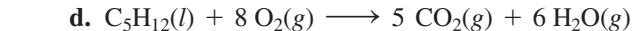
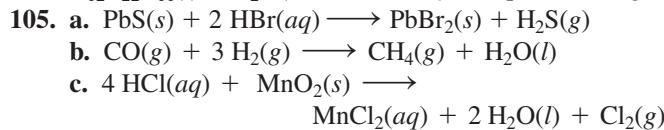
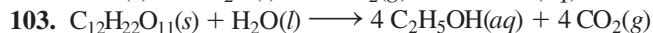
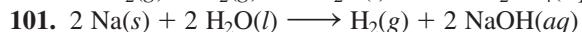
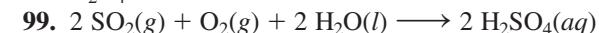
89. $C_{13}H_{18}O_2$

91. NCI_3

93. a. $C_{12}H_{14}N_2$
c. $C_{10}H_{20}N_2S_4$

95. CH_2

97. C_2H_4O



111. a. inorganic b. organic
c. organic d. inorganic

113. a. alkene b. alkane
c. alkyne d. alkane

115. a. $CH_3CH_2CH_3$ b. propane
c. $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
d. pentane

117. a. functionalized hydrocarbon, alcohol
b. hydrocarbon
c. functionalized hydrocarbon, ketone
d. functionalized hydrocarbon, amine

119. 1.50×10^{24} molecules EtOH

121. a. K_2CrO_4 , 40.27% K, 26.78% Cr, 32.95% O
b. $Pb_3(PO_4)_2$, 76.60% Pb, 7.63% P, 15.77% O
c. H_2SO_3 , 2.46% H, 39.07% S, 58.47% O
d. $CoBr_2$, 26.94% Co, 73.06% Br

123. 1.80×10^2 g Cl_2 /yr

125. M = Fe

127. estradiol = $C_{18}H_{24}O_2$

129. $C_{18}H_{20}O_2$

131. 7 H_2O

133. C_6H_9BrO

135. 1.87×10^{21} atoms

137. 92.93 amu

139. $x = 1, y = 2$

141. 41.7 mg

143. 0.224 g

145. 22.0% by mass

147. 1.6×10^7 kg Cl

149. 7.8×10^3 kg rock

151. $C_5H_{10}SI$

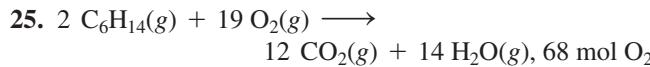
153. X_2Y_3

155. The sphere in the molecular models represents the electron cloud of the atom. On this scale, the nucleus would be too small to see.

157. The statement is incorrect because a chemical formula is based on the ratio of atoms combined, not the ratio of grams combined. The statement should read, “The chemical formula for ammonia (NH_3) indicates that ammonia contains three hydrogen atoms to each nitrogen atom.”

159. O, S, H

Chapter 4



27. a. 5.0 mol NO_2

b. 14. mol NO_2

c. 0.281 mol NO_2

d. 53.1 mol NO_2

mol SiO_2	mol C	mol SiC	mol CO
3	9	3	6
2	6	2	4
5	15	5	10
2.8	8.4	2.8	5.6
0.517	1.55	0.517	1.03

31. a. 9.3 g HBr, 0.12 g H_2

b. 6.55 g $CaCO_3$

c. 6.09 g MgO

d. 6.93 g Al_2O_3

35. a. 4.42 g HCl

c. 4.24 g H_2SO_4

37. a. Na

c. Br_2

39. 3 molecules Cl_2

41. a. 2 mol

b. 7 mol

c. 9.40 mol

43. 0.5 mol O_2

45. a. 2.5 g

b. 31.1 g

c. 1.16 g

47. 2.91 grams CO_2 remaining

49. limiting reactant: Pb^{2+} , theoretical yield: 34.5 g $PbCl_2$, percent yield: 85.3%

51. limiting reactant: NH_3 , theoretical yield: 240.5 kg

CH_4N_2O , percent yield: 70.01%

53. a. 1.17 M LiCl

b. 0.123 M $C_6H_{12}O_6$

c. 0.00453 M $NaCl$

55. a. 0.150 M NO_3^-

b. 0.300 M NO_3^-

c. 0.450 M NO_3^-

57. a. 1.3 mol

b. 1.5 mol

c. 0.211 mol

59. 37 g

61. 0.27 M

63. 6.0 L

65. 37.1 mL

67. 2.1 L

69. barium nitrate, 2.81 g $Ba(NO_3)_2$, 87.1%

71. a. yes

b. no

c. yes

d. no

73. a. soluble Ag^+ , NO_3^-

b. soluble Pb^{2+} , $C_2H_3O_2^-$

c. soluble K^+ , NO_3^-

d. soluble NH_4^+ , S^{2-}

75. a. NO REACTION

b. NO REACTION

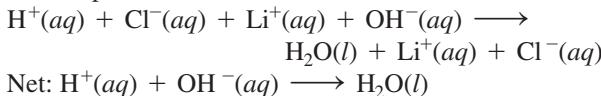
c. $CrBr_2(aq) + Na_2CO_3(aq) \longrightarrow CrCO_3(s) + 2 NaBr(aq)$

d. $3 NaOH(aq) + FeCl_3(aq) \longrightarrow Fe(OH)_3(s) + 3 NaCl(aq)$

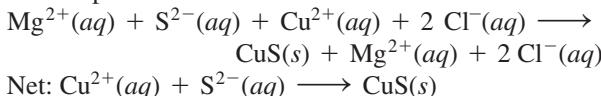
77. a. $\text{K}_2\text{CO}_3(aq) + \text{Pb}(\text{NO}_3)_2(aq) \longrightarrow \text{PbCO}_3(s) + 2 \text{KNO}_3(aq)$
 b. $\text{Li}_2\text{SO}_4(aq) + \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2(aq) \longrightarrow \text{PbSO}_4(s) + 2 \text{LiC}_2\text{H}_3\text{O}_2(aq)$
 c. $\text{Cu}(\text{NO}_3)_2(aq) + \text{MgS}(aq) \longrightarrow \text{CuS}(s) + \text{Mg}(\text{NO}_3)_2(aq)$

d. NO REACTION

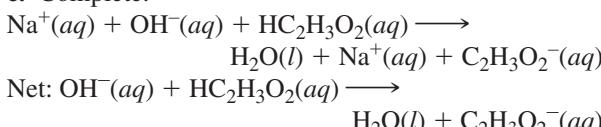
79. a. Complete:



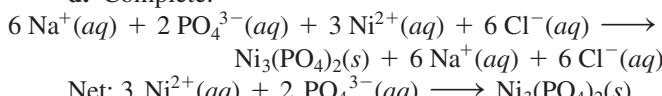
b. Complete:



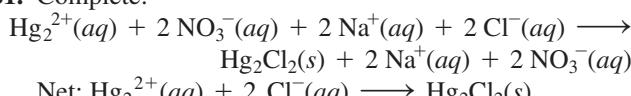
c. Complete:



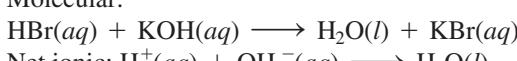
d. Complete:



81. Complete:



83. Molecular:



85. a. $\text{H}_2\text{SO}_4(aq) + \text{Ca}(\text{OH})_2(aq) \longrightarrow 2 \text{H}_2\text{O}(l) + \text{CaSO}_4(s)$
 b. $\text{HClO}_4(aq) + \text{KOH}(aq) \longrightarrow \text{H}_2\text{O}(l) + \text{KClO}_4(aq)$
 c. $\text{H}_2\text{SO}_4(aq) + 2 \text{NaOH}(aq) \longrightarrow 2 \text{H}_2\text{O}(l) + \text{Na}_2\text{SO}_4(aq)$

87. 0.1810 M HClO_4

89. a. $2 \text{HBr}(aq) + \text{NiS}(s) \longrightarrow \text{H}_2\text{S}(g) + \text{NiBr}_2(aq)$
 b. $\text{NH}_4\text{I}(aq) + \text{NaOH}(aq) \longrightarrow \text{H}_2\text{O}(l) + \text{NH}_3(g) + \text{NaI}(aq)$
 c. $2 \text{HBr}(aq) + \text{Na}_2\text{S}(aq) \longrightarrow \text{H}_2\text{S}(g) + 2 \text{NaBr}(aq)$
 d. $2 \text{HClO}_4(aq) + \text{Li}_2\text{CO}_3(aq) \longrightarrow \text{H}_2\text{O}(l) + \text{CO}_2(g) + 2 \text{LiClO}_4(aq)$

91. a. Ag: 0 b. Ag: +1
 c. Ca: +2, F: -1 d. H: +1, S: -2
 e. C: +4, O: -2 f. Cr: +6, O: -2

93. a. +2 b. +6 c. +3

95. a. redox reaction, oxidizing agent: O_2 , reducing agent: Li
 b. redox reaction, oxidizing agent: Fe^{2+} , reducing agent: Mg
 c. not a redox reaction d. not a redox reaction

97. a. $\text{S}(s) + \text{O}_2(g) \longrightarrow \text{SO}_2(g)$
 b. $2 \text{C}_3\text{H}_6(g) + 9 \text{O}_2(g) \longrightarrow 6 \text{CO}_2(g) + 6 \text{H}_2\text{O}(g)$
 c. $2 \text{Ca}(s) + \text{O}_2(g) \longrightarrow 2 \text{CaO}(g)$
 d. $\text{C}_5\text{H}_{12}\text{S}(l) + 9 \text{O}_2(g) \longrightarrow 5 \text{CO}_2(g) + \text{SO}_2(g) + 6 \text{H}_2\text{O}(g)$

99. 3.32 M

101. 1.1 g

103. 3.1 kg

105. limiting reactant: $\text{C}_7\text{H}_6\text{O}_3$, theoretical yield: 1.63 g

$\text{C}_9\text{H}_8\text{O}_4$, percent yield: 74.8%

107. b

109. a. $2 \text{HCl}(aq) + \text{Hg}_2(\text{NO}_3)_2(aq) \longrightarrow \text{Hg}_2\text{Cl}_2(s) + 2 \text{HNO}_3(aq)$
 b. $\text{KHSO}_3(aq) + \text{HNO}_3(aq) \longrightarrow \text{H}_2\text{O}(l) + \text{SO}_2(g) + \text{KNO}_3(aq)$
 c. $2 \text{NH}_4\text{Cl}(aq) + \text{Pb}(\text{NO}_3)_2(aq) \longrightarrow \text{PbCl}_2(s) + 2 \text{NH}_4\text{NO}_3(aq)$
 d. $2 \text{NH}_4\text{Cl}(aq) + \text{Ca}(\text{OH})_2(aq) \longrightarrow 2 \text{NH}_3(g) + 2 \text{H}_2\text{O}(g) + \text{CaCl}_2(aq)$

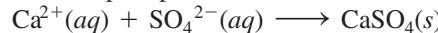
111. 22 g

113. 6.9 g

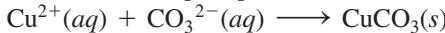
115. NaNO_3 is more economical.

117. Br is the oxidizing agent, Au is the reducing agent, 38.8 g KAuF_4

119. Ca^{2+} and Cu^{2+} present in the original solution. Net ionic for first precipitate:



Net ionic for second precipitate:



121. 0.333 g PH_3

123. 30.8 kg CO_2

125. 1.6 g C_2H_2

127. 11.8 g AgI

129. 5.5% by mass

131. 14 g KO_2 . In designing the unit you would need to consider the theoretical yield and % yield of the reaction, how changing the limiting reactant would affect the reaction, and the stoichiometry between KO_2 and O_2 to determine the mass of KO_2 required to produce enough O_2 for 10 minutes. You might also consider the speed of the reaction and whether or not the reaction produced heat. Additionally, because your body does not use 100% of the oxygen taken in with each breath, the apparatus would only need to replenish the oxygen used. The percentage of oxygen in air is about 20% and the percentage in exhaled air is about 16%, so we will assume that 4% of the air would need to be replenished with oxygen.

133. 37.9 g B_5H_9

135. a. Since the mol ratio of H_2 to NO is 5:2, the 10 mol of H_2 will require 4 mole NO, and H_2 is the limiting reactant. This eliminates answers b and c. Since there is excess NO, this eliminates d, leaving answer a.

137. a

Chapter 5

25. a. 0.832 atm

- c. 12.2 psi

27. a. 809.0 mmHg

- c. 809.0 torr

29. a. 832 mmHg

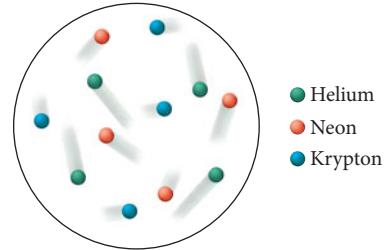
31. 4.4×10^2 mmHg

33. 58.9 mL

35. 4.22 L

37. 3.0 L The volume would not be different if the gas was argon.

- 39.** 1.16 atm
41. 2.1 mol
43. Yes, the final gauge pressure is 43.5 psi, which exceeds the maximum rating.
45. 16.2 L
47. 286 atm, 17.5 bottles purged
49. b
51. 4.76 atm
53. 37.3 L
55. 9.43 g/L
57. 44.0 g/mol
59. 4.00 g/mol
61. $P_{\text{tot}} = 434 \text{ torr}$, mass_{N₂} = 0.437 g, mass_{O₂} = 0.237 g, mass_{He} = 0.0340 g
63. 1.84 atm
65. $\chi_{\text{N}_2} = 0.627$, $\chi_{\text{O}_2} = 0.373$, $P_{\text{N}_2} = 0.687 \text{ atm}$, $P_{\text{O}_2} = 0.409 \text{ atm}$
67. $P_{\text{H}_2} = 0.921 \text{ atm}$, mass_{H₂} = 0.0539 g
69. $7.47 \times 10^{-2} \text{ g}$
71. 38 L
73. $V_{\text{H}_2} = 48.2 \text{ L}$, $V_{\text{CO}} = 24.1 \text{ L}$
75. 22.8 g NaN₃
77. 60.4%
79. F₂, 2.84 g ClF₃
81. a. yes **b. no**
c. No. Even though the argon atoms are more massive than the helium atoms, both have the same kinetic energy at a given temperature. The argon atoms therefore move more slowly and so exert the same pressure as the helium atoms.
d. He
83. F₂: $u_{\text{rms}} = 442 \text{ m/s}$, KE_{avg} = $3.72 \times 10^3 \text{ J}$; Cl₂: $u_{\text{rms}} = 324 \text{ m/s}$, KE_{avg} = $3.72 \times 10^3 \text{ J}$; Br₂: $u_{\text{rms}} = 216 \text{ m/s}$, KE_{avg} = $3.72 \times 10^3 \text{ J}$; rankings: u_{rms} : Br₂ < Cl₂ < F₂, KE_{avg}: Br₂ = Cl₂ = F₂, rate of effusion: Br₂ < Cl₂ < F₂
85. rate ²³⁸UF₆/rate ²³⁵UF₆ = 0.99574
87. krypton
89. A has the higher molar mass, B has the higher rate of effusion.
91. That the volume of gas particles is small compared to the space between them breaks down under conditions of high pressure. At high pressure the particles themselves occupy a significant portion of the total gas volume.
93. 0.05826 L (ideal); 0.0708 L (V.D.W.); Difference because of high pressure, at which Ne no longer acts ideally.
95. 97.8%
97. 27.8 g/mol
99. C₄H₁₀
101. 4.70 L
103. 2 HCl(aq) + K₂S(s) → H₂S(g) + 2 KCl(aq), 0.191 g K₂S(s)
105. 11.7 L
107. mass_{air} = 8.56 g, mass_{He} = 1.20 g, mass difference = 7.36 g
- 109.** 4.76 L/s
111. total force = 6.15×10^3 pounds; no, the can cannot withstand this force.
113. 5.8×10^3 balloons
115. 4.0 cm
117. 77.7%
119. 0.32 grams
121. 311 K
123. 5.0 g
125. C₃H₈
127. 0.39 g Ar
129. 74.0 mmHg
131. 25% N₂H₄
133. 25%
135. $P_{\text{CH}_4} = 7.30 \times 10^{-2} \text{ atm}$, $P_{\text{O}_2} = 4.20 \times 10^{-1} \text{ atm}$, $P_{\text{NO}} = 2.79 \times 10^{-3} \text{ atm}$, $P_{\text{CO}_2} = 5.03 \times 10^{-3} \text{ atm}$, $P_{\text{H}_2\text{O}} = 5.03 \times 10^{-3} \text{ atm}$, $P_{\text{NO}_2} = 2.51 \times 10^{-2} \text{ atm}$, $P_{\text{OH}} = 1.01 \times 10^{-2} \text{ atm}$, $P_{\text{tot}} = 0.542 \text{ atm}$
137. 0.42 atm
139. Because helium is less dense than air, the balloon moves in a direction opposite the direction the air inside the car is moving due to the acceleration and deceleration of the car.
141. -29%
143. a. false **b. false**
c. false **d. true**
145. four times the initial pressure
147. Although the velocity “tails” have different lengths, the average length of the tails on the helium atoms is longer than the average length of the tails on the neon atoms, which is in turn longer than the average length of the tails on the krypton atoms. The lighter the atom, the faster the tails must move on average to have the same kinetic energy.



Chapter 6

- 33. a.** $1.92 \times 10^9 \text{ J}$ **b.** $5.14 \times 10^4 \text{ cal}$
c. $2.37 \times 10^6 \text{ J}$ **d.** 0.681 Cal
35. a. $9.987 \times 10^6 \text{ J}$ **b.** $9.987 \times 10^3 \text{ kJ}$
c. 2.78 kWh
37. d
39. a. heat, + **b. work, -** **c. heat, +**
41. $-7.27 \times 10^2 \text{ kJ}$
43. 311 kJ
45. The drinks that went into cooler B had more thermal energy than the refrigerated drinks that went into cooler A. The temperature difference between the drinks in cooler B and the ice was greater than the

difference between the drinks and the ice in cooler A. More thermal energy was exchanged between the drinks and the ice in cooler B, which resulted in more melting.

47. 4.7×10^5 J
 49. a. 7.6×10^2 °C b. 4.3×10^2 °C
 c. 1.3×10^2 °C d. 49 °C
 51. -2.8×10^2 J
 53. 489 J
 55. $\Delta E = -3463$ J, $\Delta H = -3452$ kJ
 57. a. exothermic, – b. endothermic, +
 c. exothermic, –
 59. -4.30×10^3 kJ
 61. 6.46×10^4 kJ
 63. 9.5×10^2 g CO₂
 65. mass of silver 77.1 grams
 67. final temperature 28.4 °C
 69. specific heat capacity of substance A $1.10 \text{ J/g} \cdot ^\circ\text{C}$
 71. Measurement B corresponds to conditions of constant pressure. Measurement A corresponds to conditions of constant volume. When a fuel is burned under constant pressure some of the energy released does work on the atmosphere by expanding against it. Less energy is manifest as heat due to this work. When a fuel is burned under constant volume, all of the energy released by the combustion reaction is evolved as heat.
 73. -6.3×10^3 kJ/mol
 75. -1.6×10^5 J
 77. a. $-\Delta H_1$
 b. $2 \Delta H_1$
 c. $-\frac{1}{2}\Delta H_1$
 79. –23.9 kJ
 81. –173.2 kJ
 83. a. N₂(g) + 3 H₂(g) \longrightarrow 2 NH₃(g), $\Delta H_f^\circ = -45.9$ kJ/mol
 b. C(s, graphite) + O₂(g) \longrightarrow CO₂(g), $\Delta H_f^\circ = -393.5$ kJ/mol
 c. 2 Fe(s) + 3/2 O₂(g) \longrightarrow Fe₂O₃(s), $\Delta H_f^\circ = -824.2$ kJ/mol
 d. C(s, graphite) + 2 H₂(g) \longrightarrow CH₄(g), $\Delta H_f^\circ = -74.6$ kJ/mol
 85. –382.1 kJ/mol
 87. a. –137.1 kJ
 b. –41.2 kJ
 c. –137 kJ
 d. 290.7 kJ
 89. 6 CO₂(g) + 6 H₂O(l) \longrightarrow C₆H₁₂O₆(s) + 6 O₂(g), $\Delta H_{rxn}^\circ = 2803$ kJ
 91. –113.0 kJ/mol
 93. a. 5.49 g CO₂
 b. 6.46 g CO₂
 c. 6.94 g CO₂
 Natural gas, CH₄(g), contributes the least to global warming by producing the least CO₂(g) per kJ of heat produced.
 95. 2×10^{13} kg CO₂ produced per year, 150 years
 97. $\Delta E = -1.7$ J, $q = -0.5$ J, $w = -1.2$ J
 99. 78 g

101. $\Delta H = 6.0$ kJ/mol, 1.1×10^2 g
 103. 26.1 °C
 105. palmitic acid: 9.9378 Cal/g, sucrose: 3.938 Cal/g, fat contains more Cal/g than sugar
 107. $\Delta H = \Delta E + nR\Delta T$
 109. 5.7 Cal/g
 111. $\Delta E = 0$, $\Delta H = 0$, $q = -w = 3.0 \times 10^3$ J
 113. –294 kJ/mol
 115. 94.0 kJ
 117. 23.9 °C
 119. 7.3×10^3 g H₂SO₄
 121. 7.2×10^2 g
 123. 78.2 °C
 125. $C_v = \frac{3}{2}R$, $C_p = \frac{5}{2}R$
 127. $q = 1030$ kJ, $\Delta H = 1030$ kJ, $\Delta E = 952$ kJ, $w = -78$ kJ
 129. –1292 kJ
 131. d
 133. a. At constant pressure, heat can be added and work can be done on the system. $\Delta E = q + w$; therefore, $q = \Delta E - w$.
 135. The aluminum is cooler because it has a lower heat capacity (specific heat).
 137. $q = -2418$ J, $w = -5$ kJ, $\Delta H = -2418$ J/mol, $\Delta E = -2423$ J/mol
 139. b. $\Delta H > \Delta E$

Chapter 7

35. 499 s
 37. (i) d, c, b, a (ii) a, b, c, d
 39. a. 4.74×10^{14} Hz b. 5.96×10^{14} Hz
 c. 5.8×10^{18} Hz
 41. a. 3.14×10^{-19} J b. 3.95×10^{-19} J
 c. 3.8×10^{-15} J
 43. 1.03 $\times 10^{16}$ photons
 45. a. 79.8 kJ/mol b. 239 kJ/mol
 c. 798 kJ/mol



49. 3.6×10^6 m/s
 51. 5.39 nm
 53. 1.1×10^{-34} m. The wavelength of a baseball is negligible with respect to its size.
 55. $\Delta v = 1.04 \times 10^5$ m/s
 57. 2s
 59. a. $l = 0$ b. $l = 0, 1$
 c. $l = 0, 1, 2$ d. $l = 0, 1, 2, 3$
 61. c
 63. See Figures 7.25 and 7.26. The 2s and 3p orbitals would, on average, be farther from the nucleus and have more nodes than the 1s and 2p orbitals.
 65. $n = 1$
 67. 2p \longrightarrow 1s
 69. a. 122 nm, UV b. 103 nm, UV
 c. 486 nm, visible d. 434 nm, visible

71. $n = 2$

73. 344 nm

75. 6.4×10^{17} photons/s

77. 0.0547 nm

79. 91.2 nm

81. a. 4 b. 9 c. 16

83. $n = 4 \rightarrow n = 3$, $n = 5 \rightarrow n = 3$,
 $n = 6 \rightarrow n = 3$, respectively85. $4.84 \times 10^{14} \text{ s}^{-1}$

87. 11 m

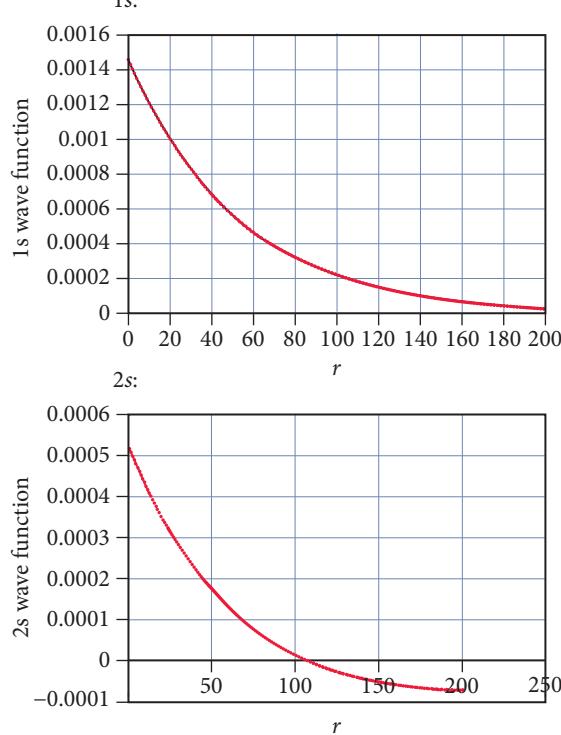
89. $6.78 \times 10^{-3} \text{ J}$

91. 632 nm

93. a. $E_1 = 2.51 \times 10^{-18} \text{ J}$, $E_2 = 1.00 \times 10^{-17} \text{ J}$,
 $E_3 = 2.26 \times 10^{-17} \text{ J}$

b. 26.5 nm, UV; 15.8 nm, UV

95.



The plot for the 2s wave function extends below the x -axis. The x -intercept represents the radial node of the orbital.

97. $7.39 \times 10^5 \text{ m/s}$ 99. $\Delta E = 1.1 \times 10^{-20} \text{ J}$, $7.0 \times 10^2 \text{ nm}$

101. 11 m

103. In the Bohr model, electrons exist in specific orbits encircling the atom. In the quantum mechanical model, electrons exist in orbitals that are really probability density maps of where the electron is likely to be found. The Bohr model is inconsistent with Heisenberg's uncertainty principle.

105. a. yes b. no
c. yes d. no

Chapter 8

41. a. $1s^2 2s^2 2p^6 3s^2 3p^2$ b. $1s^2 2s^2 2p^4$ c. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ d. $1s^2 2s^2 2p^6$

43. a.

b.

c.

d.

45. a. [Ne] $3s^2 3p^3$ b. [Ar] $4s^2 3d^{10} 4p^2$ c. [Kr] $5s^2 4d^2$ d. [Kr] $5s^2 4d^{10} 5p^5$

47. a. 1 b. 10 c. 5 d. 2

49. a. V, As b. Se c. V d. Kr

51. a. 2 b. 1 c. 10 d. 6

53. reactive metal: a, reactive nonmetal: c

55. c

57. The valence electrons of nitrogen will experience a greater effective nuclear charge. The valence electrons of both atoms are screened by two core electrons, but N has a greater number of protons and therefore a greater net nuclear charge.

59. a. 1+ b. 2+ c. 6+ d. 4+

61. a. In b. Si c. Pb d. C

63. F, S, Si, Ge, Ca, Rb

65. a. [Ne] b. [Kr] c. [Kr] d. [Ar] $3d^6$
e. [Ar] $3d^9$

67. a. [Ar] Diamagnetic

b. [Ar]
3d Paramagnetic

c. [Ar]
3d Paramagnetic

d. [Ar]
3d Paramagnetic

69. a. Li b. I⁻ c. Cr d. O²⁻71. O²⁻, F⁻, Ne, Na⁺, Mg²⁺

73. a. Br

b. Na

c. Cannot tell based on periodic trends.

d. P

75. In, Si, N, F

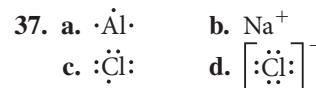
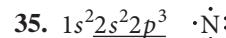
77. a. second and third b. fifth and sixth

c. sixth and seventh d. first and second

79. a. Na b. S c. C d. F

- 81.** a. Sr b. Bi
 c. Cannot tell based on periodic trends.
 d. As
- 83.** S, Se, Sb, In, Ba, Fr
- 85.** $\text{Sr}(s) + \text{I}_2(g) \longrightarrow \text{SrI}_2(s)$
- 87.** $2 \text{Li}(s) + 2 \text{H}_2\text{O}(l) \longrightarrow$
 $2 \text{Li}^+(aq) + 2 \text{OH}^-(aq) + \text{H}_2(g)$
- 89.** $\text{H}_2(g) + \text{Br}_2(g) \longrightarrow 2 \text{HBr}(g)$
- 91.** Br: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$
 Kr: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$
 Krypton's outer electron shell is filled, giving it chemical stability. Bromine is missing an electron from its outer shell and subsequently has a high electron affinity. Bromine tends to be easily reduced by gaining an electron, giving the bromide ion stability due to the filled p subshell that corresponds to krypton's chemically stable electron configuration.
- 93.** V: [Ar] $4s^2 3d^3$
 V^{3+} : [Ar] $3d^2$
 Both V and V^{3+} contain unpaired electrons in their $3d$ orbitals.
- 95.** A substitute for K^+ would need to exhibit a $1+$ electric charge and have similar mass and atomic radius. Na^+ and Rb^+ would not be good substitutes because their radii are significantly smaller and larger, respectively. Based on mass, Ca^+ and Ar^+ are the closest to K^+ . Because the first ionization energy of Ca^+ is closest to that of K^+ , Ca^+ is the best choice for a substitute. The difficulty lies in Ca's low second ionization energy, making it easily oxidized.
- 97.** Si, Ge
- 99.** a. N: [He] $2s^2 2p^3$, Mg: [Ne] $3s^2$, O: [He] $2s^2 2p^4$, F: [He] $2s^2 2p^5$, Al: [Ne] $3s^2 3p^1$
 b. Mg, Al, O, F, N c. Al, Mg, O, N, F
 d. Aluminum's first ionization energy is lower than Mg because its $3p$ electron is shielded by the $3s$ orbital. Oxygen's first ionization energy is lower than that of N because its fourth $2p$ electron experiences electron-electron repulsion by the other electron in its orbital.
- 101.** For main-group elements, atomic radii decrease across a period because the addition of a proton in the nucleus and an electron in the outermost energy level increases Z_{eff} . This does not happen in the transition metals because the electrons are added to the $n_{\text{highest}-1}$ orbital and the Z_{eff} stays roughly the same.
- 103.** Noble gases are exceptionally unreactive due to the stability of their completely filled outer quantum levels and their high ionization energies. The ionization energies of Kr, Xe, and Rn are low enough to form some compounds.
- 105.** 6A: $ns^2 np^4$, 7A: $ns^2 np^5$, group 7A elements require only one electron to achieve a noble gas configuration. Since group 6A elements require two electrons, their affinity for one electron is less negative, because one electron will merely give them an np^5 configuration.
- 107.** 85
- 109.** a. One If By Land (O, Ne, I, F, B, Y, La, Nd)
 b. Atoms are Fun (N, U, Fe, Ra, S, Mo, Ta backward)
- 111.** $1.390 \times 10^3 \text{ kJ/mol}$, 86.14 nm
- 113.** a. $d_{\text{Ar}} \approx 2 \text{ g/L}$, $d_{\text{Xe}} \approx 6.5 \text{ g/L}$
 b. $d_{\text{I}_{18}} \approx 13 \text{ g/L}$
 c. mass = $3.35 \times 10^{-23} \text{ g}/\text{Ne atom}$, density of Ne atom = $2.3 \times 10^4 \text{ g/L}$. The separation of Ne atoms relative to their size is immense.
 d. Kr: $2.69 \times 10^{22} \text{ atoms/L}$, Ne: $2.69 \times 10^{22} \text{ atoms/L}$. It seems Ar will also have $2.69 \times 10^{22} \text{ atoms/L}$. $d_{\text{Ar}} = 1.78 \text{ g/L}$. This corresponds to accepted values.
- 115.** Density increases to the right, because, though electrons are added successively across the period, they are added to the $3d$ subshell, which is not a part of the outermost principal energy level. As a result, the atomic radius does not increase significantly across the period, while mass does.
- 117.** Longest λ :
 1s 2s $2p_x$ $2p_y$ $2p_z$
- Next longest λ :
 1s 2s $2p_x$ $2p_y$ $2p_z$
- Next longest λ :
 1s 2s $2p_x$ $2p_y$ $2p_z$
- 119.** 168, noble gas
- 121.** A relatively high effective nuclear charge is found in gallium with its completed $3d$ subshell and in thallium with its completed $4f$ subshell, accounting for the relatively high first ionization energies of these elements.
- 123.** The second electron affinity requires the addition of an electron to something that is already negatively charged. The monoanions of both of these elements have relatively high electron density in a relatively small volume. As we shall see in Chapter 9 the dianions of these elements do exist in many compounds because they are stabilized by chemical bonding.
- 125.** 120, 170
- 127.** Fr, [Rn] $7s^1$, > 265, < 376, > 1.879, < 29
 a. $\text{Fr}^+(aq)$, $\text{OH}^-(aq)$, $\text{H}_2(g)$ b. $\text{Fr}_2\text{O}(s)$ c. $\text{FrCl}(s)$
- 129.** a. any group 6A element
 b. any group 5A element
 c. any group 1A element
- 131.** a. true b. true c. false d. true
- 133.** Since Ca has valence electrons of $4s^2$, it has a relatively low ionization energy to lose two electrons. F has a highly exothermic electron affinity when gaining one electron but not a second electron because of its $2s^2 2p^5$ valence electrons. Therefore, calcium and fluoride combine in a 2:1 ratio.

Chapter 9



39. a. $\text{Na}^+ \left[\begin{array}{c} \ddot{\text{F}} \\ | \\ \ddot{\text{F}} \end{array} \right]^-$ b. $\text{Ca}^{2+} \left[\begin{array}{c} \ddot{\text{O}} \\ || \\ \ddot{\text{O}} \end{array} \right]^{2-}$
 c. $\text{Sr}^{2+} \left[\begin{array}{c} \ddot{\text{Br}} \\ || \\ \ddot{\text{Br}} \end{array} \right]^-$ d. $2 \text{K}^+ \left[\begin{array}{c} \ddot{\text{O}} \\ || \\ \ddot{\text{O}} \end{array} \right]^{2-}$

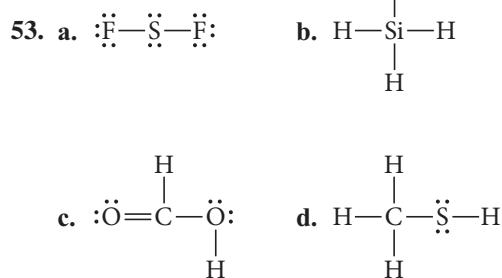
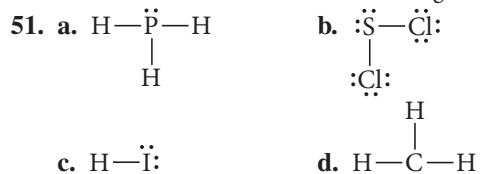
41. a. SrSe
 b. BaCl_2
 c. Na_2S
 d. Al_2O_3

43. As the size of the alkaline earth metal ions increases, so does the distance between the metal cations and oxygen anions. Therefore, the magnitude of the lattice energy decreases accordingly because the potential energy decreases as the distance increases.

45. One factor of lattice energy is the product of the charges of the two ions. The product of the ion charges for CsF is -1 while that for BaO is -4 . Because this product is four times greater, the lattice energy is also four times greater.

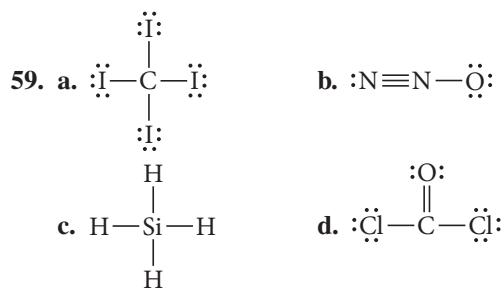
47. -708 kJ/mol

49. a. H:H , filled duets, 0 formal charge on both atoms
 b. $\ddot{\text{Cl}}:\ddot{\text{Cl}}$; filled octets, 0 formal charge on both atoms
 c. $\ddot{\text{O}}=\ddot{\text{O}}$, filled octets, 0 formal charge on both atoms
 d. $\text{:N}\equiv\text{N:}$, filled octets, 0 formal charge on both atoms

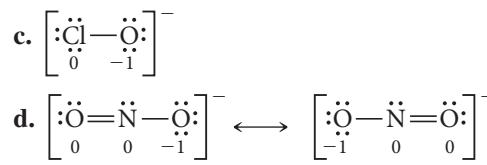
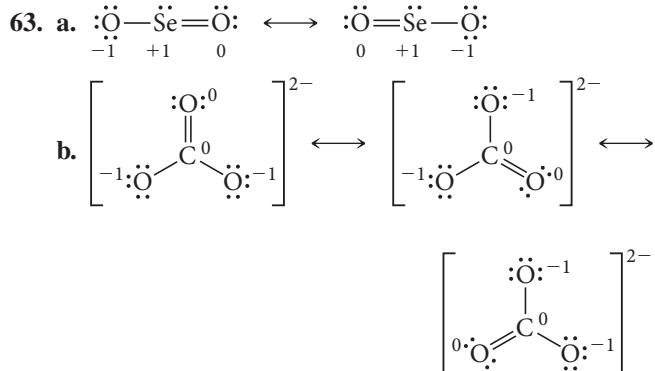


55. a. pure covalent
 c. pure covalent

57. :C=O: , 25%



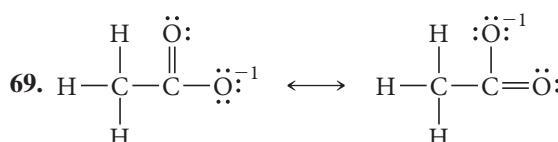
61. a. $\text{H}-\ddot{\text{N}}=\ddot{\text{N}}-\text{H}$
 b. $\text{H}-\ddot{\text{N}}-\ddot{\text{N}}-\text{H}$
 c. $\text{H}-\text{C}\equiv\text{C}-\text{H}$
 d. $\text{H}-\text{C}=\text{C}-\text{H}$



65. $\text{H}-\text{C}=\ddot{\text{S}}$ $\text{H}-\text{S}=\ddot{\text{C}}$ H_2CS is the better structure

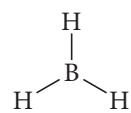
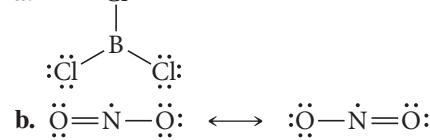
67. $\text{:O}\equiv\text{C}-\ddot{\text{O}}:$

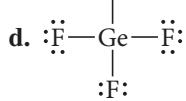
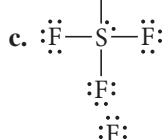
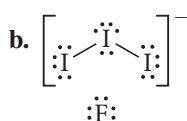
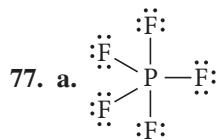
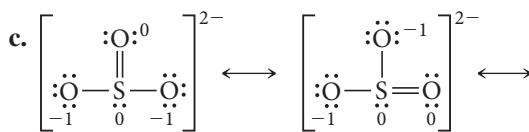
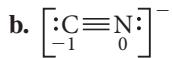
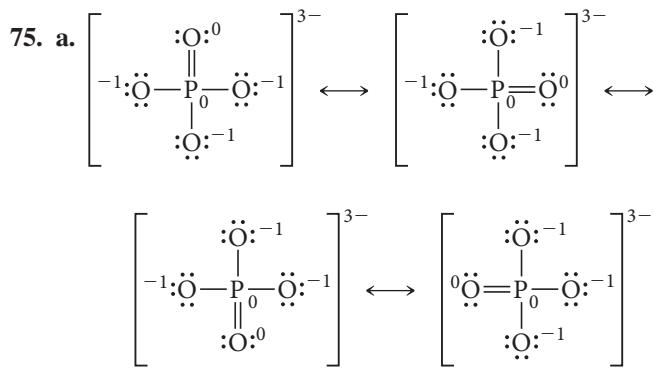
does not provide a significant contribution to the resonance hybrid as it has a $+1$ formal charge on a very electronegative atom (oxygen).



71. N has a formal charge of $+1$; O has a formal charge of -1 .

73. a.

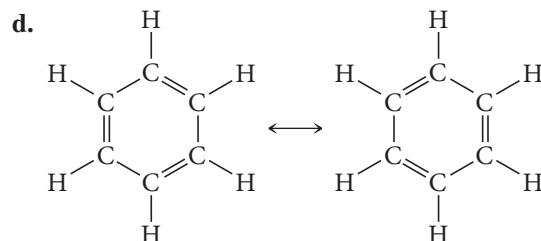
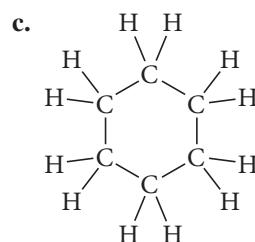
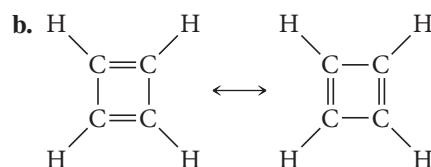
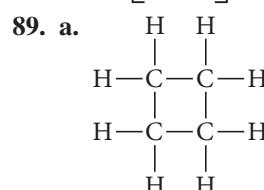
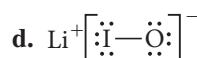
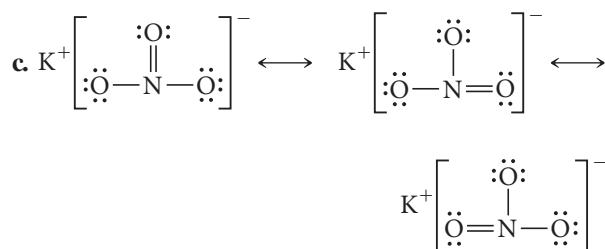
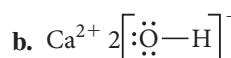
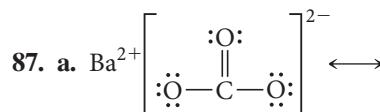
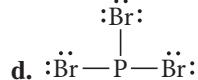
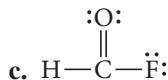
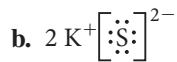
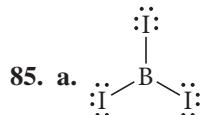


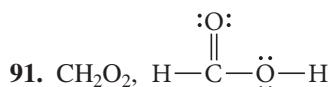


79. H_3CCH_3 , H_2CCH_2 , HCCH

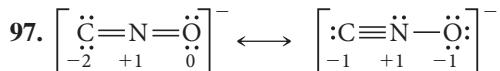
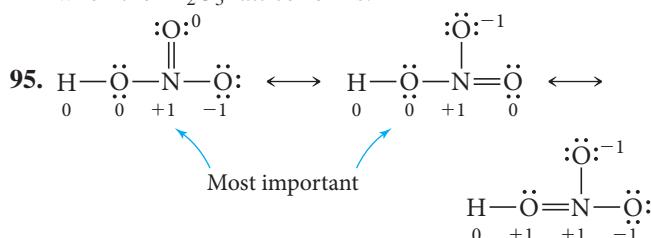
81. -128 kJ

83. -614 kJ

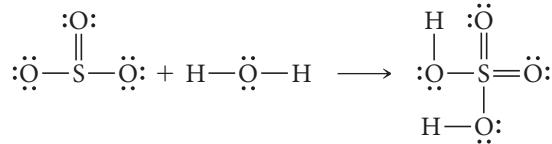
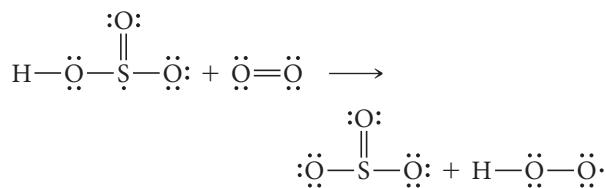
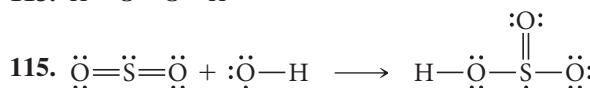
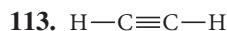
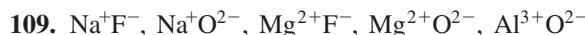
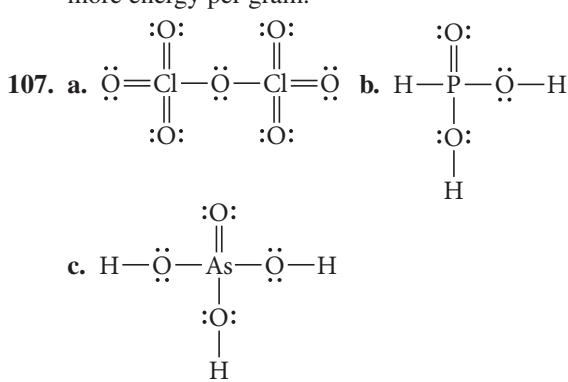
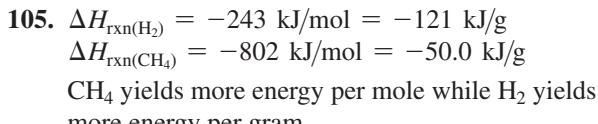
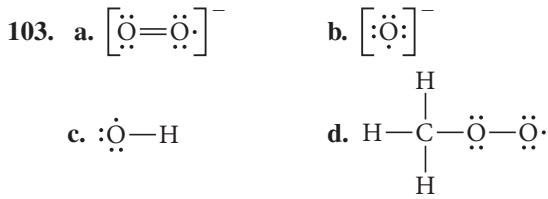
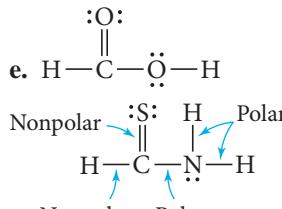
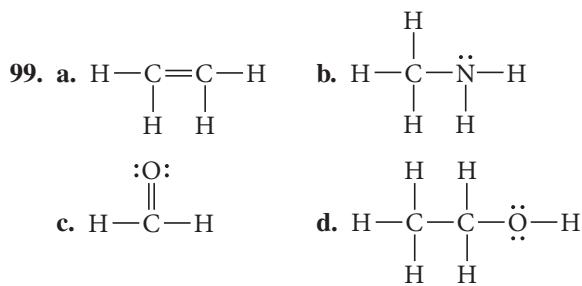




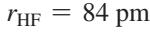
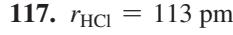
93. The reaction is exothermic due to the energy released when the Al_2O_3 lattice forms.



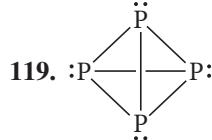
The fulminate ion is less stable because nitrogen is more electronegative than carbon and should therefore be terminal to accommodate the negative formal charge.



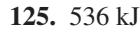
$$\Delta H_{\text{rxn}} = -172 \text{ kJ}$$



These values are close to the accepted values.



123. The oxidation number of the S atoms bonded directly to hydrogen atoms is -1 . The oxidation number of interior S atoms is 0 .



127. The compounds are energy rich because a great deal of energy is released when these compounds undergo a reaction that breaks weak bonds and forms strong ones.

129. The theory is successful because it allows us to predict and account for many chemical observations. The theory is limited because electrons cannot be treated as localized “dots.”

Chapter 10



33. a. 4 e^- groups, 4 bonding groups, 0 lone pairs
 b. 5 e^- groups, 3 bonding groups, 2 lone pairs
 c. 6 e^- groups, 5 bonding groups, 1 lone pair

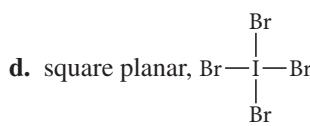
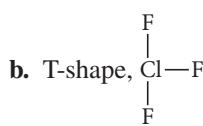
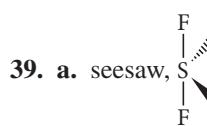
35. a. e^- geometry: tetrahedral molecular geometry: trigonal pyramidal idealized bond angle: 109.5° , deviation

b. e^- geometry: tetrahedral molecular geometry: bent idealized bond angle: 109.5° , deviation

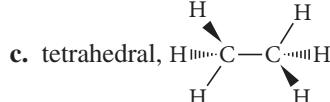
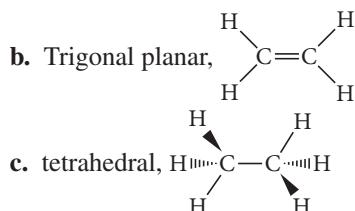
c. e^- geometry: tetrahedral molecular geometry: tetrahedral idealized bond angle: 109.5° , deviation (due to large size of Cl compared to H)

d. e^- geometry: linear molecular geometry: linear idealized bond angle: 180°

37. H_2O has a smaller bond angle due to lone pair–lone pair repulsions, the strongest electron group repulsion.



41. a. linear, $\text{H}-\text{C}\equiv\text{C}-\text{H}$

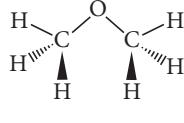
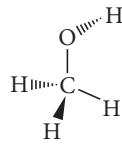


43. a. The lone pair will cause lone pair–bonding pair repulsions, pushing the three bonding pairs out of the same plane. The correct molecular geometry is trigonal pyramidal.

b. The lone pair should take an equatorial position to minimize 90° bonding pair interactions. The correct molecular geometry is seesaw.

c. The lone pairs should take positions on opposite sides of the central atom to reduce lone pair–lone pair interactions. The correct molecular geometry is square planar.

45. a. C: tetrahedral O: bent



- b. C's: tetrahedral
O: bent
c. O's: bent

47. The vectors of the polar bonds in both CO_2 and CCl_4 oppose each other with equal magnitude and sum to 0.

49. PF_3 , polar

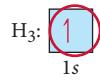
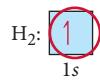
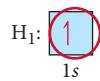
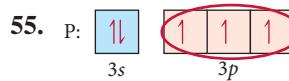
SBr_2 , nonpolar

CHCl_3 , polar

CS_2 , nonpolar

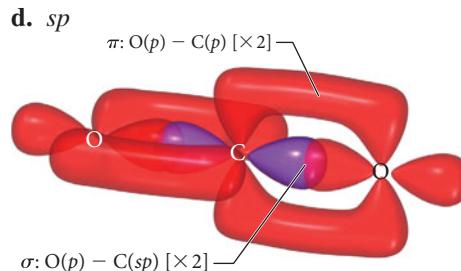
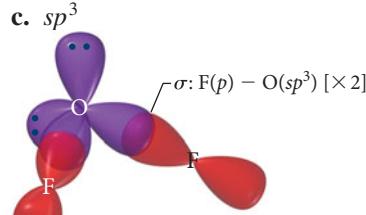
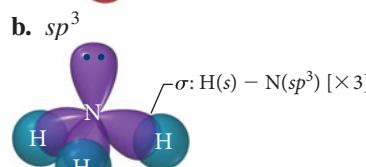
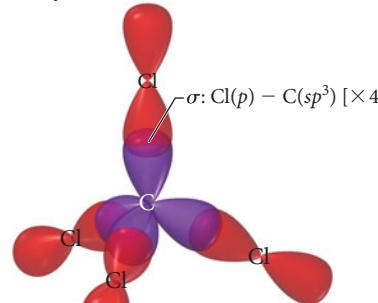
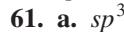
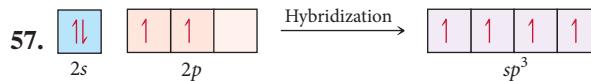
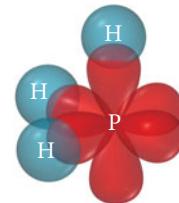
51. a. polar
b. polar
c. polar
d. nonpolar

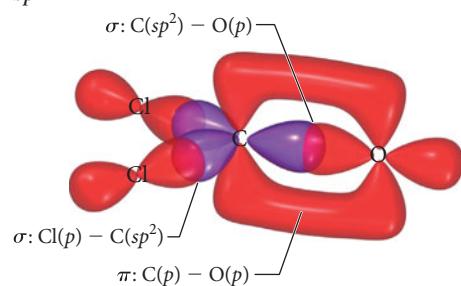
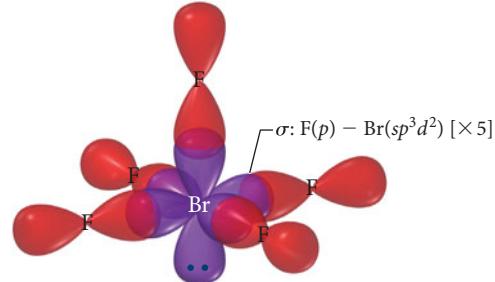
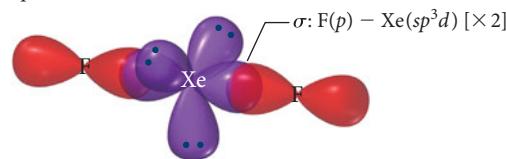
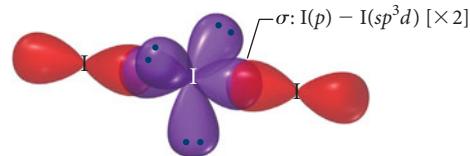
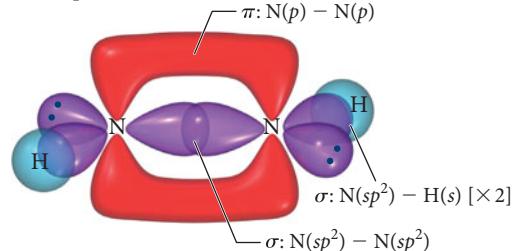
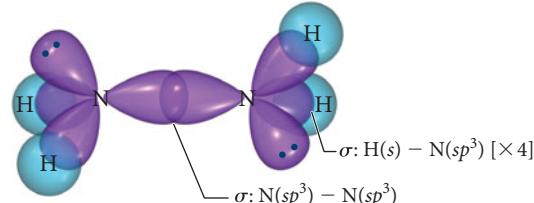
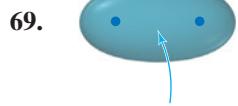
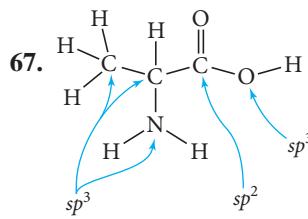
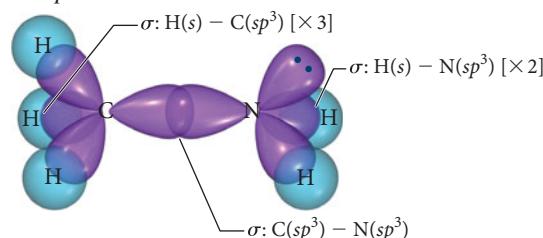
53. a. 0
b. 3
c. 1



Expected bond angle = 90°

Valence bond theory is compatible with experimentally determined bond angle of 93.3° without hybrid orbitals.



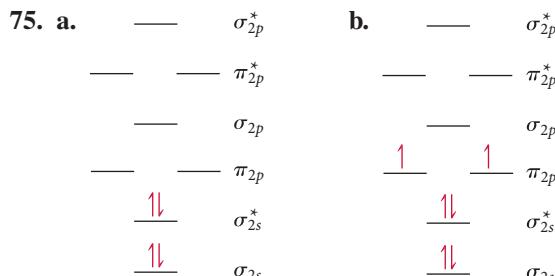
63. a. sp^2 b. sp^3d^2 c. sp^3d d. sp^3d 65. a. N's: sp^2 b. N's: sp^3 c. C: sp^3
N: sp^3 bond order $Be_2^+ = 1/2$ bond order $Be_2^- = 1/2$

Both will exist in gas phase.

73. Bonding



Antibonding

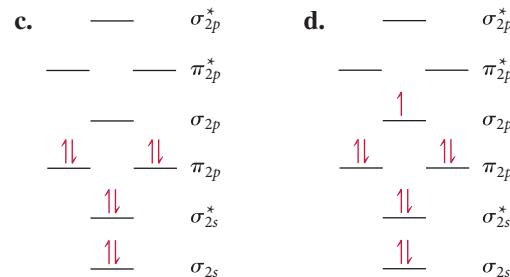


bond order = 0

diamagnetic

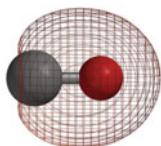
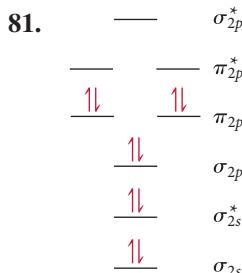
bond order = 1

paramagnetic

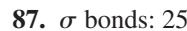
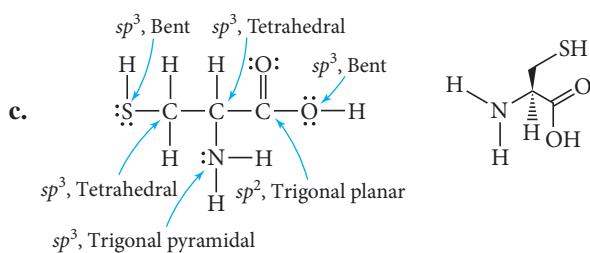
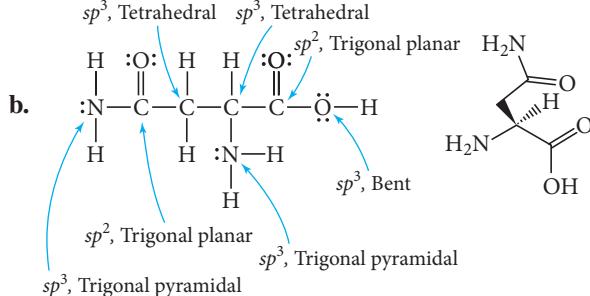
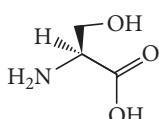
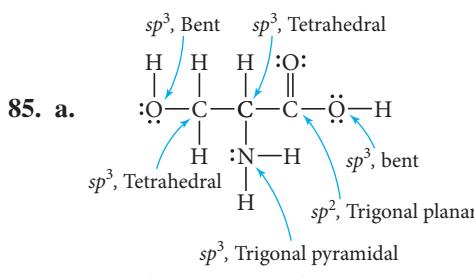
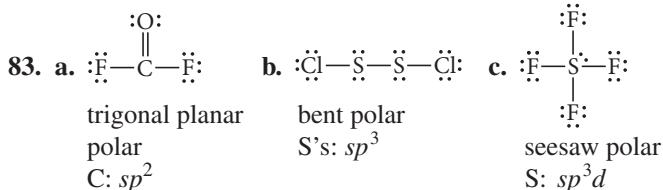
bond order = 2
diamagneticbond order = 2.5
paramagnetic

77. a. not stable
b. not stable
c. stable
d. not stable

79. C_2^- has the highest bond order, the highest bond energy, and the shortest bond length.



bond order = 3



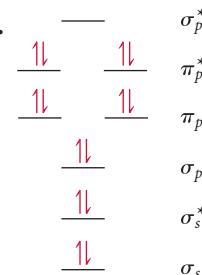
π bonds: 4

lone pairs: on O's and N (without methyl group):

*sp*² orbitals

on N's (with methyl group): sp^3 orbitals

89. a. water soluble
b. fat soluble
c. water soluble
d. fat soluble

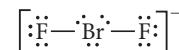


bond order = 1

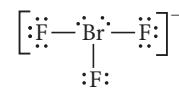
93. BrF, unhybridized, linear



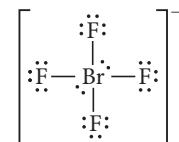
BrF_2^- has two bonds and three lone pairs on the central atom. The hybridization is sp^3d . The electron geometry is trigonal bipyramidal with the three lone pairs equatorial. The molecular geometry is linear.



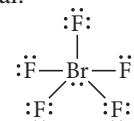
BrF_3 has three bonds and two lone pairs on the central atom. The hybridization is sp^3d . The electron geometry is trigonal bipyramidal with the two lone pairs equatorial. The molecular geometry is T-shaped.



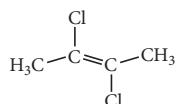
BrF_4^- has four bonds and two lone pairs on the central atom. The hybridization is sp^3d^2 . The electron geometry is octahedral with the two lone pairs on the same axis. The molecular geometry is square planar.



BrF_5 has five bonds and one lone pair on the central atom. The hybridization is $sp^3 d^2$. The electron geometry is octahedral. The molecular geometry is square pyramidal.



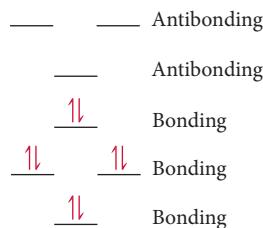
- 95.** The moments of the two Cl's cancel.



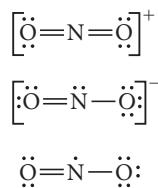
97. a. 10 b. 14 c. 2

99. According to valence bond theory, CH_4 , NH_3 , and H_2O are all sp^3 hybridized. This hybridization results in a tetrahedral electron group configuration with a 109.5° bond angle. NH_3 and H_2O deviate from this idealized bond angle because their lone electron pairs exist in their own sp^3 orbitals. The presence of lone pairs lowers the tendency for the central atom's orbitals to hybridize. As a result, as lone pairs are added, the bond angle moves further from the 109.5° hybrid angle and closer to the 90° unhybridized angle.

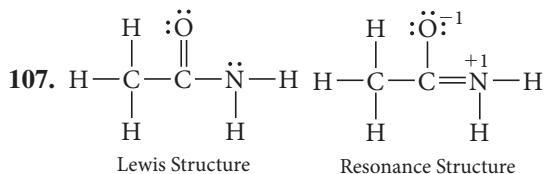
- 101.** NH₃ is stable due to its bond order of 3.



- 103.** In NO_2^+ , the central N has two electron groups, so the hybridization is sp and the ONO angle is 180° . In NO_2^- the central N has three electron groups, two bonds and one lone pair. The ideal hybridization is sp^2 but the ONO bond angle should close down a bit because of the lone pair. A bond angle around 115° is a good guess. In NO_2 there are three electron groups, but one group is a single electron. Again the ideal hybridization would be sp^2 , but since one unpaired electron must be much smaller than a lone pair or even a bonding pair, we predict that the ONO bond angle will spread and be greater than 120° . As a guess the angle is probably significantly greater than 120° .



- 105.** In addition to the $2s$ and the three $2p$ orbitals one more orbital is required to make five hybrid orbitals. The closest in energy is the $3s$ orbital. So the hybridization is s^2p^3 . VSEPR predicts trigonal bipyramidal geometry for five identical substituents.



Terminal carbon is tetrahedral, central carbon is trigonal planar, nitrogen is trigonal pyramidal (but resonance structure is trigonal planar).

- 109. a.** This is the best.

- b. This statement is similar to a but leaves out non-bonding lone-pair electron groups.
 - c. Molecular geometries are not determined by overlapping orbitals but rather by the number and type of electron groups around each central atom.

Lewis theory defines a single bond, double bond, and triple bond as a sharing of two electrons, four electrons, and six electrons, respectively, between two atoms. Valence bond theory defines a single bond as a sigma overlap of two orbitals, a double bond as a single sigma bond combined with a pi bond, and a triple bond as a double bond with an additional pi bond. Molecular orbital theory defines a single bond, double bond, and triple bond as a bond order of 1, 2, or 3, respectively, between two atoms.

Chapter 11

- 49.** a. dispersion
b. dispersion, dipole–dipole, hydrogen bonding
c. dispersion, dipole–dipole
d. dispersion

51. a. dispersion, dipole–dipole
b. dispersion, dipole–dipole, hydrogen bonding
c. dispersion
d. dispersion

53. a, b, c, d, Boiling point increases with increasing intermolecular forces. The molecules increase in their intermolecular forces as follows: a, dispersion forces; b, stronger dispersion forces (broader electron cloud); c, dispersion forces and dipole–dipole interactions; d, dispersion forces, dipole–dipole interactions, and hydrogen bonding.

55. a. CH_3OH , hydrogen bonding
b. $\text{CH}_3\text{CH}_2\text{OH}$, hydrogen bonding
c. CH_3CH_3 , greater mass, broader electron cloud causes greater dispersion forces

57. a. Br_2 , smaller mass results in weaker dispersion forces
b. H_2S , lacks hydrogen bonding
c. PH_3 , lacks hydrogen bonding

59. a. not homogeneous
b. homogeneous, dispersion, dipole–dipole, hydrogen bonding, ion–dipole
c. homogeneous, dispersion
d. homogeneous, dispersion, dipole–dipole, hydrogen bonding

61. Water. Surface tension increases with increasing intermolecular forces, and water can hydrogen bond while acetone cannot.

63. compound A

65. When the tube is clean, water experiences adhesive forces with glass that are stronger than its cohesive forces, causing it to climb the surface of a glass tube. Water does not experience strong intermolecular forces with oil, so if the tube is coated in oil, the water's cohesive forces will be greater and it will not be attracted to the surface of the tube.

67. The water in the 12 cm dish will evaporate more quickly. The vapor pressure does not change but the surface area does. The water in the dish evaporates more quickly because the greater surface area allows for more molecules to obtain enough energy at the surface and break free.

69. Water is more volatile than vegetable oil. When the water evaporates, the endothermic process results in cooling.

71. 0.405 L

73. 91 °C

75. $\Delta H_{\text{vap}} = 24.7 \text{ kJ/mol}$, bp = 239 K

77. 41 torr

79. 22.0 kJ

81. 2.7 °C

83. 30.5 kJ

85. a. solid

b. liquid

c. gas

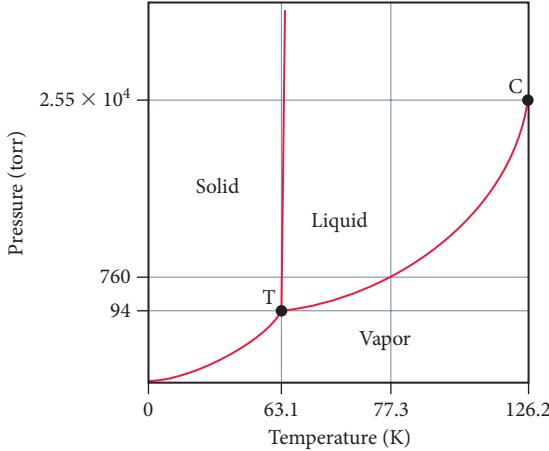
d. supercritical fluid

e. solid/liquid

f. liquid/gas

g. solid/liquid/gas

87. N₂ has a stable liquid phase at 1 atm.



89. a. 0.027 mmHg b. rhombic

91. Water has strong intermolecular forces. It is polar and experiences hydrogen bonding.

93. Water's exceptionally high specific heat capacity has a moderating effect on Earth's climate. Also, its high ΔH_{vap} causes water evaporation and condensation to have a strong effect on temperature.

95. 162 pm

97. a. 1 b. 2 c. 4

99. $l = 393 \text{ pm}$, $d = 21.3 \text{ g/cm}^3$

101. 134.5 pm

103. $6.0 \times 10^{23} \text{ atoms/mol}$

105. a. atomic b. molecular
c. ionic d. atomic

107. LiCl(s). The other three solids are held together by intermolecular forces while LiCl is held together by stronger coulombic interactions between the cations and anions of the crystal lattice.

109. a. TiO₂(s), ionic solid
b. SiCl₄(s), larger, stronger dispersion forces
c. Xe(s), larger, stronger dispersion forces
d. CaO, ions have greater charge, and therefore stronger coulombic forces

111. TiO₂

113. Cs: 1(1) = 1

Cl: 8(1/8) = 1

1 : 1

CsCl

Ba: 8(1/8) + 6(1/2) = 4

Cl: 8(1) = 8

4 : 8 = 1 : 2

BaCl₂

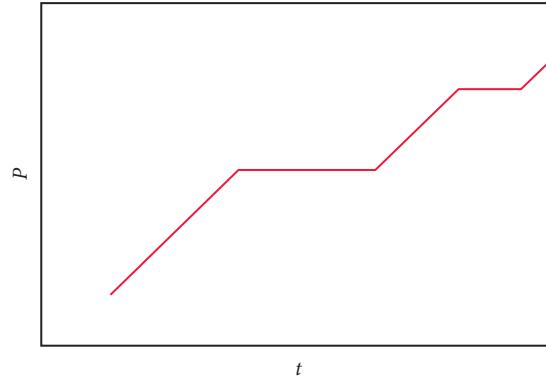
115. a

117. a. p-type b. n-type

119. The general trend is that melting point increases with increasing mass. This is due to the fact that the electrons of the larger molecules are held more loosely and a stronger dipole moment can be induced more easily. HF is the exception to the rule. It has a relatively high melting point due to hydrogen bonding.

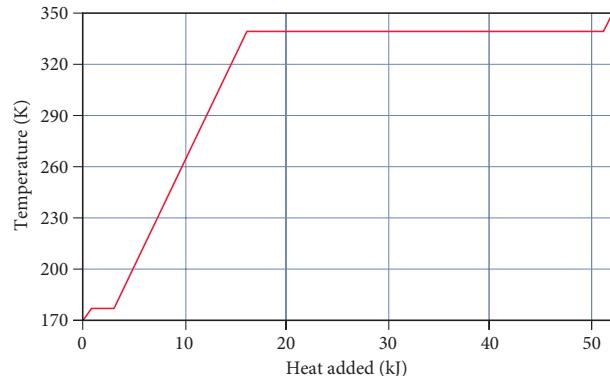
121. yes, 1.22 g

123. gas → liquid → solid



125. 26 °C

127.



129. $3.4 \times 10^3 \text{ g H}_2\text{O}$

131. CsCl has a higher melting point than AgI because of its higher coordination number. In CsCl, one anion bonds to eight cations (and vice versa) while in AgI, one anion bonds to only four cations.

133. a. 4r

b. $c^2 = a^2 + b^2$ $c = 4r$, $a = l$, $b = l$

$$(4r)^2 = l^2 + l^2$$

$$16r^2 = 2l^2$$

$$8r^2 = l^2$$

$$l = \sqrt[3]{8r^2}$$

$$l = 2\sqrt{2}r$$

135. 8 atoms/unit

137. a. $\text{CO}_2(s) \longrightarrow \text{CO}_2(g)$ at 195 K
 b. $\text{CO}_2(s) \longrightarrow$ triple point at 216 K $\longrightarrow \text{CO}_2(g)$
 just above 216 K
 c. $\text{CO}_2(s) \longrightarrow \text{CO}_2(l)$ at somewhat above
 216 K $\longrightarrow \text{CO}_2(g)$ at around 250 K
 d. $\text{CO}_2(s) \longrightarrow \text{CO}_2(g) \longrightarrow$ supercritical fluid

139. 55.843 g/mol

141. 2.00 g/cm³

143. Decreasing the pressure will decrease the temperature of liquid nitrogen. Because the nitrogen is boiling, its temperature must be constant at a given pressure. As the pressure decreases, the boiling point decreases, and therefore so does the temperature. If the pressure drops below the pressure of the triple point, the phase change will shift from vaporization to sublimation and the liquid nitrogen will become solid.

145. body diagonal = $\sqrt{6}r$,
 radius = $(\sqrt{3} - \sqrt{2})r/\sqrt{2} = 0.2247r$

147. 70.7 L

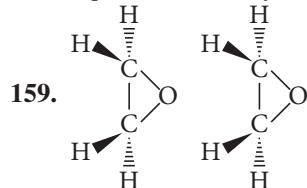
149. 0.48 atm

151. The water within a container with a larger surface area will evaporate more quickly because there is more surface area for the molecules to evaporate from. Vapor pressure is the pressure of the gas when it is in dynamic equilibrium with the liquid. The vapor pressure is dependent only on the substance and the temperature. The larger the surface area, the more quickly it will reach the dynamic state.

153. The triple point will be at a lower temperature since the fusion equilibrium line has a positive slope. This means that we will be increasing both temperature and pressure as we travel from the triple point to the normal melting point.

155. The liquid segment will have the least steep slope because it takes the most kJ/mol to raise the temperature of the phase.

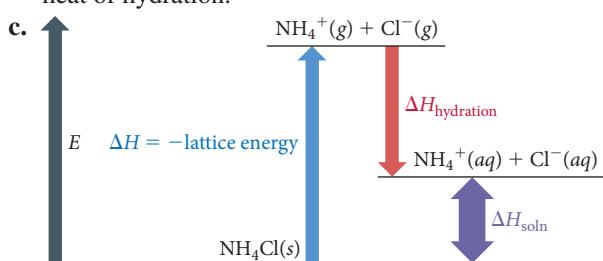
157. There are substantial intermolecular attractions in the liquid, but virtually none in the gas.



Chapter 12

29. a. hexane, toluene, or CCl_4 ; dispersion forces
 b. water, methanol; dispersion, dipole–dipole,
 hydrogen bonding
 c. hexane, toluene, or CCl_4 ; dispersion forces
 d. water, acetone, methanol, ethanol; dispersion,
 ion–dipole
31. $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{OH}$
33. a. water; dispersion, dipole–dipole, hydrogen bonding
 b. hexane; dispersion
 c. water; dispersion, dipole–dipole
 d. water; dispersion, dipole–dipole, hydrogen bonding

35. a. endothermic
 b. The lattice energy is greater in magnitude than the heat of hydration.



- c. The solution forms because chemical systems tend toward greater entropy.

37. -797 kJ/mol

39. $\Delta H_{\text{soln}} = -6 \times 10^1$ kJ/mol, -7 kJ of energy evolved

41. unsaturated

43. About 31 g will precipitate.

45. Boiling water releases any O_2 dissolved in it. The solubility of gases decreases with increasing temperature.

47. As pressure increases, nitrogen will more easily dissolve in blood. To reverse this process, divers should ascend to lower pressures.

49. 1.1 g

51. 1.92 M, 2.0 m, 10.4%

53. 0.340 L

55. 1.6×10^2 g

57. 1.4×10^4 g

59. Add water to 7.31 mL of concentrated solution until a total volume of 1.15 L is acquired.

61. a. Add water to 3.73 g KCl to a volume of 100 mL.

b. Add 3.59 g KCl to 96.41 g H_2O .

c. Add 5.0 g KCl to 95 g H_2O .

63. a. 0.417 M b. 0.444 m c. 7.41% by mass
 d. 0.00794 e. 0.794% by mole

65. 0.89 M

67. 15 m, 0.22

69. The level has decreased more in the beaker filled with pure water. The dissolved salt in the seawater decreases the vapor pressure and subsequently lowers the rate of vaporization.

71. 30.7 torr

73. a. $P_{\text{hept}} = 24.4$ torr, $P_{\text{oct}} = 5.09$ torr

b. 29.5 torr

c. 80.8% heptane by mass, 19.2% octane by mass

d. The vapor is richer in the more volatile component.

75. $P_{\text{chl}} = 51.9$ torr, $P_{\text{ace}} = 274$ torr, $P_{\text{tot}} = 326$ torr.

The solution is not ideal. The chloroform–acetone interactions are stronger than the chloroform–chloroform and acetone–acetone interactions.

77. freezing point (fp) = -1.27 °C, bp = 100.349 °C

79. freezing point (fp) = 1.0 °C, boiling point (bp) = 82.4 °C

81. 1.8×10^2 g/mol

83. 26.1 atm

85. 6.36×10^3 g/mol

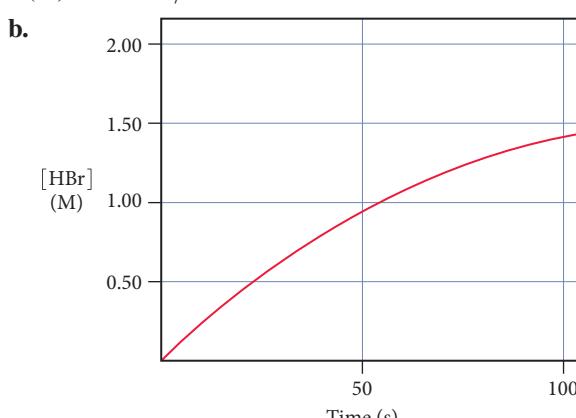
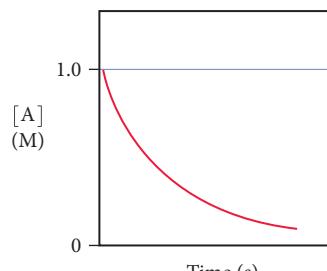
87. a. fp = -0.558 °C, bp = 100.154 °C

b. fp = -1.98 °C, bp = 100.546 °C

c. fp = -2.5 °C, bp = 100.70 °C

89. 157 g

- 91.** a. $-0.632\text{ }^{\circ}\text{C}$
 b. 5.4 atm
 c. $100.18\text{ }^{\circ}\text{C}$
- 93.** 2.3
- 95.** 3.4
- 97.** 23.0 torr
- 99.** Chloroform is polar and has stronger solute–solvent interactions than nonpolar carbon tetrachloride.
- 101.** $\Delta H_{\text{soln}} = 51\text{ kJ/mol}$, $-8.7\text{ }^{\circ}\text{C}$
- 103.** $2.2 \times 10^{-3}\text{ M/atm}$
- 105.** $1.3 \times 10^4\text{ L}$
- 107.** 0.24 g
- 109.** $-24\text{ }^{\circ}\text{C}$
- 111.** a. 1.1% by mass/V
 b. 1.6% by mass/V
 c. 5.3% by mass/V
- 113.** 2.484
- 115.** 0.229 atm
- 117.** $\chi_{\text{CHCl}_3}(\text{original}) = 0.657$,
 $P_{\text{CHCl}_3}(\text{condensed}) = 0.346\text{ atm}$
- 119.** 1.74 M
- 121.** $\text{C}_6\text{H}_{14}\text{O}_2$
- 123.** 12 grams
- 125.** $6.4 \times 10^{-3}\text{ L}$
- 127.** 22.4% glucose by mass, 77.6% sucrose by mass
- 129.** $P_{\text{iso}} = 0.131\text{ atm}$, $P_{\text{pro}} = 0.068\text{ atm}$. The major intermolecular attractions are between the OH groups. The OH group at the end of the chain in propyl alcohol is more accessible than the one in the middle of the chain in isopropyl alcohol. In addition, the molecular shape of propyl alcohol is a straight chain of carbon atoms, while that of isopropyl alcohol is a branched chain and is more like a ball. The contact area between two ball-like objects is smaller than that of two chain-like objects. The smaller contact area in isopropyl alcohol means the molecules don't attract each other as strongly as do those of propyl alcohol. As a result of both of these factors, the vapor pressure of isopropyl alcohol is higher.
- 131.** 0.0097 m
- 133.** Na_2CO_3 0.050 M, NaHCO_3 0.075 M
- 135.** The water should not be immediately cycled back into the river. As the water was warmed, dissolved oxygen would have been released, since the amount of a gas able to be dissolved into a liquid decreases as the temperature of the liquid increases. As such, the water returned to the river would lack dissolved oxygen if it was still hot. To preserve the dissolved oxygen necessary for the survival of fish and other aquatic life, the water must first be cooled.
- 137.** b. NaCl
- Chapter 13**
- 25.** a. Rate = $-\frac{1}{2} \frac{\Delta[\text{HBr}]}{\Delta t} = \frac{\Delta[\text{H}_2]}{\Delta t} = \frac{\Delta[\text{Br}_2]}{\Delta t}$
 b. $1.8 \times 10^{-3}\text{ M/s}$
 c. 0.040 mol Br_2
- 27.** a. Rate = $-\frac{1}{2} \frac{\Delta[\text{A}]}{\Delta t} = -\frac{\Delta[\text{B}]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{C}]}{\Delta t}$
 b. $\frac{\Delta[\text{B}]}{\Delta t} = -0.0500\text{ M/s}$, $\frac{\Delta[\text{C}]}{\Delta t} = 0.150\text{ M/s}$
- 29.**

$\Delta[\text{Cl}_2]/\Delta t$	$\Delta[\text{F}_2]/\Delta t$	$\Delta[\text{ClF}_3]/\Delta t$	Rate
-0.012 M/s	-0.036 M/s	0.024 M/s	0.012 M/s
- 31.** a. $0 \longrightarrow 10\text{ s}$: Rate = $8.7 \times 10^{-3}\text{ M/s}$
 $40 \longrightarrow 50\text{ s}$: Rate = $6.0 \times 10^{-3}\text{ M/s}$
 b. $1.4 \times 10^{-2}\text{ M/s}$
- 33.** a. (i) $1.0 \times 10^{-2}\text{ M/s}$
 (ii) $8.5 \times 10^{-3}\text{ M/s}$
 (iii) 0.013 M/s
- b.** 
- 35.** a. first order
b. 
- c.** Rate = $k[\text{A}]^1$, $k = 0.010\text{ s}^{-1}$
d. s^{-1} **e.** $\text{M}^{-1}\text{s}^{-1}$ **f.** $\text{M} \cdot \text{s}^{-1}$
- 37.** a. s^{-1} **b.** $\text{M}^{-1}\text{s}^{-1}$ **c.** $\text{M} \cdot \text{s}^{-1}$
- 39.** a. Rate = $k[\text{A}][\text{B}]^2$ **b.** third order
 c. 2 **d.** 4
 e. 1 **f.** 8
- 41.** second order, Rate = $5.25\text{ M}^{-1}\text{s}^{-1}[\text{A}]^2$
43. Rate = $k[\text{NO}_2][\text{F}_2]$, $k = 2.57\text{ M}^{-1}\text{s}^{-1}$, second order
- 45.** a. zero order
 b. first order
 c. second order
- 47.** second order, $k = 2.25 \times 10^{-2}\text{ M}^{-1}\text{s}^{-1}$, $[\text{AB}]$ at $25\text{ s} = 0.619\text{ M}$
- 49.** first order, $k = 1.12 \times 10^{-2}\text{ s}^{-1}$, Rate = $2.8 \times 10^{-3}\text{ M/s}$
- 51.** a. $4.5 \times 10^{-3}\text{ s}^{-1}$ **b.** Rate = $4.5 \times 10^{-3}\text{ s}^{-1}[\text{A}]$
 c. $1.5 \times 10^2\text{ s}$ **d.** $[\text{A}] = 0.0908\text{ M}$
- 53.** a. $4.88 \times 10^3\text{ s}$ **b.** $9.8 \times 10^3\text{ s}$
 c. $1.7 \times 10^3\text{ s}$ **d.** 0.146 M at 200 s , 0.140 M at 500 s
- 55.** $6.8 \times 10^8\text{ yrs}$; $1.8 \times 10^{17}\text{ atoms}$