

**CHECK**

The units (J) are correct for work. The sign of the work is negative, as it should be for an expansion: work is done on the surroundings by the expanding balloon.

**FOR PRACTICE 6.4**

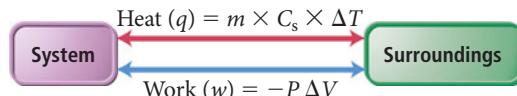
A cylinder equipped with a piston expands against an external pressure of 1.58 atm. If the initial volume is 0.485 L and the final volume is 1.245 L, how much work (in J) is done?

**FOR MORE PRACTICE 6.4**

When fuel is burned in a cylinder equipped with a piston, the volume expands from 0.255 L to 1.45 L against an external pressure of 1.02 atm. In addition, 875 J is emitted as heat. What is  $\Delta E$  for the burning of the fuel?

## 6.5 Measuring $\Delta E$ for Chemical Reactions: Constant-Volume Calorimetry

We now have a complete picture of how a system exchanges energy with its surroundings via heat and pressure-volume work:



Recall from Section 6.3 that the change in internal energy that occurs during a chemical reaction ( $\Delta E$ ) is a measure of *all of the energy* (heat and work) exchanged with the surroundings ( $\Delta E = q + w$ ). Therefore, we can measure the changes in temperature (to calculate heat) and the changes in volume (to calculate work) that occur during a chemical reaction, and then sum them together to calculate  $\Delta E$ . However, an easier way to obtain the value of  $\Delta E$  for a chemical reaction is to force all of the energy change associated with a reaction to manifest itself as heat rather than work. We can then measure the temperature change caused by the heat flow.

Recall that  $\Delta E = q + w$  and that  $w = -P \Delta V$ . If a reaction is carried out at constant volume, then  $\Delta V = 0$  and  $w = 0$ . The heat evolved (or given off), called the *heat at constant volume* ( $q_v$ ), is then equal to  $\Delta E_{\text{rxn}}$ .

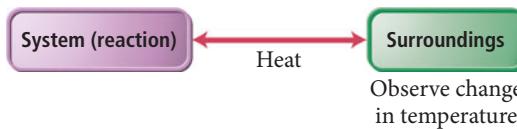
$$\Delta E_{\text{rxn}} = q_v + w$$

[6.9]

Equals zero  
at constant volume

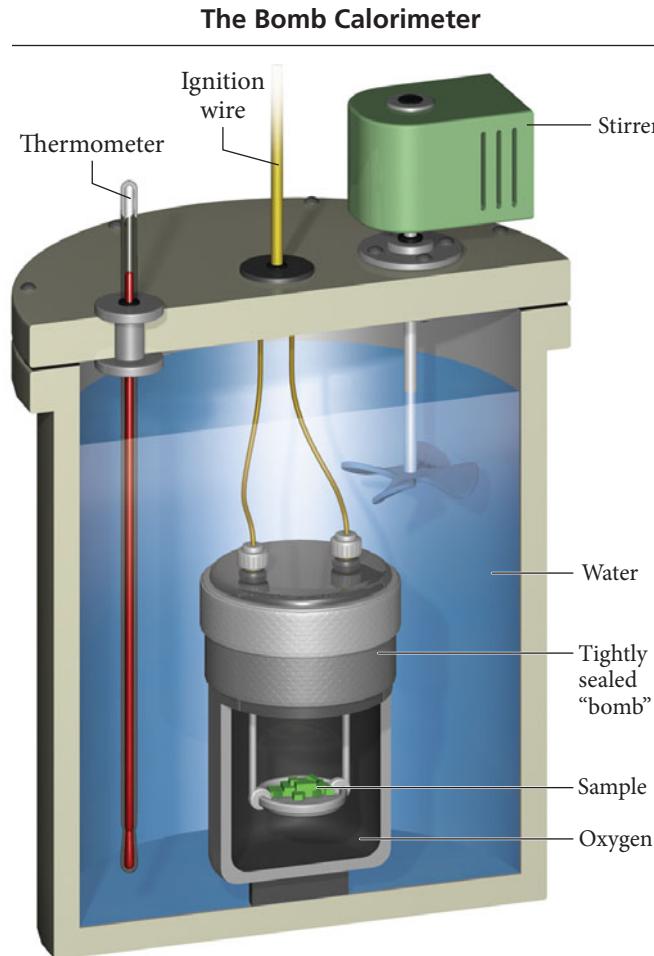
$$\Delta E_{\text{rxn}} = q_v$$

We can measure the heat evolved in a chemical reaction using *calorimetry*. In **calorimetry**, we measure the thermal energy exchanged between the reaction (defined as the system) and the surroundings by observing the change in temperature of the surroundings.



The magnitude of the temperature change in the surroundings depends on the magnitude of  $\Delta E$  for the reaction and on the heat capacity of the surroundings.

Figure 6.8 ► shows a **bomb calorimeter**, a piece of equipment designed to measure  $\Delta E$  for combustion reactions. In a bomb calorimeter, the reaction occurs in a sealed



◀ FIGURE 6.8 The Bomb Calorimeter

A bomb calorimeter measures changes in internal energy for combustion reactions.

container called a *bomb*, which ensures that the reaction occurs at constant volume. To use a bomb calorimeter, we put the sample to be burned (of known mass) into a cup equipped with an ignition wire. We then seal the cup into the bomb, which is filled with oxygen gas, and place the bomb in a water-filled, insulated container. The container is equipped with a stirrer and a thermometer. Finally, we ignite the sample with a wire coil and monitor the temperature with the thermometer. The temperature change ( $\Delta T$ ) is related to the heat absorbed by the entire calorimeter assembly ( $q_{\text{cal}}$ ) by the equation:

$$q_{\text{cal}} = C_{\text{cal}} \times \Delta T \quad [6.10]$$

where  $C_{\text{cal}}$  is the heat capacity of the entire calorimeter assembly (which is usually determined in a separate measurement involving the burning of a substance that gives off a known amount of heat). If no heat escapes from the calorimeter, the amount of heat gained by the calorimeter exactly equals that released by the reaction (the two are equal in magnitude but opposite in sign):

$$q_{\text{cal}} = -q_{\text{rxn}} \quad [6.11]$$

Since the reaction occurs under conditions of constant volume,  $q_{\text{rxn}} = q_v = \Delta E_{\text{rxn}}$ . This measured quantity is the change in the internal energy of the reaction for the specific amount of reactant burned. To get  $\Delta E_{\text{rxn}}$  per mole of a particular reactant—a more general quantity—we divide by the number of moles that actually reacted, as shown in Example 6.5.

The heat capacity of the calorimeter,  $C_{\text{cal}}$ , has units of energy over temperature; its value accounts for all of the heat absorbed by all of the components within the calorimeter (including the water).

### EXAMPLE 6.5 Measuring $\Delta E_{\text{rxn}}$ in a Bomb Calorimeter



When 1.010 g of sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) undergoes combustion in a bomb calorimeter, the temperature rises from  $24.92^\circ\text{C}$  to  $28.33^\circ\text{C}$ . Find  $\Delta E_{\text{rxn}}$  for the combustion of sucrose in kJ/mol sucrose. The heat capacity of the bomb calorimeter, determined in a separate experiment, is 4.90 kJ/ $^\circ\text{C}$ . (You can ignore the heat capacity of the small sample of sucrose because it is negligible compared to the heat capacity of the calorimeter.)

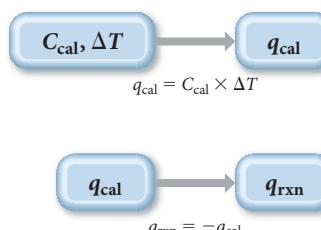
**SORT** You are given the mass of sucrose, the heat capacity of the calorimeter, and the initial and final temperatures. You are asked to find the change in internal energy for the reaction.

**GIVEN:** 1.010 g  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ,  $T_i = 24.92^\circ\text{C}$ ,  $T_f = 28.33^\circ\text{C}$ ,  $C_{\text{cal}} = 4.90 \text{ kJ}/^\circ\text{C}$

**FIND:**  $\Delta E_{\text{rxn}}$

**STRATEGIZE** The conceptual plan has three parts. In the first part, use the temperature change and the heat capacity of the calorimeter to find  $q_{\text{cal}}$ .

#### CONCEPTUAL PLAN



In the second part, use  $q_{\text{cal}}$  to get  $q_{\text{rxn}}$  (which just involves changing the sign). Since the bomb calorimeter ensures constant volume,  $q_{\text{rxn}}$  is equivalent to  $\Delta E_{\text{rxn}}$  for the amount of sucrose burned.

In the third part, divide  $q_{\text{rxn}}$  by the number of moles of sucrose to get  $\Delta E_{\text{rxn}}$  per mole of sucrose.

$$\Delta E_{\text{rxn}} = \frac{q_{\text{rxn}}}{\text{mol } \text{C}_{12}\text{H}_{22}\text{O}_{11}}$$

#### RELATIONSHIPS USED

$$q_{\text{cal}} = C_{\text{cal}} \times \Delta T = -q_{\text{rxn}}$$

molar mass  $\text{C}_{12}\text{H}_{22}\text{O}_{11} = 342.3 \text{ g/mol}$

**SOLVE** Gather the necessary quantities in the correct units and substitute these into the equation to calculate  $q_{\text{cal}}$ .

#### SOLUTION

$$\begin{aligned} \Delta T &= T_f - T_i \\ &= 28.33^\circ\text{C} - 24.92^\circ\text{C} = 3.41^\circ\text{C} \end{aligned}$$

$$q_{\text{cal}} = C_{\text{cal}} \times \Delta T$$

$$q_{\text{cal}} = 4.90 \frac{\text{kJ}}{^\circ\text{C}} \times 3.41^\circ\text{C} = 16.7 \text{ kJ}$$

$$q_{\text{rxn}} = -q_{\text{cal}} = -16.7 \text{ kJ}$$

$$\begin{aligned} \Delta E_{\text{rxn}} &= \frac{q_{\text{rxn}}}{\text{mol } \text{C}_{12}\text{H}_{22}\text{O}_{11}} \\ &= \frac{-16.7 \text{ kJ}}{1.010 \text{ g } \text{C}_{12}\text{H}_{22}\text{O}_{11} \times \frac{1 \text{ mol } \text{C}_{12}\text{H}_{22}\text{O}_{11}}{342.3 \text{ g } \text{C}_{12}\text{H}_{22}\text{O}_{11}}} \\ &= -5.66 \times 10^3 \text{ kJ/mol } \text{C}_{12}\text{H}_{22}\text{O}_{11} \end{aligned}$$

Find  $q_{\text{rxn}}$  by taking the negative of  $q_{\text{cal}}$ .

Find  $\Delta E_{\text{rxn}}$  per mole of sucrose by dividing  $q_{\text{rxn}}$  by the number of moles of sucrose (calculated from the given mass of sucrose and its molar mass).

**CHECK** The units of the answer (kJ) are correct for a change in internal energy. The sign of  $\Delta E_{\text{rxn}}$  is negative, as it should be for a combustion reaction that gives off energy.

#### FOR PRACTICE 6.5

When 1.550 g of liquid hexane ( $\text{C}_6\text{H}_{14}$ ) undergoes combustion in a bomb calorimeter, the temperature rises from  $25.87^\circ\text{C}$  to  $38.13^\circ\text{C}$ . Find  $\Delta E_{\text{rxn}}$  for the reaction in kJ/mol hexane. The heat capacity of the bomb calorimeter, determined in a separate experiment, is 5.73 kJ/ $^\circ\text{C}$ .

#### FOR MORE PRACTICE 6.5

The combustion of toluene has a  $\Delta E_{\text{rxn}}$  of  $-3.91 \times 10^3 \text{ kJ/mol}$ . When 1.55 g of toluene ( $\text{C}_7\text{H}_8$ ) undergoes combustion in a bomb calorimeter, the temperature rises from  $23.12^\circ\text{C}$  to  $37.57^\circ\text{C}$ . Find the heat capacity of the bomb calorimeter.

## 6.6 Enthalpy: The Heat Evolved in a Chemical Reaction at Constant Pressure

We have just seen that when a chemical reaction occurs in a sealed container under conditions of constant volume, the energy evolves only as heat. However, when a chemical reaction occurs open to the atmosphere under conditions of constant pressure—for example, a reaction occurring in an open beaker or the burning of natural gas on a stove—the energy can evolve as both heat and work. As we have also seen,  $\Delta E_{rxn}$  is a measure of the *total energy change* (both heat and work) that occurs during the reaction. However, in many cases, we are interested only in the heat exchanged, not the work done. For example, when we burn natural gas on a stove to cook food, we do not really care how much work the combustion reaction does on the atmosphere by expanding against it—we just want to know how much heat is given off to cook the food. Under conditions of constant pressure, a thermodynamic quantity called *enthalpy* represents exactly this.

We define the **enthalpy ( $H$ )** of a system as the sum of its internal energy and the product of its pressure and volume:

$$H = E + PV \quad [6.12]$$

Since internal energy, pressure, and volume are all state functions, enthalpy is also a state function. The *change in enthalpy ( $\Delta H$ )* for any process occurring under constant pressure is given by the expression:

$$\Delta H = \Delta E + P \Delta V \quad [6.13]$$

To better understand this expression, we can interpret the two terms on the right with the help of relationships already familiar to us. We saw previously that  $\Delta E = q + w$ . If we represent the heat at constant pressure as  $q_p$ , then the change in internal energy at constant pressure is  $\Delta E = q_p + w$ . In addition, from our definition of pressure–volume work, we know that  $P \Delta V = -w$ . Substituting these expressions into the expression for  $\Delta H$  gives us the following expression:

$$\begin{aligned} \Delta H &= \Delta E + P \Delta V \\ &= (q_p + w) + P \Delta V \\ &= q_p + w - w \\ \Delta H &= q_p \end{aligned} \quad [6.14]$$

We can see that  $\Delta H$  is equal to  $q_p$ , the heat at constant pressure.

Conceptually (and often numerically),  $\Delta H$  and  $\Delta E$  are similar: they both represent changes in a state function for the system. However,  $\Delta E$  is a measure of *all of the energy* (heat and work) exchanged with the surroundings, while  $\Delta H$  is a measure of only the heat exchanged under conditions of constant pressure. For chemical reactions that do not exchange much work with the surroundings—that is, those that do not cause a large change in reaction volume as they occur— $\Delta H$  and  $\Delta E$  are nearly identical in value. For chemical reactions that produce or consume large amounts of gas, and therefore result in large volume changes,  $\Delta H$  and  $\Delta E$  can be slightly different in value.

### Conceptual Connection 6.5 The Difference between $\Delta H$ and $\Delta E$

Lighters are usually fueled by butane ( $C_4H_{10}$ ). When 1 mole of butane burns at constant pressure, it produces 2658 kJ of heat and does 3 kJ of work. What are the values of  $\Delta H$  and  $\Delta E$  for the combustion of one mole of butane?

The signs of  $\Delta H$  and  $\Delta E$  follow the same conventions. A positive  $\Delta H$  indicates that heat flows into the system as the reaction occurs. A chemical reaction with a positive  $\Delta H$ , called an **endothermic reaction**, absorbs heat from its surroundings. A chemical cold pack, often used to ice athletic injuries, is a good example of an endothermic reaction. When a barrier separating the reactants in a chemical cold pack is broken, the substances mix, react, and absorb heat from the surroundings. The surroundings—including, say, your bruised wrist—get *colder* because they *lose* energy as the cold pack absorbs it.



▲ The reaction that occurs in a chemical cold pack is endothermic—it absorbs energy from the surroundings. The combustion of natural gas is an exothermic reaction—it releases energy to the surroundings.

A chemical reaction with a negative  $\Delta H$ , called an **exothermic reaction**, gives off heat to its surroundings. The reaction occurring in the chemical hand warmer discussed in Section 6.1 is a good example of an exothermic reaction. As the reaction occurs, heat is given off into the surroundings (including your hand and glove), making them warmer. The burning of natural gas is another example of an exothermic reaction. As the gas burns, it gives off energy, raising the temperature of its surroundings.

#### *Summarizing Enthalpy:*

- ▶ The value of  $\Delta H$  for a chemical reaction is the amount of heat absorbed or evolved in the reaction under conditions of constant pressure.
- ▶ An endothermic reaction has a *positive  $\Delta H$*  and absorbs heat from the surroundings. An endothermic reaction feels cold to the touch.
- ▶ An exothermic reaction has a *negative  $\Delta H$*  and gives off heat to the surroundings. An exothermic reaction feels warm to the touch.

### EXAMPLE 6.6 Exothermic and Endothermic Processes

Identify each process as endothermic or exothermic and indicate the sign of  $\Delta H$ .

- sweat evaporating from skin
- water freezing in a freezer
- wood burning in a fire

#### SOLUTION

- Sweat evaporating from skin cools the skin and is therefore endothermic, with a positive  $\Delta H$ . The skin must supply heat to the perspiration in order for it to continue to evaporate.
- Water freezing in a freezer releases heat and is therefore exothermic, with a negative  $\Delta H$ . The refrigeration system in the freezer must remove this heat for the water to continue to freeze.
- Wood burning in a fire releases heat and is therefore exothermic, with a negative  $\Delta H$ .

#### FOR PRACTICE 6.6

Identify each process as endothermic or exothermic and indicate the sign of  $\Delta H$ .

- an ice cube melting
- nail polish remover quickly evaporating after it is accidentally spilled on the skin
- gasoline burning within the cylinder of an automobile engine

## Exothermic and Endothermic Processes: A Molecular View

When a chemical system undergoes a change in enthalpy, where does the energy come from or go to? For example, we just saw that an exothermic chemical reaction gives off *thermal energy*—what is the source of that energy?

First, we know that the emitted thermal energy *does not* come from the original thermal energy of the system. Recall from Section 6.2 that the thermal energy of a system is the total kinetic energy of the atoms and molecules that compose the system. This kinetic energy *cannot* be the source of the energy given off in an exothermic reaction because if the atoms and molecules that compose the system were to lose kinetic energy, their temperature would necessarily fall—the system would get colder. Yet we know that in exothermic reactions, the temperature of the system and the surroundings rises. So there must be some other source of energy.

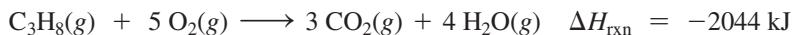
Recall also from Section 6.2 that the internal energy of a chemical system is the sum of its kinetic energy and its *potential energy*. This potential energy is the source in an exothermic chemical reaction. Under normal circumstances, chemical potential energy (or simply chemical energy) arises primarily from the electrostatic forces between the protons and electrons that compose the atoms and molecules within the system. In an exothermic reaction, some bonds break and new ones form, and the nuclei and electrons reorganize into an arrangement with lower potential energy. As the molecules rearrange, their potential energy converts into thermal energy, the heat emitted in the reaction. In an endothermic reaction, the opposite happens: as some bonds break and others form, the nuclei and electrons reorganize into an arrangement with higher potential energy, absorbing thermal energy in the process.

### Conceptual Connection 6.6 Exothermic and Endothermic Reactions

If an endothermic reaction absorbs heat, then why does it feel cold to the touch?

## Stoichiometry Involving $\Delta H$ : Thermochemical Equations

The enthalpy change for a chemical reaction, abbreviated  $\Delta H_{\text{rxn}}$ , is also called the **enthalpy of reaction** or **heat of reaction** and is an extensive property, one that depends on the amount of material undergoing the reaction. In other words, the amount of heat generated or absorbed when a chemical reaction occurs depends on the *amounts* of reactants that actually react. We usually specify  $\Delta H_{\text{rxn}}$  in combination with the balanced chemical equation for the reaction. *The magnitude of  $\Delta H_{\text{rxn}}$  is for the stoichiometric amounts of reactants and products for the reaction as written.* For example, consider the balanced equation and  $\Delta H_{\text{rxn}}$  for the combustion of propane, the main component of LP gas:

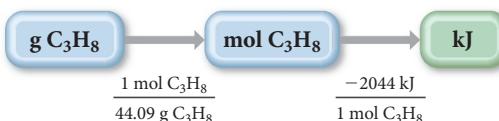


The equation tells us that when 1 mol of  $\text{C}_3\text{H}_8$  reacts with 5 mol of  $\text{O}_2$  to form 3 mol of  $\text{CO}_2$  and 4 mol of  $\text{H}_2\text{O}$ , 2044 kJ of heat is emitted. We can write these relationships in the same way that we expressed stoichiometric relationships in Chapter 4, as ratios between two quantities. For example, for the reactants, we write the following ratios:

$$1 \text{ mol C}_3\text{H}_8 : -2044 \text{ kJ} \quad \text{or} \quad 5 \text{ mol O}_2 : -2044 \text{ kJ}$$

The ratios indicate that 2044 kJ of heat evolves when 1 mol of  $\text{C}_3\text{H}_8$  and 5 mol of  $\text{O}_2$  completely react. We can use these ratios to construct conversion factors between amounts of reactants or products and the quantity of heat emitted (for exothermic reactions) or absorbed (for endothermic reactions). To find out how much heat is

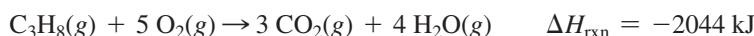
emitted upon the combustion of a certain mass in grams of C<sub>3</sub>H<sub>8</sub>, we use the following conceptual plan:



We use the molar mass to convert between grams and moles, and the stoichiometric relationship between moles of C<sub>3</sub>H<sub>8</sub> and the heat of reaction to convert between moles and kilojoules, as shown in Example 6.7.

### EXAMPLE 6.7 Stoichiometry Involving ΔH

An LP gas tank in a home barbecue contains 13.2 kg of propane, C<sub>3</sub>H<sub>8</sub>. Calculate the heat (in kJ) associated with the complete combustion of all of the propane in the tank.



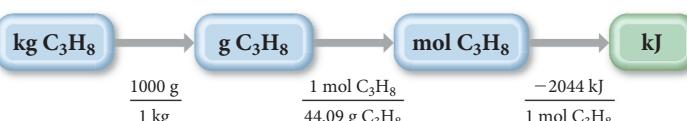
**SORT** You are given the mass of propane and asked to find the heat evolved in its combustion.

**STRATEGIZE** Starting with kg C<sub>3</sub>H<sub>8</sub>, convert to g C<sub>3</sub>H<sub>8</sub> and then use the molar mass of C<sub>3</sub>H<sub>8</sub> to find the number of moles. Next, use the stoichiometric relationship between mol C<sub>3</sub>H<sub>8</sub> and kJ to determine the heat evolved.

**GIVEN:** 13.2 kg C<sub>3</sub>H<sub>8</sub>

**FIND:** *q*

#### CONCEPTUAL PLAN



#### RELATIONSHIPS USED

$$1000 \text{ g} = 1 \text{ kg}$$

$$\text{molar mass C}_3\text{H}_8 = 44.09 \text{ g/mol}$$

$$1 \text{ mol C}_3\text{H}_8 : -2044 \text{ kJ} \text{ (from balanced equation)}$$

**SOLVE** Follow the conceptual plan to solve the problem. Begin with 13.2 kg C<sub>3</sub>H<sub>8</sub> and multiply by the appropriate conversion factors to arrive at kJ.

#### SOLUTION

$$13.2 \text{ kg C}_3\text{H}_8 \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol C}_3\text{H}_8}{44.09 \text{ g C}_3\text{H}_8} \times \frac{-2044 \text{ kJ}}{1 \text{ mol C}_3\text{H}_8} \\ = -6.12 \times 10^5 \text{ kJ}$$

**CHECK** The units of the answer (kJ) are correct for energy. The answer is negative, as it should be for heat evolved by the reaction.

#### FOR PRACTICE 6.7

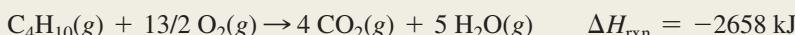
Ammonia reacts with oxygen according to the equation:



Calculate the heat (in kJ) associated with the complete reaction of 155 g of NH<sub>3</sub>.

#### FOR MORE PRACTICE 6.7

What mass of butane in grams is necessary to produce  $1.5 \times 10^3$  kJ of heat? What mass of CO<sub>2</sub> is produced?



## 6.7 Constant-Pressure Calorimetry: Measuring $\Delta H_{\text{rxn}}$

For many aqueous reactions, we can measure  $\Delta H_{\text{rxn}}$  fairly simply using a **coffee-cup calorimeter** shown in Figure 6.9 ▶. The calorimeter consists of two Styrofoam coffee cups, one inserted into the other, to provide insulation from the laboratory environment. The calorimeter is equipped with a thermometer and a stirrer. The reaction occurs in a specifically measured quantity of solution within the calorimeter, so that the mass of the solution is known. During the reaction, the heat evolved (or absorbed) causes a temperature change in the solution, which the thermometer measures. If we know the specific heat capacity of the solution, normally assumed to be that of water, we can calculate  $q_{\text{soln}}$ , the heat absorbed by or lost from the solution (which is acting as the surroundings) using the equation:

$$q_{\text{soln}} = m_{\text{soln}} \times C_{s,\text{soln}} \times \Delta T$$

The insulated calorimeter prevents heat from escaping, so we assume that the heat gained by the solution equals that lost by the reaction (or vice versa):

$$q_{\text{rxn}} = -q_{\text{soln}}$$

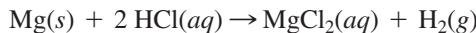
Since the reaction happens under conditions of constant pressure (open to the atmosphere),  $q_{\text{rxn}} = q_p = \Delta H_{\text{rxn}}$ . This measured quantity is the heat of reaction for the specific amount (which is measured ahead of time) of reactants that reacted. To get  $\Delta H_{\text{rxn}}$  per mole of a particular reactant—a more general quantity—we divide by the number of moles that actually reacted, as shown in Example 6.8.

### Summarizing Calorimetry:

- ▶ Bomb calorimetry occurs at constant *volume* and measures  $\Delta E$  for a reaction.
- ▶ Coffee-cup calorimetry occurs at constant *pressure* and measures  $\Delta H$  for a reaction.

### EXAMPLE 6.8 Measuring $\Delta H_{\text{rxn}}$ in a Coffee-Cup Calorimeter

Magnesium metal reacts with hydrochloric acid according to the balanced equation:



In an experiment to determine the enthalpy change for this reaction, 0.158 g of Mg metal is combined with enough HCl to make 100.0 mL of solution in a coffee-cup calorimeter. The HCl is sufficiently concentrated so that the Mg completely reacts. The temperature of the solution rises from 25.6 °C to 32.8 °C as a result of the reaction. Find  $\Delta H_{\text{rxn}}$  for the reaction as written. Use 1.00 g/mL as the density of the solution and  $C_{s,\text{soln}} = 4.18 \text{ J/g} \cdot ^\circ\text{C}$  as the specific heat capacity of the solution.

**SORT** You are given the mass of magnesium, the volume of solution, the initial and final temperatures, the density of the solution, and the heat capacity of the solution. You are asked to find the change in enthalpy for the reaction.

**GIVEN:** 0.158 g Mg  
100.0 mL soln

$$T_i = 25.6 \text{ } ^\circ\text{C}$$

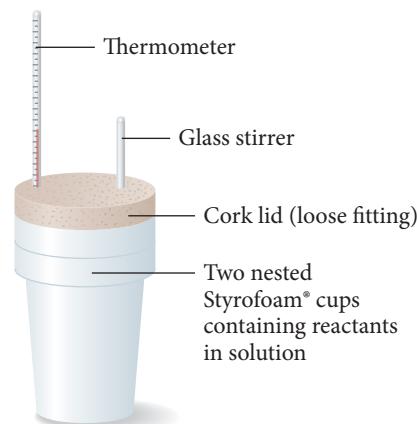
$$T_f = 32.8 \text{ } ^\circ\text{C}$$

$$d = 1.00 \text{ g/mL}$$

$$C_{s,\text{soln}} = 4.18 \text{ J/g} \cdot ^\circ\text{C}$$

**FIND:**  $\Delta H_{\text{rxn}}$

### The Coffee-Cup Calorimeter



▲ FIGURE 6.9 The Coffee-Cup Calorimeter A coffee-cup calorimeter measures enthalpy changes for chemical reactions in solution.

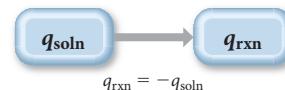
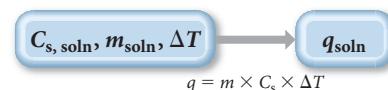
This equation assumes that no heat is lost to the calorimeter itself. If heat absorbed by the calorimeter is accounted for, the equation becomes  $q_{\text{rxn}} = +(q_{\text{soln}} + q_{\text{cal}})$ .

**STRATEGIZE** The conceptual plan has three parts. In the first part, use the temperature change and the other given quantities, together with the equation  $q = m \times C_s \times \Delta T$ , to find  $q_{\text{soln}}$ .

In the second part, use  $q_{\text{soln}}$  to get  $q_{\text{rxn}}$  (which simply involves changing the sign). Because the pressure is constant,  $q_{\text{rxn}}$  is equivalent to  $\Delta H_{\text{rxn}}$  for the amount of magnesium that reacts.

In the third part, divide  $q_{\text{rxn}}$  by the number of moles of magnesium to get  $\Delta H_{\text{rxn}}$  per mole of magnesium.

### CONCEPTUAL PLAN



$$\Delta H_{\text{rxn}} = \frac{q_{\text{rxn}}}{\text{mol Mg}}$$

### RELATIONSHIPS USED

$$q = m \times C_s \times \Delta T$$

$$q_{\text{rxn}} = -q_{\text{soln}}$$

**SOLVE** Gather the necessary quantities in the correct units for the equation  $q = m \times C_s \times \Delta T$  and substitute these into the equation to calculate  $q_{\text{soln}}$ . Notice that the sign of  $q_{\text{soln}}$  is positive, meaning that the solution absorbed heat from the reaction.

Find  $q_{\text{rxn}}$  by taking the negative of  $q_{\text{soln}}$ . Notice that  $q_{\text{rxn}}$  is negative, as expected for an exothermic reaction.

Finally, find  $\Delta H_{\text{rxn}}$  per mole of magnesium by dividing  $q_{\text{rxn}}$  by the number of moles of magnesium that reacts. Find the number of moles of magnesium from the given mass of magnesium and its molar mass.

Since the stoichiometric coefficient for magnesium in the balanced chemical equation is 1, the calculated value represents  $\Delta H_{\text{rxn}}$  for the reaction as written.

### SOLUTION

$$C_{s,\text{soln}} = 4.18 \text{ J/g} \cdot ^\circ\text{C}$$

$$m_{\text{soln}} = 100.0 \text{ mL soln} \times \frac{1.00 \text{ g}}{1 \text{ mL soln}} = 1.00 \times 10^2 \text{ g}$$

$$\Delta T = T_f - T_i$$

$$= 32.8 \text{ }^\circ\text{C} - 25.6 \text{ }^\circ\text{C} = 7.2 \text{ }^\circ\text{C}$$

$$q_{\text{soln}} = m_{\text{soln}} \times C_{s,\text{soln}} \times \Delta T$$

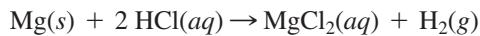
$$= 1.00 \times 10^2 \text{ g} \times 4.18 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \times 7.2 \text{ }^\circ\text{C} = 3.0 \times 10^3 \text{ J}$$

$$q_{\text{rxn}} = -q_{\text{soln}} = -3.0 \times 10^3 \text{ J}$$

$$\Delta H_{\text{rxn}} = \frac{q_{\text{rxn}}}{\text{mol Mg}}$$

$$= \frac{-3.0 \times 10^3 \text{ J}}{0.158 \text{ g Mg} \times \frac{1 \text{ mol Mg}}{24.31 \text{ g Mg}}}$$

$$= -4.6 \times 10^5 \text{ J/mol Mg}$$

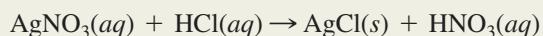


$$\Delta H_{\text{rxn}} = -4.6 \times 10^5 \text{ J}$$

**CHECK** The units of the answer (J) are correct for the change in enthalpy of a reaction. The sign is negative, as expected for an exothermic reaction.

### FOR PRACTICE 6.8

The addition of hydrochloric acid to a silver nitrate solution precipitates silver chloride according to the reaction:



When 50.0 mL of 0.100 M  $\text{AgNO}_3$  is combined with 50.0 mL of 0.100 M HCl in a coffee-cup calorimeter, the temperature changes from 23.40 °C to 24.21 °C. Calculate  $\Delta H_{\text{rxn}}$  for the reaction as written. Use 1.00 g/mL as the density of the solution and  $C = 4.18 \text{ J/g} \cdot ^\circ\text{C}$  as the specific heat capacity.

**Conceptual Connection** 6.7 Constant-Pressure versus Constant-Volume Calorimetry

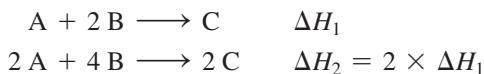
The same reaction, with exactly the same amount of reactant, is conducted in a bomb calorimeter and in a coffee-cup calorimeter. In one measurement,  $q_{rxn} = -12.5 \text{ kJ}$  and in the other  $q_{rxn} = -11.8 \text{ kJ}$ . Which value was obtained in the bomb calorimeter? (Assume that the reaction has a positive  $\Delta V$  in the coffee-cup calorimeter.)

## 6.8 Relationships Involving $\Delta H_{rxn}$

The change in enthalpy for a reaction is always associated with a *particular* reaction. If we change the reaction in well-defined ways, then  $\Delta H_{rxn}$  also changes in well-defined ways. We now turn our attention to three quantitative relationships between a chemical equation and  $\Delta H_{rxn}$ .

- If a chemical equation is multiplied by some factor, then  $\Delta H_{rxn}$  is also multiplied by the same factor.**

Recall from Section 6.6 that  $\Delta H_{rxn}$  is an extensive property; it depends on the quantity of reactants undergoing reaction. Recall also that  $\Delta H_{rxn}$  is usually reported for a reaction involving stoichiometric amounts of reactants. For example, for a reaction  $A + 2B \longrightarrow C$ ,  $\Delta H_{rxn}$  is typically reported as the amount of heat emitted or absorbed when 1 mol A reacts with 2 mol B to form 1 mol C. Therefore, if a chemical equation is multiplied by a factor, then  $\Delta H_{rxn}$  is also multiplied by the same factor. For example,



- If a chemical equation is reversed, then  $\Delta H_{rxn}$  changes sign.**

Recall from Section 6.6 that  $\Delta H_{rxn}$  is a state function, which means that its value depends only on the initial and final states of the system.

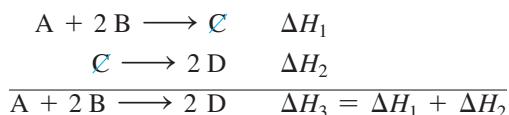
$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

When a reaction is reversed, the final state becomes the initial state and vice versa. Consequently,  $\Delta H_{rxn}$  changes sign:



- If a chemical equation can be expressed as the sum of a series of steps, then  $\Delta H_{rxn}$  for the overall equation is the sum of the heats of reactions for each step.**

This last relationship, known as **Hess's law**, also follows from the enthalpy of reaction being a state function. Since  $\Delta H_{rxn}$  is dependent only on the initial and final states, and not on the pathway the reaction follows,  $\Delta H$  obtained from summing the individual steps that lead to an overall reaction must be the same as  $\Delta H$  for that overall reaction. For example,

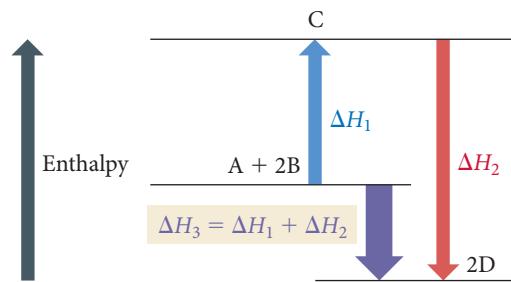


We illustrate Hess's law with the energy level diagram shown in Figure 6.10 ▶.

These three quantitative relationships make it possible to determine  $\Delta H$  for a reaction without directly measuring it in the laboratory. (For some reactions, direct measurement can be difficult.) If we can find

### Hess's Law

The change in enthalpy for a stepwise process is the sum of the enthalpy changes of the steps.

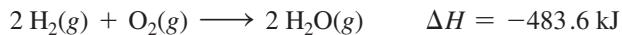
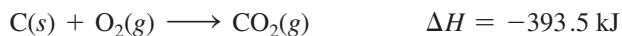


**FIGURE 6.10** Hess's Law The change in enthalpy for a stepwise process is the sum of the enthalpy changes of the steps.

related reactions (with known  $\Delta H$ 's) that sum to the reaction of interest, we can find  $\Delta H$  for the reaction of interest. For example, the following reaction between  $C(s)$  and  $H_2O(g)$  is an industrially important method of generating hydrogen gas:



We can find  $\Delta H_{rxn}$  from the following reactions with known  $\Delta H$ 's:



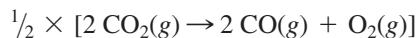
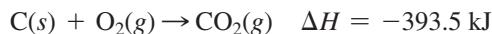
We just have to determine how to sum these reactions to get the overall reaction of interest. We do this by manipulating the reactions with known  $\Delta H$ 's in such a way as to get the reactants of interest on the left, the products of interest on the right, and other species to cancel.

Since the first reaction has  $C(s)$  as a reactant, and the reaction of interest also has  $C(s)$  as a reactant, we write the first reaction unchanged.

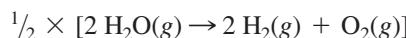
The second reaction has 2 mol of  $CO(g)$  as a reactant. However, the reaction of interest has 1 mol of  $CO(g)$  as a product. Therefore, we reverse the second reaction, change the sign of  $\Delta H$ , and multiply the reaction and  $\Delta H$  by  $\frac{1}{2}$ .

The third reaction has  $H_2(g)$  as a reactant. In the reaction of interest, however,  $H_2(g)$  is a product. Therefore, we reverse the equation and change the sign of  $\Delta H$ . In addition, to obtain coefficients that match the reaction of interest, and to cancel  $O_2$ , we must multiply the reaction and  $\Delta H$  by  $\frac{1}{2}$ .

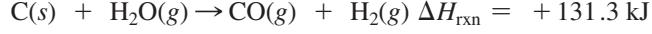
Lastly, we rewrite the three reactions after multiplying through by the indicated factors and show how they sum to the reaction of interest.  $\Delta H$  for the reaction of interest is then just the sum of the  $\Delta H$ 's for the steps.



$$\Delta H = \frac{1}{2} \times (+566.0 \text{ kJ})$$

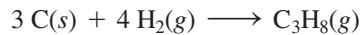


$$\Delta H = \frac{1}{2} \times (+483.6 \text{ kJ})$$

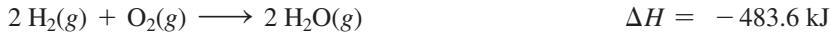


### EXAMPLE 6.9 Hess's Law

Find  $\Delta H_{rxn}$  for the reaction:



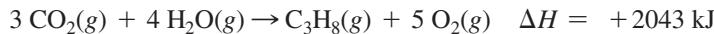
Use these reactions with known  $\Delta H$ 's:



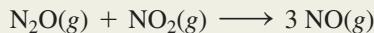
### SOLUTION

To work this and other Hess's law problems, manipulate the reactions with known  $\Delta H$ 's in such a way as to get the reactants of interest on the left, the products of interest on the right, and other species to cancel.

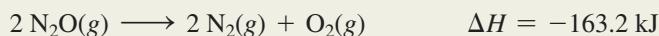
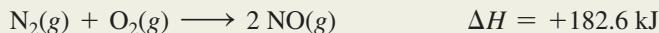
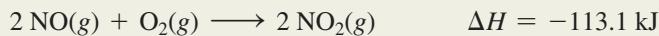
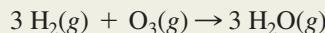
The first reaction has  $C_3H_8$  as a reactant, and the reaction of interest has  $C_3H_8$  as a product, so you can reverse the first reaction and change the sign of  $\Delta H$ .



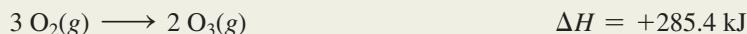
The second reaction has C as a reactant and CO <sub>2</sub> as a product, just as required in the reaction of interest. However, the coefficient for C is 1, and in the reaction of interest, the coefficient for C is 3. You need to multiply this equation and its ΔH by 3.	$3 \times [C(s) + O_2(g) \rightarrow CO_2(g)] \quad \Delta H = 3 \times (-393.5 \text{ kJ})$
The third reaction has H <sub>2</sub> (g) as a reactant, as required. However, the coefficient for H <sub>2</sub> is 2, and in the reaction of interest, the coefficient for H <sub>2</sub> is 4. Multiply this reaction and its ΔH by 2.	$2 \times [2 H_2(g) + O_2(g) \rightarrow 2 H_2O(g)] \quad \Delta H = 2 \times (-483.6 \text{ kJ})$
Lastly, rewrite the three reactions after multiplying through by the indicated factors and show how they sum to the reaction of interest. ΔH for the reaction of interest is the sum of the ΔH's for the steps.	$\begin{array}{l} 3CO_2(g) + 4H_2O(g) \rightarrow C_3H_8(g) + 5O_2(g) \\ 3C(s) + 3O_2(g) \rightarrow 3CO_2(g) \\ 4H_2(g) + 2O_2(g) \rightarrow 4H_2O(g) \\ \hline 3C(s) + 4H_2(g) \rightarrow C_3H_8(g) \end{array} \quad \begin{array}{l} \Delta H = +2043 \text{ kJ} \\ \Delta H = -1181 \text{ kJ} \\ \Delta H = -967.2 \text{ kJ} \\ \Delta H_{rxn} = -105 \text{ kJ} \end{array}$

**FOR PRACTICE 6.9**Find ΔH<sub>rxn</sub> for the reaction:

Use these reactions with known ΔH's:

**FOR MORE PRACTICE 6.9**Find ΔH<sub>rxn</sub> for the reaction:

Use these reactions with known ΔH's:



## 6.9 Determining Enthalpies of Reaction from Standard Enthalpies of Formation

We have examined two ways to determine ΔH for a chemical reaction: experimentally through calorimetry and inferentially through Hess's law. We now turn to a third and more convenient way to determine ΔH for a large number of chemical reactions: from tabulated *standard enthalpies of formation*.

### Standard States and Standard Enthalpy Changes

Recall that ΔH is the *change* in enthalpy for a chemical reaction—the difference in enthalpy between the products and the reactants. Since we are interested in changes in enthalpy (and not in absolute values of enthalpy itself), we are free to define the *zero* of enthalpy as conveniently as possible. Returning to our mountain-climbing analogy, a change in altitude (like a change in enthalpy) is an absolute quantity. Altitude itself (like enthalpy), however, is a relative quantity, defined relative to some standard (such as sea level in the case of altitude). We must define a similar, albeit slightly more complex, standard for enthalpy. This standard has three parts: the **standard state**, the **standard enthalpy change** (ΔH°), and the **standard enthalpy of formation** (ΔH<sub>f</sub>°).

The standard state was changed in 1997 to a pressure of 1 bar, which is very close to 1 atm (1 atm = 1.013 bar). Both standards are now in common use.

## 1. Standard State

- *For a Gas:* The standard state for a gas is the pure gas at a pressure of exactly 1 atmosphere.
- *For a Liquid or Solid:* The standard state for a liquid or solid is the pure substance in its most stable form at a pressure of 1 atm and at the temperature of interest (often taken to be 25 °C).
- *For a Substance in Solution:* The standard state for a substance in solution is a concentration of exactly 1 M.

## 2. Standard Enthalpy Change ( $\Delta H^\circ$ )

- The change in enthalpy for a process when all reactants and products are in their standard states. The degree sign indicates standard states.

## 3. Standard Enthalpy of Formation ( $\Delta H_f^\circ$ )

- *For a Pure Compound:* The change in enthalpy when one mole of the compound forms from its constituent elements in their standard states.
- *For a Pure Element in Its Standard State:*  $\Delta H_f^\circ = 0$ .

The standard enthalpy of formation is also called the **standard heat of formation**.

Assigning the value of zero to the standard enthalpy of formation for an element in its standard state is the equivalent of assigning an altitude of zero to sea level. Once we assume sea level is zero, we can then measure all subsequent changes in altitude relative to sea level. Similarly, we can measure all changes in enthalpy relative to those of pure elements in their standard states. For example, consider the standard enthalpy of formation of methane gas at 25 °C:



For methane, as with most compounds,  $\Delta H_f^\circ$  is negative. Continuing our analogy, if we think of pure elements in their standard states as being at *sea level*, then most compounds lie *below sea level*. The chemical equation for the enthalpy of formation of a compound is always written to form one mole of the compound, so  $\Delta H_f^\circ$  has the units of kJ/mol. Table 6.5 lists  $\Delta H_f^\circ$  values for some selected compounds. A more complete list can be found in Appendix IIB.

**TABLE 6.5 Standard Enthalpies (or Heats) of Formation,  $\Delta H_f^\circ$ , at 298 K**

Formula	$\Delta H_f^\circ$ (kJ/mol)	Formula	$\Delta H_f^\circ$ (kJ/mol)	Formula	$\Delta H_f^\circ$ (kJ/mol)
<b>Bromine</b>		$\text{C}_3\text{H}_8\text{O}(\text{l, isopropanol})$	-318.1	<b>Oxygen</b>	
$\text{Br}(\text{g})$	111.9	$\text{C}_6\text{H}_6(\text{l})$	49.1	$\text{O}_2(\text{g})$	0
$\text{Br}_2(\text{l})$	0	$\text{C}_6\text{H}_{12}\text{O}_6(\text{s, glucose})$	-1273.3	$\text{O}_3(\text{g})$	142.7
$\text{HBr}(\text{g})$	-36.3	$\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s, sucrose})$	-2226.1	$\text{H}_2\text{O}(\text{g})$	-241.8
<b>Calcium</b>		<b>Chlorine</b>		$\text{H}_2\text{O}(\text{l})$	-285.8
$\text{Ca}(\text{s})$	0	$\text{Cl}(\text{g})$	121.3	<b>Silver</b>	
$\text{CaO}(\text{s})$	-634.9	$\text{Cl}_2(\text{g})$	0	$\text{Ag}(\text{s})$	0
$\text{CaCO}_3(\text{s})$	-1207.6	$\text{HCl}(\text{g})$	-92.3	$\text{AgCl}(\text{s})$	-127.0
<b>Carbon</b>		<b>Fluorine</b>		<b>Sodium</b>	
$\text{C}(\text{s, graphite})$	0	$\text{F}(\text{g})$	79.38	$\text{Na}(\text{s})$	0
$\text{C}(\text{s, diamond})$	1.88	$\text{F}_2(\text{g})$	0	$\text{Na}(\text{g})$	107.5
$\text{CO}(\text{g})$	-110.5	$\text{HF}(\text{g})$	-273.3	$\text{NaCl}(\text{s})$	-411.2
$\text{CO}_2(\text{g})$	-393.5	<b>Hydrogen</b>		$\text{Na}_2\text{CO}_3(\text{s})$	-1130.7
$\text{CH}_4(\text{g})$	-74.6	$\text{H}(\text{g})$	218.0	$\text{NaHCO}_3(\text{s})$	-950.8
$\text{CH}_3\text{OH}(\text{l})$	-238.6	$\text{H}_2(\text{g})$	0	<b>Sulfur</b>	
$\text{C}_2\text{H}_2(\text{g})$	227.4	<b>Nitrogen</b>		$\text{S}_8(\text{s, rhombic})$	0
$\text{C}_2\text{H}_4(\text{g})$	52.4	$\text{N}_2(\text{g})$	0	$\text{S}_8(\text{s, monoclinic})$	0.3
$\text{C}_2\text{H}_6(\text{g})$	-84.68	$\text{NH}_3(\text{g})$	-45.9	$\text{SO}_2(\text{g})$	-296.8
$\text{C}_2\text{H}_5\text{OH}(\text{l})$	-277.6	$\text{NH}_4\text{NO}_3(\text{s})$	-365.6	$\text{SO}_3(\text{g})$	-395.7
$\text{C}_3\text{H}_8(\text{g})$	-103.85	$\text{NO}(\text{g})$	91.3	$\text{H}_2\text{SO}_4(\text{l})$	-814.0
$\text{C}_3\text{H}_6\text{O}(\text{l, acetone})$	-248.4	$\text{N}_2\text{O}(\text{g})$	81.6		

### EXAMPLE 6.10 Standard Enthalpies of Formation

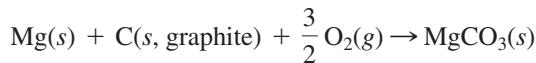
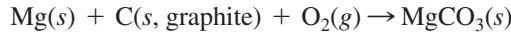
Write equations for the formation of (a)  $\text{MgCO}_3(s)$  and (b)  $\text{C}_6\text{H}_{12}\text{O}_6(s)$  from their respective elements in their standard states. Include the value of  $\Delta H_f^\circ$  for each equation.

#### SOLUTION

a.  $\text{MgCO}_3(s)$

Write the equation with the elements in  $\text{MgCO}_3$  in their standard states as the reactants and 1 mol of  $\text{MgCO}_3$  as the product.

Balance the equation and look up  $\Delta H_f^\circ$  in Appendix IIB. (Use fractional coefficients so that the product of the reaction is 1 mol of  $\text{MgCO}_3$ .)

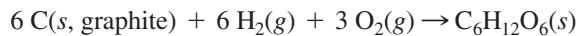
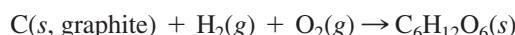


$$\Delta H_f^\circ = -1095.8 \text{ kJ/mol}$$

b.  $\text{C}_6\text{H}_{12}\text{O}_6(s)$

Write the equation with the elements in  $\text{C}_6\text{H}_{12}\text{O}_6$  in their standard states as the reactants and 1 mol of  $\text{C}_6\text{H}_{12}\text{O}_6$  as the product.

Balance the equation and look up  $\Delta H_f^\circ$  in Appendix IIB.



$$\Delta H_f^\circ = -1273.3 \text{ kJ/mol}$$

#### FOR PRACTICE 6.10

Write equations for the formation of (a)  $\text{NaCl}(s)$  and (b)  $\text{Pb}(\text{NO}_3)_2(s)$  from their respective elements in their standard states. Include the value of  $\Delta H_f^\circ$  for each equation.

### Calculating the Standard Enthalpy Change for a Reaction

We have just seen that the standard enthalpy of formation corresponds to the *formation* of a compound from its constituent elements in their standard states:



Therefore, the *negative* of the standard enthalpy of formation corresponds to the *decomposition* of a compound into its constituent elements in their standard states:

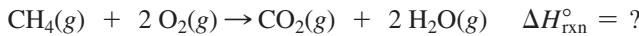


We can use these two concepts—the decomposition of a compound into its elements and the formation of a compound from its elements—to calculate the enthalpy change of any reaction by mentally taking the reactants through two steps. In the first step we *decompose the reactants* into their constituent elements in their standard states; in the second step we *form the products* from the constituent elements in their standard states.



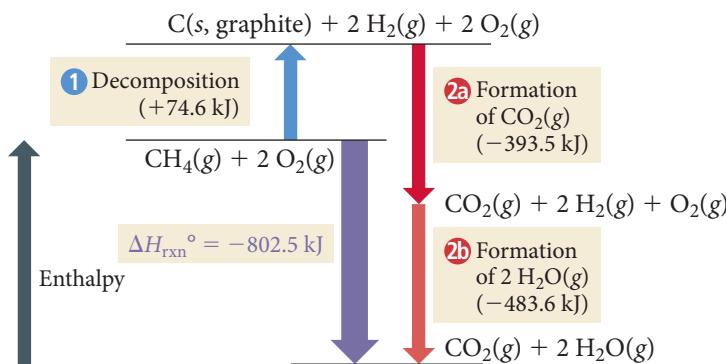
In these equations,  $\Sigma$  means “the sum of” so that  $\Delta H_1$  is the sum of the negatives of the heats of formation of the reactants and  $\Delta H_2$  is the sum of the heats of formation of the products.

We can demonstrate this procedure by calculating the standard enthalpy change ( $\Delta H_{\text{rxn}}^\circ$ ) for the combustion of methane:



The energy changes associated with the decomposition of the reactants and the formation of the products are shown in Figure 6.11 ▶. The first step (1) is the decomposition of 1 mol of methane into its constituent elements in their standard states. We can obtain the

### Calculating the Enthalpy Change for the Combustion of Methane

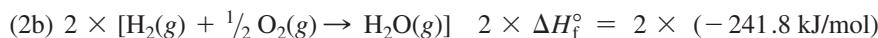


▲ FIGURE 6.11 Calculating the Enthalpy Change for the Combustion of Methane

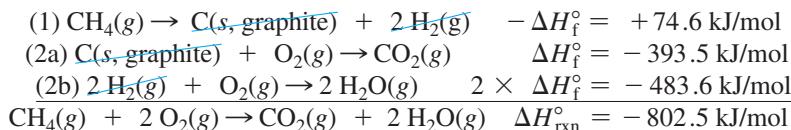
change in enthalpy for this step by reversing the enthalpy of formation equation for methane and changing the sign of  $\Delta H_f^\circ$ :



The second step, the formation of the products from their constituent elements, has two parts: (a) the formation of 1 mol CO<sub>2</sub> and (b) the formation of 2 mol H<sub>2</sub>O. Since part (b) forms 2 mol H<sub>2</sub>O, we multiply the  $\Delta H_f^\circ$  for that step by 2.



As we know from Hess's law, the enthalpy of reaction for the overall reaction is the sum of the enthalpies of reaction of the individual steps:



We can streamline and generalize this process as follows:

**To calculate  $\Delta H_{rxn}^\circ$ , subtract the enthalpies of formation of the reactants multiplied by their stoichiometric coefficients from the enthalpies of formation of the products multiplied by their stoichiometric coefficients.**

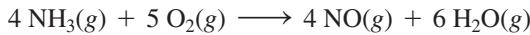
In the form of an equation,

$$\Delta H_{rxn}^\circ = \sum n_p \Delta H_f^\circ(\text{products}) - \sum n_r \Delta H_f^\circ(\text{reactants}) \quad [6.15]$$

In this equation,  $n_p$  represents the stoichiometric coefficients of the products,  $n_r$  represents the stoichiometric coefficients of the reactants, and  $\Delta H_f^\circ$  represents the standard enthalpies of formation. Keep in mind when using this equation that elements in their standard states have  $\Delta H_f^\circ = 0$ . Examples 6.11 and 6.12 demonstrate this process.

**EXAMPLE 6.11**  $\Delta H_{\text{rxn}}^{\circ}$  and Standard Enthalpies of Formation

Use the standard enthalpies of formation to determine  $\Delta H_{\text{rxn}}^{\circ}$  for the reaction:



**SORT** You are given the balanced equation and asked to find the enthalpy of reaction.

**STRATEGIZE** To calculate  $\Delta H_{\text{rxn}}^{\circ}$  from standard enthalpies of formation, subtract the heats of formation of the reactants multiplied by their stoichiometric coefficients from the heats of formation of the products multiplied by their stoichiometric coefficients.

**SOLVE** Begin by looking up (in Appendix IIB) the standard enthalpy of formation for each reactant and product. Remember that the standard enthalpy of formation of pure elements in their standard state is zero. Calculate  $\Delta H_{\text{rxn}}^{\circ}$  by substituting into the equation.

**GIVEN:**  $4 \text{ NH}_3(g) + 5 \text{ O}_2(g) \longrightarrow 4 \text{ NO}(g) + 6 \text{ H}_2\text{O}(g)$

**FIND:**  $\Delta H_{\text{rxn}}^{\circ}$

**CONCEPTUAL PLAN**

$$\Delta H_{\text{rxn}}^{\circ} = \sum n_p \Delta H_f^{\circ}(\text{products}) - \sum n_r \Delta H_f^{\circ}(\text{reactants})$$

**SOLUTION**

Reactant or product	$\Delta H_f^{\circ}$ (kJ/mol, from Appendix IIB)
$\text{NH}_3(g)$	-45.9
$\text{O}_2(g)$	0.0
$\text{NO}(g)$	+91.3
$\text{H}_2\text{O}(g)$	-241.8

$$\begin{aligned}\Delta H_{\text{rxn}}^{\circ} &= \sum n_p \Delta H_f^{\circ}(\text{products}) - \sum n_r \Delta H_f^{\circ}(\text{reactants}) \\ &= [4(\Delta H_f^{\circ}, \text{NO}(g)) + 6(\Delta H_f^{\circ}, \text{H}_2\text{O}(g))] - [4(\Delta H_f^{\circ}, \text{NH}_3(g)) + 5(\Delta H_f^{\circ}, \text{O}_2(g))] \\ &= [4(+91.3 \text{ kJ}) + 6(-241.8 \text{ kJ})] - [4(-45.9 \text{ kJ}) + 5(0.0 \text{ kJ})] \\ &= -1085.6 \text{ kJ} - (-183.6 \text{ kJ}) \\ &= -902.0 \text{ kJ}\end{aligned}$$

**CHECK** The units of the answer (kJ) are correct. The answer is negative, which means that the reaction is exothermic.

**FOR PRACTICE 6.11**

The thermite reaction, in which powdered aluminum reacts with iron oxide, is highly exothermic.



Use standard enthalpies of formation to find  $\Delta H_{\text{rxn}}^{\circ}$  for the thermite reaction.

► The reaction of powdered aluminum with iron oxide, known as the thermite reaction, releases a large amount of heat.



### EXAMPLE 6.12 $\Delta H_{\text{rxn}}^{\circ}$ and Standard Enthalpies of Formation

A city of 100,000 people uses approximately  $1.0 \times 10^{11}$  kJ of energy per day. Suppose all of that energy comes from the combustion of liquid octane ( $\text{C}_8\text{H}_{18}$ ) to form gaseous water and gaseous carbon dioxide. Use standard enthalpies of formation to calculate  $\Delta H_{\text{rxn}}^{\circ}$  for the combustion of octane and then determine how many kilograms of octane would be necessary to provide this amount of energy.

<p><b>SORT</b> You are given the amount of energy used and asked to find the mass of octane required to produce the energy.</p> <p><b>STRATEGIZE</b> The conceptual plan has three parts. In the first part, write a balanced equation for the combustion of octane.</p> <p>In the second part, calculate <math>\Delta H_{\text{rxn}}^{\circ}</math> from the <math>\Delta H_f^{\circ}</math>'s of the reactants and products.</p> <p>In the third part, convert from kilojoules of energy to moles of octane using the conversion factor found in step 2, and then convert from moles of octane to mass of octane using the molar mass.</p>	<p><b>GIVEN:</b> <math>1.0 \times 10^{11}</math> kJ  <b>FIND:</b> kg <math>\text{C}_8\text{H}_{18}</math></p> <p><b>CONCEPTUAL PLAN</b></p> <p>(1) Write the balanced equation.</p> <p>(2)   <math display="block">\Delta H_{\text{rxn}}^{\circ} = \sum n_p \Delta H_f^{\circ} (\text{products}) - \sum n_r \Delta H_f^{\circ} (\text{reactants})</math></p> <p>(3)   Conversion factor to be determined from steps 1 and 2  <math display="block">\frac{114.22 \text{ g } \text{C}_8\text{H}_{18}}{1 \text{ mol } \text{C}_8\text{H}_{18}}</math>      <math display="block">\frac{1 \text{ kg}}{1000 \text{ g}}</math></p> <p><b>RELATIONSHIPS USED</b></p> <p>molar mass <math>\text{C}_8\text{H}_{18} = 114.22 \text{ g/mol}</math>  <math>1 \text{ kg} = 1000 \text{ g}</math></p>										
<p><b>SOLVE</b> Begin by writing the balanced equation for the combustion of octane. For convenience, do not clear the <math>25/2</math> fraction in order to keep the coefficient on octane as 1.</p>	<p><b>SOLUTION STEP 1</b></p> $\text{C}_8\text{H}_{18}(l) + \frac{25}{2} \text{O}_2(g) \longrightarrow 8 \text{CO}_2(g) + 9 \text{H}_2\text{O}(g)$										
<p>Look up (in Appendix IIB) the standard enthalpy of formation for each reactant and product and then calculate <math>\Delta H_{\text{rxn}}^{\circ}</math>.</p>	<p><b>SOLUTION STEP 2</b></p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="background-color: #f2e0bd; padding: 2px;">Reactant or product</th> <th style="background-color: #f2e0bd; padding: 2px;"><math>\Delta H_f^{\circ}</math> (kJ/mol from Appendix IIB)</th> </tr> </thead> <tbody> <tr> <td style="padding: 2px;"><math>\text{C}_8\text{H}_{18}(l)</math></td> <td style="padding: 2px; text-align: right;">−250.1</td> </tr> <tr> <td style="padding: 2px;"><math>\text{O}_2(g)</math></td> <td style="padding: 2px; text-align: right;">0.0</td> </tr> <tr> <td style="padding: 2px;"><math>\text{CO}_2(g)</math></td> <td style="padding: 2px; text-align: right;">−393.5</td> </tr> <tr> <td style="padding: 2px;"><math>\text{H}_2\text{O}(g)</math></td> <td style="padding: 2px; text-align: right;">−241.8</td> </tr> </tbody> </table> $\begin{aligned} \Delta H_{\text{rxn}}^{\circ} &= \sum n_p \Delta H_f^{\circ} (\text{products}) - \sum n_r \Delta H_f^{\circ} (\text{reactants}) \\ &= [8(\Delta H_f^{\circ}, \text{CO}_2(g)) + 9(\Delta H_f^{\circ}, \text{H}_2\text{O}(g))] \\ &\quad - \left[ 1(\Delta H_f^{\circ}, \text{C}_8\text{H}_{18}(l)) + \frac{25}{2}(\Delta H_f^{\circ}, \text{O}_2(g)) \right] \\ &= [8(-393.5 \text{ kJ}) + 9(-241.8 \text{ kJ})] - \left[ 1(-250.1 \text{ kJ}) + \frac{25}{2}(0.0 \text{ kJ}) \right] \\ &= -5324.2 \text{ kJ} - (-250.1 \text{ kJ}) \\ &= -5074.1 \text{ kJ} \end{aligned}$	Reactant or product	$\Delta H_f^{\circ}$ (kJ/mol from Appendix IIB)	$\text{C}_8\text{H}_{18}(l)$	−250.1	$\text{O}_2(g)$	0.0	$\text{CO}_2(g)$	−393.5	$\text{H}_2\text{O}(g)$	−241.8
Reactant or product	$\Delta H_f^{\circ}$ (kJ/mol from Appendix IIB)										
$\text{C}_8\text{H}_{18}(l)$	−250.1										
$\text{O}_2(g)$	0.0										
$\text{CO}_2(g)$	−393.5										
$\text{H}_2\text{O}(g)$	−241.8										

From steps 1 and 2 build a conversion factor between mol C<sub>8</sub>H<sub>18</sub> and kJ.

Follow step 3 of the conceptual plan. Begin with  $-1.0 \times 10^{11}$  kJ (since the city uses this much energy, the reaction must emit it, and therefore the sign is negative) and follow the steps to determine kg octane.

### SOLUTION STEP 3

$$\begin{aligned} 1 \text{ mol C}_8\text{H}_{18} &: -5074.1 \text{ kJ} \\ -1.0 \times 10^{11} \text{ kJ} &\times \frac{1 \text{ mol C}_8\text{H}_{18}}{-5074.1 \text{ kJ}} \times \frac{114.22 \text{ g C}_8\text{H}_{18}}{1 \text{ mol C}_8\text{H}_{18}} \\ &\times \frac{1 \text{ kg}}{1000 \text{ g}} = 2.3 \times 10^6 \text{ kg C}_8\text{H}_{18} \end{aligned}$$

### CHECK

The units of the answer (kg C<sub>8</sub>H<sub>18</sub>) are correct. The answer is positive, as it should be for mass. The magnitude is fairly large, as you would expect since this amount of octane is supposed to provide the energy for an entire city.

### FOR PRACTICE 6.12

The chemical hand warmers described in Section 6.1 produce heat when they are removed from their airtight plastic wrappers. Recall that they utilize the oxidation of iron to form iron oxide according to the reaction  $4 \text{ Fe}(s) + 3 \text{ O}_2(g) \longrightarrow 2 \text{ Fe}_2\text{O}_3(s)$ .

Calculate  $\Delta H_{\text{rxn}}^\circ$  for this reaction and calculate how much heat is produced from a hand warmer containing 15.0 g of iron powder.

## 6.10 Energy Use and the Environment

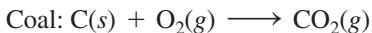
In this chapter, we have learned about the relationship between chemical reactions and energy changes. As noted earlier, our society derives the majority of its energy from the energy changes associated with burning fossil fuels. Fossil fuels have traditionally been regarded as convenient sources of energy due to their abundance and portability and because they undergo combustion reactions that have large negative enthalpies of reaction (the reactions are highly exothermic). However, the burning of fossil fuels also has some serious environmental impacts.

### Energy Consumption

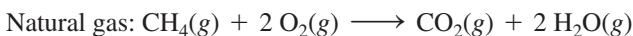
According to the U.S. Department of Energy, the United States currently consumes close to 100 quads (1 quad = 1 quadrillion British thermal units =  $1.06 \times 10^{18}$  J) of energy per year in the categories shown in this chart.

This corresponds to over 100,000 kWh of energy use per person per year. If we used physical laborers to do the equivalent amount of work, we would need about 120 people. In other words, the average American employs the work output of 120 people, day and night, all year long! For this reason, Americans enjoy one of the highest standards of living in the world. However, as we learned earlier in the chapter, when it comes to energy, there is no free lunch. Our consumption of energy has significant environmental consequences.

Most U.S. energy comes from the combustion of fossil fuels, as shown in Figure 6.12 ▶. Fossil fuels include petroleum, natural gas, and coal, all of which have been considered convenient fuels because they are relatively abundant in Earth's crust (and therefore are relatively inexpensive), they are easily transportable, and their combustion is highly exothermic. The reactions for the combustion of the main or representative components of several fossil fuels, and the associated enthalpies of reaction, are:



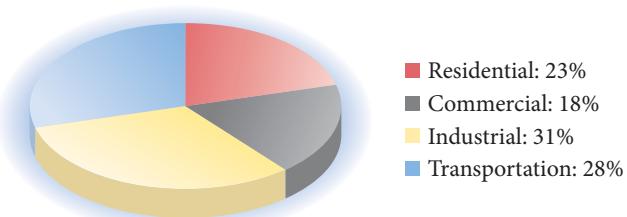
$$\Delta H_{\text{rxn}}^\circ = -393.5 \text{ kJ}$$



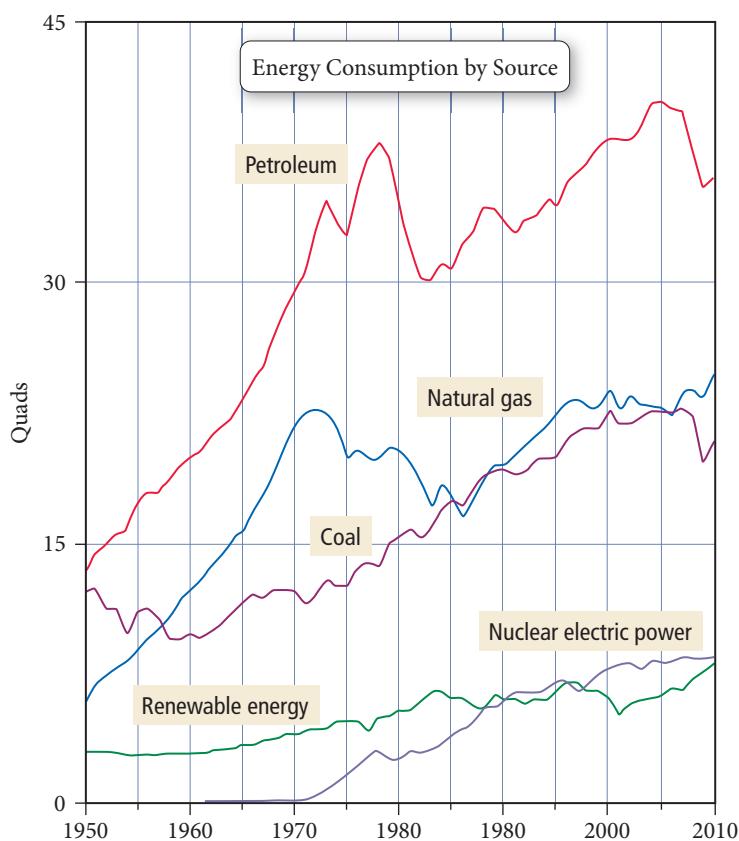
$$\Delta H_{\text{rxn}}^\circ = -802.3 \text{ kJ}$$



$$\Delta H_{\text{rxn}}^\circ = -5074.1 \text{ kJ}$$



Source: U.S. Energy Information Administration. *Annual Energy Review*. 2010.



▲ FIGURE 6.12 Energy Consumption by Source

Source: U.S. Energy Information Administration. *Annual Energy Review*. 2010.

## Environmental Problems Associated with Fossil Fuel Use

One of the main problems associated with the burning of fossil fuels is that even though they are abundant in Earth's crust, they are also finite. Fossil fuels originate from ancient plant and animal life and are a nonrenewable energy source—once they are all burned, they cannot be replenished. At current rates of consumption, oil and natural gas supplies will be depleted in 50 to 100 years. While there is enough coal to last much longer, it is a dirtier fuel (it produces more pollution) and, because it is a solid, is less convenient (more difficult to transport and use) than petroleum and natural gas.

The other major problems associated with fossil fuel use stem from the products of combustion. The chemical equations shown for fossil fuel combustion all produce carbon dioxide and water. However, these equations represent the reactions under ideal conditions and do not account for impurities in the fuel, side reactions, and incomplete combustion. When these are taken into account, we can identify three major environmental problems associated with the emissions of fossil fuel combustion: air pollution, acid rain, and global climate change. We discussed acid rain in Chapter 3 (see *Chemistry in the Environment: Acid Rain* in Section 3.6). Here we will address air pollution and global climate change, which we first touched on in Section 4.1.

## Air Pollution

The air in all major cities in the world is polluted. Pollution comes from a number of sources including electricity generation, motor vehicle emissions, and industrial waste. There are many different kinds of air pollutants.

**Sulfur Oxides ( $\text{SO}_x$ )** Sulfur oxides include  $\text{SO}_2$  and  $\text{SO}_3$ , produced primarily during coal-fired electricity generation and industrial metal refining. The sulfur oxides are lung and eye irritants that affect the respiratory system and are the main precursors of acid rain (see Section 3.6).

**Carbon Monoxide (CO)** Carbon monoxide is formed during the incomplete combustion of fossil fuels (petroleum, natural gas, and coal). It is emitted mainly by motor vehicles. In humans and other animals, carbon monoxide displaces oxygen in the blood, forcing the heart and lungs to work harder. At high levels, CO can cause sensory impairment, decreased thinking ability, unconsciousness, and even death.

**Nitrogen Oxides ( $\text{NO}_x$ )** The nitrogen oxides include  $\text{NO}$  and  $\text{NO}_2$ , emitted by motor vehicles, fossil fuel-based electricity generation plants, and any high-temperature combustion process occurring in air. Nitrogen dioxide is an orange-brown gas that causes the dark haze over polluted cities. Nitrogen oxides are eye and lung irritants and precursors of acid rain.

**Ozone ( $\text{O}_3$ )** Ozone is produced when some of the products of fossil fuel combustion, especially nitrogen oxides and unburned volatile organic compounds (VOCs), react in the presence of sunlight. The products of this reaction, which include ozone, are called *photochemical smog*. Ozone produced in this way—sometimes called ground-level ozone—should not be confused with upper atmospheric or *stratospheric* ozone. Although ozone is always the same molecule ( $\text{O}_3$ ), stratospheric ozone is a natural part of our environment that protects Earth from harmful ultraviolet light. Stratospheric ozone does not harm us because we are not directly exposed to it. Ground-level ozone, on the other hand, is a pollutant to which we are directly exposed; it is an eye and lung irritant, and prolonged exposure can cause permanent lung damage.

In the United States, the U.S. Environmental Protection Agency (EPA) has established limits on these pollutants. Beginning in the 1970s, the U.S. Congress passed the Clean Air Act and its amendments, requiring U.S. cities to reduce their pollution and maintain levels below the standards set by the EPA. As a result of this legislation, pollutant levels in U.S. cities have decreased over the last 30 years, even as the number of vehicles has increased. For example, according to the EPA's 2010 National Air Quality and Emissions Trends Report, the levels of the major pollutants in the air of U.S. cities have decreased significantly during the period 1980–2010 as shown in Table 6.6.

Although the levels of pollutants (especially ozone) in some cities are still above what the EPA considers safe, real progress has been made. These trends demonstrate that legislation can improve our environment.

## Global Climate Change

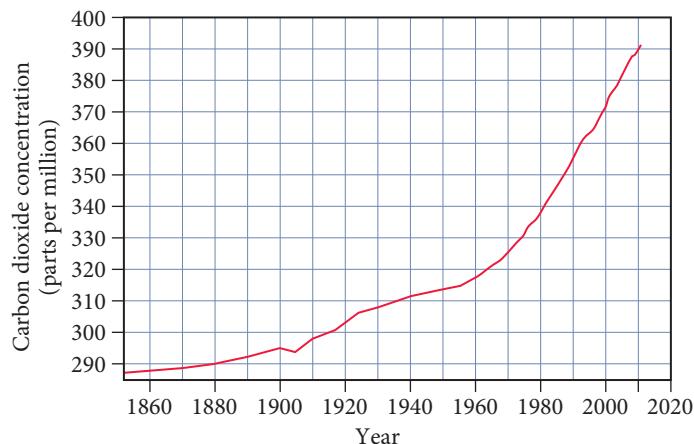
One of the main products of fossil fuel combustion is carbon dioxide. Carbon dioxide is a greenhouse gas; it allows visible light from the sun to enter Earth's atmosphere but prevents heat (in the form of infrared light) from escaping. In doing so, carbon dioxide acts as a blanket, keeping Earth warm, which, in moderation, is a very good thing and allows life as we know it to exist on our planet. However, because of fossil fuel combustion, carbon dioxide levels in the atmosphere have been steadily increasing, as shown in Figure 6.13 ▶. This increase is expected to change the global climate and raise Earth's average temperature. Current observations suggest that Earth has already warmed by about 0.7 °C in the last century due to an approximately 38% increase in atmospheric carbon dioxide. Computer models suggest that the warming could worsen if carbon dioxide emissions are not curbed. The possible effects of this warming include heightened storm severity, increasing numbers of floods and droughts, major shifts in agricultural zones, rising sea levels and coastal flooding, and profound changes in habitats that could result in the extinction of some plant and animal species.

**TABLE 6.6 Changes in National Average Pollutant Levels, 1980–2010**

Pollutant	Change (%) in Average Level
SO <sub>2</sub>	-76
CO	-82
NO <sub>2</sub>	-52
O <sub>3</sub>	-28

\*Source: EPA's 2010 National Air Quality and Emissions Trends Report.

## Atmospheric Carbon Dioxide



**▲ FIGURE 6.13** The Rise in Atmospheric Carbon Dioxide Atmospheric carbon dioxide levels have been steadily increasing as a result of fossil fuel combustion.

### EXAMPLE 6.13 Fossil Fuels and Climate Change

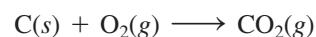
One way to evaluate fuels with respect to global warming is to determine how much heat they release during combustion relative to how much CO<sub>2</sub> they produce. The greater the heat relative to the amount of CO<sub>2</sub>, the better the fuel. Use the combustion reactions of carbon, natural gas, and octane, in combination with the enthalpy of combustion for each reaction (all given earlier), to calculate the heat (in kJ) released by each fuel per 1.00 kg of CO<sub>2</sub> produced.

**SORT** You are given the mass of CO<sub>2</sub> emitted and asked to find the energy output for three different fuels.

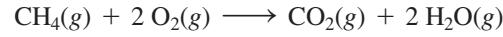
**GIVEN:** 1.00 kg CO<sub>2</sub>

**FIND:** kJ

**STRATEGIZE** You must first write the thermochemical equations for the combustion of each fuel given in Section 6.10.



$$\Delta H_{\text{rxn}}^\circ = -393.5 \text{ kJ}$$



$$\Delta H_{\text{rxn}}^\circ = -802.3 \text{ kJ}$$



$$\Delta H_{\text{rxn}}^\circ = -5074.1 \text{ kJ}$$

The conceptual plan has two parts. In the first part, use the molar mass of CO<sub>2</sub> to convert from mass of CO<sub>2</sub> to moles of CO<sub>2</sub>. This step is the same for each fuel.

In the second part, use the stoichiometric relationship between moles of CO<sub>2</sub> produced and kilojoules of energy released to calculate the energy output. Repeat the second part for each fuel using the appropriate stoichiometric relationship from the balanced equations.

### SOLVE

Begin by converting kg CO<sub>2</sub> to mol CO<sub>2</sub>.

Then, for each fuel, convert mol CO<sub>2</sub> to kJ.

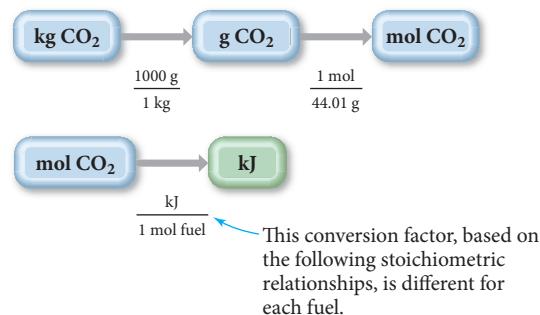
As you can see from the heat released in the production of 1 kg CO<sub>2</sub>, natural gas, CH<sub>4</sub>, provides the most energy per kg CO<sub>2</sub>; therefore, it is the best fuel with respect to climate change.

**CHECK** Each answer is in kJ, as it should be for heat produced. Each answer is negative, as expected for exothermic combustion reactions.

### FOR PRACTICE 6.13

What mass of CO<sub>2</sub> (in kg) does the combustion of a 15-gallon tank of gasoline release into the atmosphere? Assume the gasoline is pure octane (C<sub>8</sub>H<sub>18</sub>) and that it has a density of 0.70 g /mL.

### CONCEPTUAL PLAN



### STOICHIOMETRIC RELATIONSHIPS

For C: 1 mol CO<sub>2</sub> : -393.5 kJ

For CH<sub>4</sub>: 1 mol CO<sub>2</sub> : -802.3 kJ

For C<sub>8</sub>H<sub>18</sub>: 8 mol CO<sub>2</sub> : -5074.1 kJ

### OTHER RELATIONSHIPS USED

1 kg = 1000 g

molar mass CO<sub>2</sub> = 44.01 g/mol

### SOLUTION

$$1.00 \text{ kg CO}_2 \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} = 22.72 \text{ mol CO}_2$$

For C:

$$22.72 \text{ mol CO}_2 \times \frac{-393.5 \text{ kJ}}{1 \text{ mol CO}_2} = -8.94 \times 10^3 \text{ kJ}$$

For CH<sub>4</sub>:

$$22.72 \text{ mol CO}_2 \times \frac{-802.3 \text{ kJ}}{1 \text{ mol CO}_2} = -1.82 \times 10^4 \text{ kJ}$$

For C<sub>8</sub>H<sub>18</sub>:

$$22.72 \text{ mol CO}_2 \times \frac{-5074.1 \text{ kJ}}{8 \text{ mol CO}_2} = -1.44 \times 10^4 \text{ kJ}$$



## Chemistry in the Environment

### Renewable Energy

Because of their finite supply and environmental impacts, fossil fuels will not be our major source of energy in the future. What will replace them? Although the answer is not clear, several alternative energy technologies are beginning to emerge. Unlike fossil fuels, these technologies are renewable, and we can use them indefinitely.

Our planet's greatest source of renewable energy is the sun. If we could capture and harness just a small fraction of the total

sunlight falling on Earth, we could meet our energy needs several times over. The main problem with solar energy, however,

is diffuseness—the sun's

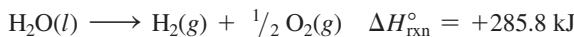


▲ Honda's 2009 FCX Clarity, a fuel cell vehicle that runs on hydrogen gas and produces only water as exhaust.

energy falls over an enormous area. How do we concentrate and store it? In California, some of the state's electricity is generated by parabolic troughs, solar power towers, and dish/engines.

These devices use reflective surfaces to focus the sun's energy and produce enough heat to generate electricity. Although the direct cost of generating electricity this way is higher than using fossil fuels, the benefits to the environment are obvious. In addition, with time, the costs are expected to fall.

Another way to capture the sun's energy is in chemical bonds. For example, solar energy could be used to drive the decomposition of water:



The hydrogen gas produced could be stored until needed to provide energy by re-forming water in the reverse reaction:



This reaction can be carried out in an electrochemical device called a fuel cell. In a fuel cell, hydrogen and oxygen gases combine to form water and produce electricity. In 2007, Honda introduced the FCX, a fuel cell four-passenger vehicle with a 240-mile range and a top speed of 100 mph. The automobile is selectively available for lease, primarily in Southern California. The main challenge for the FCX and other fuel cell vehicles is refueling. The FCX requires hydrogen fuel, which can only be obtained at a small number of refueling stations. Other automakers have similar prototype models in development.



Parabolic troughs



Solar power tower



Dish/engine

▲ The sun's energy, concentrated by reflective surfaces in various arrangements, can produce enough heat to generate electricity.

## CHAPTER IN REVIEW

### Self Assessment Quiz

- Q1.** A chemical system produces 155 kJ of heat and does 22 kJ of work. What is  $\Delta E$  for the *surroundings*?
- 177 kJ
  - 177 kJ
  - 133 kJ
  - 133 kJ
- Q2.** Which sample is most likely to undergo the smallest change in temperature upon the absorption of 100 kJ of heat?
- 15 g water
  - 15 g lead
  - 50 g water
  - 50 g lead
- Q3.** How much heat must be absorbed by a 15.0 g sample of water to raise its temperature from 25.0 °C to 55.0 °C? (For water,  $C_s = 4.18 \text{ J/g } ^\circ\text{C}$ .)
- 1.57 kJ
  - 1.88 kJ
  - 3.45 kJ
  - 107 J
- Q4.** A 12.5 g sample of granite initially at 82.0 °C is immersed into 25.0 g of water initially at 22.0 °C. What is the final temperature of both substances when they reach thermal equilibrium? (For water,  $C_s = 4.18 \text{ J/g } ^\circ\text{C}$  and for granite,  $C_s = 0.790 \text{ J/g } ^\circ\text{C}$ .)
- 52.0 °C
  - $1.55 \times 10^3 \text{ } ^\circ\text{C}$
  - 15.7 °C
  - 27.2 °C

Other renewable energy sources are hydroelectric power and wind power. Hydroelectric power plants—which generate approximately 8% of U.S. electricity—harness the gravitational potential energy of water held behind a dam. Water is released at a controlled rate. As it falls, it acquires kinetic energy that is used to spin a turbine, generating electricity. Wind power plants—which produce about 2% of U.S. electricity—consist of hundreds of turbines that are spun by the wind to generate electricity. Both of these technologies are cost competitive with fossil fuels, have no emissions, and are completely renewable.

Our energy future will probably involve a combination of these technologies and some new ones, combined with a focus on greater efficiency and conservation. One thing, however, is clear—the future of fossil fuels is limited.



▲ Wind turbines such as these generate about 2% of U.S. electricity.

- Q5.** A cylinder with a moving piston expands from an initial volume of 0.250 L against an external pressure of 2.00 atm. The expansion does 288 J of work on the surroundings. What is the final volume of the cylinder?
- 1.42 L
  - 1.17 L
  - 144 L
  - 1.67 L

- Q6.** When a 3.80 g sample of liquid octane ( $C_8H_{18}$ ) is burned in a bomb calorimeter, the temperature of the calorimeter rises by  $27.3\text{ }^{\circ}\text{C}$ . The heat capacity of the calorimeter, measured in a separate experiment, is  $6.18\text{ kJ/ }^{\circ}\text{C}$ . Determine the enthalpy of combustion for octane in units of  $\text{kJ/mol}$  octane.
- $-5.07 \times 10^3\text{ kJ/mol}$
  - $5.07 \times 10^3\text{ kJ/mol}$
  - $-44.4 \times 10^3\text{ kJ/mol}$
  - $-16.7 \times 10^3\text{ kJ/mol}$

- Q7.** Hydrogen gas reacts with oxygen to form water.



Determine the minimum mass of hydrogen gas required to produce 226 kJ of heat.

- 8.63 g
- 1.88 g
- 0.942 g
- 0.935 g

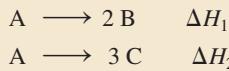
- Q8.** Manganese reacts with hydrochloric acid to produce manganese(II) chloride and hydrogen gas.



When 0.625 g Mn is combined with enough hydrochloric acid to make 100.0 mL of solution in a coffee-cup calorimeter, all of the Mn reacts, raising the temperature of the solution from  $23.5\text{ }^{\circ}\text{C}$  to  $28.8\text{ }^{\circ}\text{C}$ . Find  $\Delta H_{\text{rxn}}$  for the reaction as written. (Assume that the specific heat capacity of the solution is  $4.18\text{ J/g }^{\circ}\text{C}$  and the density is 1.00 g/mL.)

- 195 kJ
- 3.54 kJ
- 1.22 kJ
- 2.21 kJ

- Q9.** Consider the reactions:



What is  $\Delta H$  for the reaction  $2\text{ B} \longrightarrow 3\text{ C}$ ?

- $\Delta H_1 + \Delta H_2$
- $\Delta H_1 - \Delta H_2$
- $\Delta H_2 - \Delta H_1$
- $2 \times (\Delta H_1 + \Delta H_2)$

- Q10.** Use standard enthalpies of formation to determine  $\Delta H_{\text{rxn}}^{\circ}$  for the reaction:



- 541.2 kJ
- 2336 kJ
- 541.2 kJ
- 24.8 kJ

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

- Q11.** Two substances, A and B, of equal mass but at different temperatures come into thermal contact. The specific heat capacity of substance A is twice the specific heat capacity of substance B. Which statement is true of the temperature of the two substances when they reach thermal equilibrium? (Assume no heat loss other than the thermal transfer between the substances.)

- The final temperature of both substances will be closer to the initial temperature of substance A than the initial temperature of substance B.
- The final temperature of both substances will be closer to the initial temperature of substance B than the initial temperature of substance A.
- The final temperature of both substances will be exactly midway between the initial temperatures of substance A and substance B.
- The final temperature of substance B will be greater than the final temperature of substance A.

- Q12.** Which process is endothermic?

- The evaporation of water from the skin.
- The burning of candle wax.
- The oxidation of iron in a chemical hand warmer.
- The combustion of natural gas in a stove.

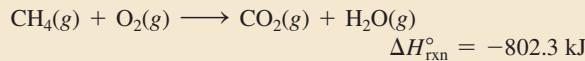
- Q13.** Which fuel is not a fossil fuel?

- coal
- hydrogen
- natural gas
- petroleum

- Q14.** The standard enthalpy of formation for glucose [ $C_6H_{12}O_6(s)$ ] is  $-1273.3\text{ kJ/mol}$ . What is the correct formation equation corresponding to this  $\Delta H_f^{\circ}$ ?

- $6\text{C(s, graphite)} + 6\text{H}_2\text{O}(g) \longrightarrow \text{C}_6\text{H}_{12}\text{O}_6(s, \text{glucose})$
- $6\text{C(s, graphite)} + 6\text{H}_2\text{O}(l) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(s, \text{glucose})$
- $6\text{C(s, graphite)} + 6\text{H}_2(l) + 3\text{O}_2(l) \longrightarrow \text{C}_6\text{H}_{12}\text{O}_6(s, \text{glucose})$
- $6\text{C(s, graphite)} + 6\text{H}_2(g) + 3\text{O}_2(g) \longrightarrow \text{C}_6\text{H}_{12}\text{O}_6(s, \text{glucose})$

- Q15.** Natural gas burns in air to form carbon dioxide and water, releasing heat.



What minimum mass of  $\text{CH}_4$  is required to heat 55 g of water by  $25\text{ }^{\circ}\text{C}$ ? (Assume 100% heating efficiency.)

- 0.115 g
- $2.25 \times 10^3\text{ g}$
- 115 g
- 8.70 g

## Key Terms

### Section 6.1

thermochemistry (247)

### Section 6.2

energy (248)

work (248)

heat (248)

kinetic energy (248)

thermal energy (248)

potential energy (248)

chemical energy (248)

law of conservation of energy (248)

system (249)

surroundings (249)

joule (J) (250)

calorie (cal) (250)

Calorie (Cal) (250)

kilowatt-hour (kWh) (250)

### Section 6.3

first law of thermodynamics (250)

internal energy ( $E$ ) (251)

state function (251)

**Section 6.4**

thermal equilibrium (256)  
heat capacity (*C*) (257)  
specific heat capacity (*C<sub>s</sub>*) (257)  
molar heat capacity (257)  
pressure–volume work (260)

**Section 6.5**

calorimetry (262)  
bomb calorimeter (262)

**Section 6.6**

enthalpy (*H*) (265)  
endothermic reaction (265)  
exothermic reaction (266)

enthalpy (heat) of reaction  
( $\Delta H_{rxn}$ ) (267)

**Section 6.7**

coffee-cup calorimeter (269)

**Section 6.8**

Hess's law (271)

**Section 6.9**

standard state (273)  
standard enthalpy change  
( $\Delta H^\circ$ ) (273)  
standard enthalpy of formation  
( $\Delta H_f^\circ$ ) (273)  
standard heat of formation (274)

## Key Concepts

### The Nature of Energy and Thermodynamics (6.2, 6.3)

- Energy, which is measured in the SI unit of joules (J), is the capacity to do work.
- Work is the result of a force acting through a distance.
- Many different kinds of energy exist, including kinetic energy, thermal energy, potential energy, and chemical energy, a type of potential energy associated with the relative positions of electrons and nuclei in atoms and molecules.
- The first law of thermodynamics states that energy can be converted from one form to another, but the total amount of energy is always conserved.
- The internal energy (*E*) of a system is the sum of all of its kinetic and potential energy. Internal energy is a state function, which means that it depends only on the state of the system and not on the pathway by which it got to that state.
- A chemical system exchanges energy with its surroundings through heat (the transfer of thermal energy caused by a temperature difference) or work. The total change in internal energy is the sum of these two quantities.

### Heat and Work (6.4)

- We quantify heat with the equation  $q = m \times C_s \times \Delta T$ . In this expression,  $C_s$  is the specific heat capacity, the amount of heat required to change the temperature of 1 g of the substance by 1 °C. Compared to most substances, water has a very high heat capacity—it takes a lot of heat to change its temperature.
- The type of work most characteristic of chemical reactions is pressure–volume work, which occurs when a gas expands against an external pressure. Pressure–volume work can be quantified with the equation  $w = -P\Delta V$ .
- The change in internal energy ( $\Delta E$ ) that occurs during a chemical reaction is the sum of the heat ( $q$ ) exchanged and the work ( $w$ ) done:  $\Delta E = q + w$

### Enthalpy (6.6)

- The heat evolved in a chemical reaction occurring at constant pressure is the change in enthalpy ( $\Delta H$ ) for the reaction. Like internal energy, enthalpy is a state function.
- An endothermic reaction has a positive enthalpy of reaction; an exothermic reaction has a negative enthalpy of reaction.
- The enthalpy of reaction can be used to determine stoichiometrically the heat evolved when a specific amount of reactant reacts.

### Calorimetry (6.5, 6.7)

- Calorimetry is a method of measuring  $\Delta E$  or  $\Delta H$  for a reaction.
- In bomb calorimetry, the reaction is carried out under conditions of constant volume, so  $\Delta E = q_v$ . The temperature change of the calorimeter can therefore be used to calculate  $\Delta E$  for the reaction.
- When a reaction takes place at constant pressure, energy may be released both as heat and as work.
- In coffee-cup calorimetry, a reaction is carried out under atmospheric pressure in a solution, so  $q = \Delta H$ . The temperature change of the solution is then used to calculate  $\Delta H$  for the reaction.

### Calculating $\Delta H_{rxn}$ (6.8, 6.9)

- The enthalpy of reaction ( $\Delta H_{rxn}$ ) can be calculated from known thermochemical data using the following relationships: (a) when a reaction is multiplied by a factor,  $\Delta H_{rxn}$  is multiplied by the same factor; (b) when a reaction is reversed,  $\Delta H_{rxn}$  changes sign; and (c) if a chemical reaction can be expressed as a sum of two or more steps,  $\Delta H_{rxn}$  is the sum of the  $\Delta H$ 's for the individual steps (Hess's law). Together, these relationships can be used to determine the enthalpy change of an unknown reaction from reactions with known enthalpy changes.
- A second method to calculate  $\Delta H_{rxn}$  from known thermochemical data involves using tabulated standard enthalpies of formation for the reactants and products of the reaction. These are usually tabulated for substances in their standard states, and the enthalpy of reaction is called the standard enthalpy of reaction ( $\Delta H_{rxn}^\circ$ ). For any reaction, ( $\Delta H_{rxn}^\circ$ ) is obtained by subtracting the sum of the enthalpies of formation of the reactants multiplied by their stoichiometric coefficients from the sum of the enthalpies of formation of the products multiplied by their stoichiometric coefficients.

### Environmental Problems Associated with Fossil Fuel Use (6.10)

- Fossil fuels are nonrenewable fuels; once they are consumed, they cannot be replaced.
- At current rates of consumption, natural gas and petroleum reserves will be depleted in 50–100 years.
- In addition to their limited supply, the products of the combustion of fossil fuels—directly or indirectly formed—contribute to environmental problems including air pollution, acid rain, and global climate change, which involves an increase in Earth's average temperature caused by CO<sub>2</sub> emission.

## Key Equations and Relationships

### Kinetic Energy (6.2)

$$KE = \frac{1}{2}mv^2$$

### Change in Internal Energy ( $\Delta E$ ) of a Chemical System (6.3)

$$\Delta E = E_{products} - E_{reactants}$$

### Energy Flow between System and Surroundings (6.3)

$$\Delta E_{system} = -\Delta E_{surroundings}$$

### Relationship between Internal Energy ( $\Delta E$ ), Heat ( $q$ ), and Work ( $w$ ) (6.3)

$$\Delta E = q + w$$

Relationship between Heat ( $q$ ), Temperature ( $T$ ), and Heat Capacity ( $C$ ) (6.4)

$$q = C \times \Delta T$$

Relationship between Heat ( $q$ ), Mass ( $m$ ), Temperature ( $T$ ), and Specific Heat Capacity of a Substance ( $C_s$ ) (6.4)

$$q = m \times C_s \times \Delta T$$

Relationship between Work ( $w$ ), Force ( $F$ ), and Distance ( $D$ ) (6.4)

$$w = F \times D$$

Relationship between Work ( $w$ ), Pressure ( $P$ ), and Change in Volume ( $\Delta V$ ) (6.4)

$$w = -P \Delta V$$

Change in Internal Energy ( $\Delta E$ ) of System at Constant Volume (6.5)

$$\Delta E = q_v$$

Heat of a Bomb Calorimeter ( $q_{\text{cal}}$ ) (6.5)

$$q_{\text{cal}} = C_{\text{cal}} \times \Delta T$$

Heat Exchange between a Calorimeter and a Reaction (6.5)

$$q_{\text{cal}} = -q_{\text{rxn}}$$

Relationship between Enthalpy ( $\Delta H$ ), Internal Energy ( $\Delta E$ ), Pressure ( $P$ ), and Volume ( $V$ ) (6.6)

$$\Delta H = \Delta E + P \Delta V$$

$$\Delta H = q_p$$

Relationship between Enthalpy of a Reaction ( $\Delta H_{\text{rxn}}^\circ$ ) and the Heats of Formation ( $\Delta H_f^\circ$ ) (6.9)

$$\Delta H_{\text{rxn}}^\circ = \sum n_p \Delta H_f^\circ (\text{products}) - \sum n_r \Delta H_f^\circ (\text{reactants})$$

## Key Learning Outcomes

### Chapter Objectives

Calculating Internal Energy from Heat and Work (6.3)



### Assessment

Example 6.1 For Practice 6.1 Exercises 41–44

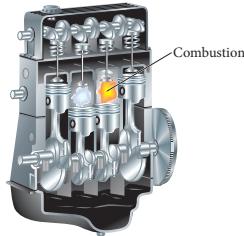
Finding Heat from Temperature Changes (6.4)

Example 6.2 For Practice 6.2 For More Practice 6.2 Exercises 47–50

Determining Quantities in Thermal Energy Transfer (6.4)

Example 6.3 For Practice 6.3 Exercises 65–70

Finding Work from Volume Changes (6.4)



Example 6.4 For Practice 6.4 For More Practice 6.4 Exercises 51, 52

Using Bomb Calorimetry to Calculate  $\Delta E_{\text{rxn}}$  (6.5)

Example 6.5 For Practice 6.5 For More Practice 6.5 Exercises 53, 54

Predicting Endothermic and Exothermic Processes (6.6)



Example 6.6 For Practice 6.6 Exercises 57, 58

Determining Heat from  $\Delta H$  and Stoichiometry (6.6)

Examples 6.7, 6.13 For Practice 6.7, 6.13 For More Practice 6.7 Exercises 59–64

Finding  $\Delta H_{\text{rxn}}$  Using Calorimetry (6.7)

Example 6.8 For Practice 6.8 Exercises 75, 76

Finding  $\Delta H_{\text{rxn}}$  Using Hess's Law (6.8)

Example 6.9 For Practice 6.9 For More Practice 6.9 Exercises 79–82

Finding  $\Delta H_{\text{rxn}}^\circ$  Using Standard Enthalpies of Formation (6.9)

Examples 6.10, 6.11, 6.12 For Practice 6.10, 6.11, 6.12 Exercises 83–92

# EXERCISES

## Review Questions

1. What is thermochemistry? Why is it important?
2. What is energy? What is work? List some examples of each.
3. What is kinetic energy? What is potential energy? List some examples of each.
4. What is the law of conservation of energy? How does it relate to energy exchanges between a thermodynamic system and its surroundings?
5. What is the SI unit of energy? List some other common units of energy.
6. What is the first law of thermodynamics? What are its implications?
7. A friend claims to have constructed a machine that creates electricity but requires no energy input. Explain why you should be suspicious of your friend's claim.
8. What is a state function? List some examples of state functions.
9. What is internal energy? Is internal energy a state function?
10. If energy flows out of a chemical system and into the surroundings, what is the sign of  $\Delta E_{\text{system}}$ ?
11. If the internal energy of the products of a reaction is higher than the internal energy of the reactants, what is the sign of  $\Delta E$  for the reaction? In which direction does energy flow?
12. What is heat? Explain the difference between heat and temperature.
13. How is the change in internal energy of a system related to heat and work?
14. Explain how the sum of heat and work can be a state function, even though heat and work are themselves not state functions.
15. What is heat capacity? Explain the difference between heat capacity and specific heat capacity.
16. Explain how the high specific heat capacity of water can affect the weather in coastal regions.
17. If two objects, A and B, of different temperature come into direct contact, what is the relationship between the heat lost by one object and the heat gained by the other? What is the relationship between the temperature changes of the two objects? (Assume that the two objects do not lose any heat to anything else.)
18. What is pressure-volume work? How is it calculated?
19. What is calorimetry? Explain the difference between a coffee-cup calorimeter and a bomb calorimeter. What is each designed to measure?
20. What is the change in enthalpy ( $\Delta H$ ) for a chemical reaction? How is  $\Delta H$  different from  $\Delta E$ ?
21. Explain the difference between an exothermic and an endothermic reaction. Give the sign of  $\Delta H$  for each type of reaction.
22. From a molecular viewpoint, where does the energy emitted in an exothermic chemical reaction come from? Why does the reaction mixture undergo an increase in temperature even though energy is emitted?
23. From a molecular viewpoint, where does the energy absorbed in an endothermic chemical reaction go? Why does the reaction mixture undergo a decrease in temperature even though energy is absorbed?
24. Is the change in enthalpy for a reaction an extensive property? Explain the relationship between  $\Delta H$  for a reaction and the amounts of reactants and products that undergo reaction.
25. Explain how the value of  $\Delta H$  for a reaction changes upon each operation:
  - a. multiplying the reaction by a factor.
  - b. reversing the reaction.
 Why do these relationships hold?
26. What is Hess's law? Why is it useful?
27. What is a standard state? What is the standard enthalpy change for a reaction?
28. What is the standard enthalpy of formation for a compound? For a pure element in its standard state?
29. How do you calculate  $\Delta H_{\text{rxn}}^{\circ}$  from tabulated standard enthalpies of formation?
30. What are the main sources of the energy consumed in the United States?
31. What are the main environmental problems associated with fossil fuel use?
32. Explain global climate change. What causes global warming? What is the evidence that global warming is occurring?

## Problems by Topic

### Energy Units

33. Convert between energy units:
 

<b>a.</b> 534 kWh to J	<b>b.</b> 215 kJ to Cal	<b>c.</b> 567 Cal to J	<b>d.</b> $2.85 \times 10^3$ J to cal
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34. Convert between energy units:
 

<b>a.</b> 231 cal to kJ	<b>b.</b> $132 \times 10^4$ kJ to kcal	<b>c.</b> $4.99 \times 10^3$ kJ to kWh	<b>d.</b> $2.88 \times 10^4$ J to Cal
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35. Suppose that a person eats 2387 Calories per day. Convert this amount of energy into each unit:
 

<b>a.</b> J	<b>b.</b> kJ	<b>c.</b> kWh
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36. A particular frost-free refrigerator uses about 745 kWh of electrical energy per year. Express this amount of energy in each unit:
 

<b>a.</b> J	<b>b.</b> kJ	<b>c.</b> Cal
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### Internal Energy, Heat, and Work

37. Which statement is true of the internal energy of a system and its surroundings during an energy exchange with a negative  $\Delta E_{\text{sys}}$ ?
  - a. The internal energy of the system increases and the internal energy of the surroundings decreases.
  - b. The internal energy of both the system and the surroundings increases.
  - c. The internal energy of both the system and the surroundings decreases.
  - d. The internal energy of the system decreases and the internal energy of the surroundings increases.
38. During an energy exchange, a chemical system absorbs energy from its surroundings. What is the sign of  $\Delta E_{\text{sys}}$  for this process? Explain.

- 39.** Identify each energy exchange as primarily heat or work and determine whether the sign of  $\Delta E$  is positive or negative for the system.
- Sweat evaporates from skin, cooling the skin. (The evaporating sweat is the system.)
  - A balloon expands against an external pressure. (The contents of the balloon is the system.)
  - An aqueous chemical reaction mixture is warmed with an external flame. (The reaction mixture is the system.)
- 40.** Identify each energy exchange as primarily heat or work and determine whether the sign of  $\Delta E$  is positive or negative for the system.
- A rolling billiard ball collides with another billiard ball. The first billiard ball (defined as the system) stops rolling after the collision.
  - A book is dropped to the floor. (The book is the system.)
  - A father pushes his daughter on a swing. (The daughter and the swing are the system.)
- 41.** A system releases 622 kJ of heat and does 105 kJ of work on the surroundings. What is the change in internal energy of the system?
- 42.** A system absorbs 196 kJ of heat and the surroundings do 117 kJ of work on the system. What is the change in internal energy of the system?
- 43.** The gas in a piston (defined as the system) warms and absorbs 655 J of heat. The expansion performs 344 J of work on the surroundings. What is the change in internal energy for the system?
- 44.** The air in an inflated balloon (defined as the system) warms over a toaster and absorbs 115 J of heat. As it expands, it does 77 kJ of work. What is the change in internal energy for the system?

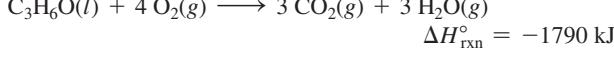
### Heat, Heat Capacity, and Work

- 45.** We pack two identical coolers for a picnic, placing twenty-four 12-ounce soft drinks and 5 pounds of ice in each. However, the drinks that we put into cooler A were refrigerated for several hours before they were packed in the cooler, while the drinks that we put into cooler B were at room temperature. When we open the two coolers 3 hours later, most of the ice in cooler A is still present, while nearly all of the ice in cooler B has melted. Explain this difference.
- 46.** A kilogram of aluminum metal and a kilogram of water are each warmed to 75 °C and placed in two identical insulated containers. One hour later, the two containers are opened and the temperature of each substance is measured. The aluminum has cooled to 35 °C while the water has cooled only to 66 °C. Explain this difference.
- 47.** How much heat is required to warm 1.50 L of water from 25.0 °C to 100.0 °C? (Assume a density of 1.0 g/mL for the water.)
- 48.** How much heat is required to warm 1.50 kg of sand from 25.0 °C to 100.0 °C?
- 49.** Suppose that 25 g of each substance is initially at 27.0 °C. What is the final temperature of each substance upon absorbing 2.35 kJ of heat?
- |                    |                  |
|--------------------|------------------|
| <b>a.</b> gold     | <b>b.</b> silver |
| <b>c.</b> aluminum | <b>d.</b> water  |
- 50.** An unknown mass of each substance, initially at 23.0 °C, absorbs  $1.95 \times 10^3$  J of heat. The final temperature is recorded as indicated. Find the mass of each substance.
- Pyrex glass ( $T_f = 55.4$  °C)
  - sand ( $T_f = 62.1$  °C)
  - ethanol ( $T_f = 44.2$  °C)
  - water ( $T_f = 32.4$  °C)
- 51.** How much work (in J) is required to expand the volume of a pump from 0.0 L to 2.5 L against an external pressure of 1.1 atm?

- 52.** The average human lung expands by about 0.50 L during each breath. If this expansion occurs against an external pressure of 1.0 atm, how much work (in J) is done during the expansion?
- 53.** The air within a piston equipped with a cylinder absorbs 565 J of heat and expands from an initial volume of 0.10 L to a final volume of 0.85 L against an external pressure of 1.0 atm. What is the change in internal energy of the air within the piston?
- 54.** A gas is compressed from an initial volume of 5.55 L to a final volume of 1.22 L by an external pressure of 1.00 atm. During the compression the gas releases 124 J of heat. What is the change in internal energy of the gas?

### Enthalpy and Thermochemical Stoichiometry

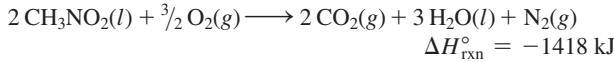
- 55.** When 1 mol of a fuel burns at constant pressure, it produces 3452 kJ of heat and does 11 kJ of work. What are  $\Delta E$  and  $\Delta H$  for the combustion of the fuel?
- 56.** The change in internal energy for the combustion of 1.0 mol of octane at a pressure of 1.0 atm is 5084.3 kJ. If the change in enthalpy is 5074.1 kJ, how much work is done during the combustion?
- 57.** Determine whether each process is exothermic or endothermic and indicate the sign of  $\Delta H$ .
- natural gas burning on a stove
  - isopropyl alcohol evaporating from skin
  - water condensing from steam
- 58.** Determine whether each process is exothermic or endothermic and indicate the sign of  $\Delta H$ .
- dry ice evaporating
  - a sparkler burning
  - the reaction that occurs in a chemical cold pack used to ice athletic injuries
- 59.** Consider the thermochemical equation for the combustion of acetone ( $C_3H_6O$ ), the main ingredient in nail polish remover.



If a bottle of nail polish remover contains 177 mL of acetone, how much heat is released by its complete combustion? The density of acetone is 0.788 g/mL.

- 60.** What mass of natural gas ( $CH_4$ ) must burn to emit 267 kJ of heat?
- $$CH_4(g) + 2 O_2(g) \longrightarrow CO_2(g) + 2 H_2O(g) \quad \Delta H_{rxn}^\circ = -802.3 \text{ kJ}$$

- 61.** Nitromethane ( $CH_3NO_2$ ) burns in air to produce significant amounts of heat.



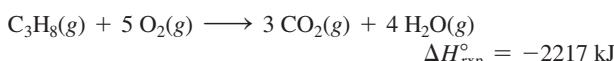
How much heat is produced by the complete reaction of 5.56 kg of nitromethane?

- 62.** Titanium reacts with iodine to form titanium(III) iodide, emitting heat.



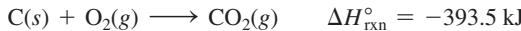
Determine the masses of titanium and iodine that react if  $1.55 \times 10^3$  kJ of heat is emitted by the reaction.

- 63.** The propane fuel ( $C_3H_8$ ) used in gas barbeques burns according to the thermochemical equation:



If a pork roast must absorb  $1.6 \times 10^3$  kJ to fully cook, and if only 10% of the heat produced by the barbecue is actually absorbed by the roast, what mass of CO<sub>2</sub> is emitted into the atmosphere during the grilling of the pork roast?

64. Charcoal is primarily carbon. Determine the mass of CO<sub>2</sub> produced by burning enough carbon (in the form of charcoal) to produce  $5.00 \times 10^2$  kJ of heat.

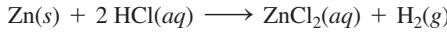


### Thermal Energy Transfer

65. A silver block, initially at 58.5 °C, is submerged into 100.0 g of water at 24.8 °C, in an insulated container. The final temperature of the mixture upon reaching thermal equilibrium is 26.2 °C. What is the mass of the silver block?
66. A 32.5 g iron rod, initially at 22.7 °C, is submerged into an unknown mass of water at 63.2 °C, in an insulated container. The final temperature of the mixture upon reaching thermal equilibrium is 59.5 °C. What is the mass of the water?
67. A 31.1 g wafer of pure gold, initially at 69.3 °C, is submerged into 64.2 g of water at 27.8 °C in an insulated container. What is the final temperature of both substances at thermal equilibrium?
68. A 2.85 g lead weight, initially at 10.3 °C, is submerged in 7.55 g of water at 52.3 °C in an insulated container. What is the final temperature of both substances at thermal equilibrium?
69. Two substances, A and B, initially at different temperatures, come into contact and reach thermal equilibrium. The mass of substance A is 6.15 g and its initial temperature is 20.5 °C. The mass of substance B is 25.2 g and its initial temperature is 52.7 °C. The final temperature of both substances at thermal equilibrium is 46.7 °C. If the specific heat capacity of substance B is 1.17 J/g · °C, what is the specific heat capacity of substance A?
70. A 2.74 g sample of a substance suspected of being pure gold is warmed to 72.1 °C and submerged into 15.2 g of water initially at 24.7 °C. The final temperature of the mixture is 26.3 °C. What is the heat capacity of the unknown substance? Could the substance be pure gold?

### Calorimetry

71. Exactly 1.5 g of a fuel burns under conditions of constant pressure and then again under conditions of constant volume. In measurement A the reaction produces 25.9 kJ of heat, and in measurement B the reaction produces 23.3 kJ of heat. Which measurement (A or B) corresponds to conditions of constant pressure? Which one corresponds to conditions of constant volume? Explain.
72. In order to obtain the largest possible amount of heat from a chemical reaction in which there is a large increase in the number of moles of gas, should you carry out the reaction under conditions of constant volume or constant pressure? Explain.
73. When 0.514 g of biphenyl (C<sub>12</sub>H<sub>10</sub>) undergoes combustion in a bomb calorimeter, the temperature rises from 25.8 °C to 29.4 °C. Find  $\Delta E_{\text{rxn}}$  for the combustion of biphenyl in kJ/mol biphenyl. The heat capacity of the bomb calorimeter, determined in a separate experiment, is 5.86 kJ/°C.
74. Mothballs are composed primarily of the hydrocarbon naphthalene (C<sub>10</sub>H<sub>8</sub>). When 1.025 g of naphthalene burns in a bomb calorimeter, the temperature rises from 24.25 °C to 32.33 °C. Find  $\Delta E_{\text{rxn}}$  for the combustion of naphthalene. The heat capacity of the calorimeter, determined in a separate experiment, is 5.11 kJ/°C.
75. Zinc metal reacts with hydrochloric acid according to the balanced equation:



When 0.103 g of Zn(s) is combined with enough HCl to make 50.0 mL of solution in a coffee-cup calorimeter, all of the zinc reacts, raising the temperature of the solution from 22.5 °C to 23.7 °C. Find  $\Delta H_{\text{rxn}}$  for this reaction as written. (Use 1.0 g/mL for the density of the solution and 4.18 J/g · °C as the specific heat capacity.)

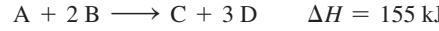
76. Instant cold packs used to ice athletic injuries on the field contain ammonium nitrate and water separated by a thin plastic divider. When the divider is broken, the ammonium nitrate dissolves according to the endothermic reaction:



In order to measure the enthalpy change for this reaction, 1.25 g of NH<sub>4</sub>NO<sub>3</sub> is dissolved in enough water to make 25.0 mL of solution. The initial temperature is 25.8 °C and the final temperature (after the solid dissolves) is 21.9 °C. Calculate the change in enthalpy for the reaction in kJ. (Use 1.0 g/mL as the density of the solution and 4.18 J/g · °C as the specific heat capacity.)

### Quantitative Relationships Involving $\Delta H$ and Hess's Law

77. For each generic reaction, determine the value of  $\Delta H_2$  in terms of  $\Delta H_1$ .
- a. A + B → 2 C       $\Delta H_1$   
2 C → A + B       $\Delta H_2 = ?$
  - b. A +  $\frac{1}{2}$ B → C       $\Delta H_1$   
2 A + B → 2 C       $\Delta H_2 = ?$
  - c. A → B + 2 C       $\Delta H_1$   
 $\frac{1}{2}$ B + C →  $\frac{1}{2}$ A       $\Delta H_2 = ?$
78. Consider the generic reaction:



Determine the value of  $\Delta H$  for each related reaction:

- a. 3 A + 6 B → 3 C + 9 D
- b. C + 3 D → A + 2 B
- c.  $\frac{1}{2}$ C +  $\frac{3}{2}$ D →  $\frac{1}{2}$ A + B

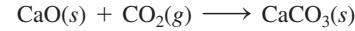
79. Calculate  $\Delta H_{\text{rxn}}$  for the reaction:



Use the following reactions and given  $\Delta H$ 's.

- |   |                                |
|---|--------------------------------|
| 2 Fe(s) + $\frac{3}{2}$ O <sub>2</sub> (g) → Fe <sub>2</sub> O <sub>3</sub> (s) | $\Delta H = -824.2 \text{ kJ}$ |
| CO(g) + $\frac{1}{2}$ O <sub>2</sub> (g) → CO <sub>2</sub> (g)                  | $\Delta H = -282.7 \text{ kJ}$ |

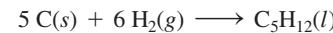
80. Calculate  $\Delta H_{\text{rxn}}$  for the reaction:



Use the following reactions and given  $\Delta H$ 's.

- |  |                                 |
|--|---------------------------------|
| Ca(s) + CO <sub>2</sub> (g) + $\frac{1}{2}$ O <sub>2</sub> (g) → CaCO <sub>3</sub> (s) | $\Delta H = -812.8 \text{ kJ}$  |
| 2 Ca(s) + O <sub>2</sub> (g) → 2 CaO(s)  | $\Delta H = -1269.8 \text{ kJ}$ |

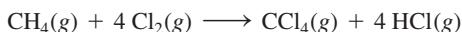
81. Calculate  $\Delta H_{\text{rxn}}$  for the reaction:



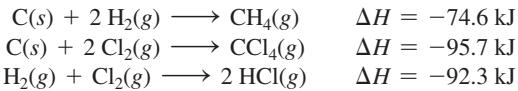
Use the following reactions and given  $\Delta H$ 's.

- |   |                                 |
|---|---------------------------------|
| C <sub>5</sub> H <sub>12</sub> (l) + 8 O <sub>2</sub> (g) → 5 CO <sub>2</sub> (g) + 6 H <sub>2</sub> O(g) | $\Delta H = -3244.8 \text{ kJ}$ |
| C(s) + O <sub>2</sub> (g) → CO <sub>2</sub> (g)   | $\Delta H = -393.5 \text{ kJ}$  |
| 2 H <sub>2</sub> (g) + O <sub>2</sub> (g) → 2 H <sub>2</sub> O(g)   | $\Delta H = -483.5 \text{ kJ}$  |

82. Calculate  $\Delta H_{rxn}$  for the reaction:



Use the following reactions and given  $\Delta H^\circ$ 's.



### Enthalpies of Formation and $\Delta H$

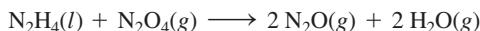
83. Write an equation for the formation of each compound from its elements in their standard states, and find  $\Delta H_f^\circ$  for each from Appendix IIB.

a.  $\text{NH}_3(g)$       b.  $\text{CO}_2(g)$       c.  $\text{Fe}_2\text{O}_3(s)$       d.  $\text{CH}_4(g)$

84. Write an equation for the formation of each compound from its elements in their standard states, and find  $\Delta H_{rxn}^\circ$  for each from Appendix IIB.

a.  $\text{NO}_2(g)$       b.  $\text{MgCO}_3(s)$   
c.  $\text{C}_2\text{H}_4(g)$       d.  $\text{CH}_3\text{OH}(l)$

85. Hydrazine ( $\text{N}_2\text{H}_4$ ) is a fuel used by some spacecraft. It is normally oxidized by  $\text{N}_2\text{O}_4$  according to the equation:



Calculate  $\Delta H_{rxn}^\circ$  for this reaction using standard enthalpies of formation.

86. Pentane ( $\text{C}_5\text{H}_{12}$ ) is a component of gasoline that burns according to the following balanced equation:



Calculate  $\Delta H_{rxn}^\circ$  for this reaction using standard enthalpies of formation. (The standard enthalpy of formation of liquid pentane is  $-146.8 \text{ kJ/mol}$ .)

87. Use standard enthalpies of formation to calculate  $\Delta H_{rxn}^\circ$  for each reaction:

a.  $\text{C}_2\text{H}_4(g) + \text{H}_2(g) \longrightarrow \text{C}_2\text{H}_6(g)$   
b.  $\text{CO}(g) + \text{H}_2\text{O}(g) \longrightarrow \text{H}_2(g) + \text{CO}_2(g)$   
c.  $3 \text{NO}_2(g) + \text{H}_2\text{O}(l) \longrightarrow 2 \text{HNO}_3(aq) + \text{NO}(g)$   
d.  $\text{Cr}_2\text{O}_3(s) + 3 \text{CO}(g) \longrightarrow 2 \text{Cr}(s) + 3 \text{CO}_2(g)$

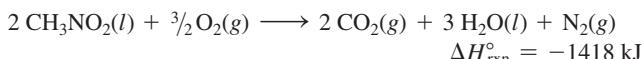
88. Use standard enthalpies of formation to calculate  $\Delta H_{rxn}^\circ$  for each reaction:

a.  $2 \text{H}_2\text{S}(g) + 3 \text{O}_2(g) \longrightarrow 2 \text{H}_2\text{O}(l) + 2 \text{SO}_2(g)$   
b.  $\text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \longrightarrow \text{SO}_3(g)$   
c.  $\text{C}(s) + \text{H}_2\text{O}(g) \longrightarrow \text{CO}(g) + \text{H}_2(g)$   
d.  $\text{N}_2\text{O}_4(g) + 4 \text{H}_2(g) \longrightarrow \text{N}_2(g) + 4 \text{H}_2\text{O}(g)$

89. During photosynthesis, plants use energy from sunlight to form glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) and oxygen from carbon dioxide and water. Write a balanced equation for photosynthesis and calculate  $\Delta H_{rxn}^\circ$ .

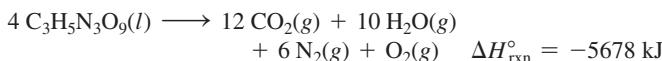
90. Ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) can be made from the fermentation of crops and has been used as a fuel additive to gasoline. Write a balanced equation for the combustion of ethanol and calculate  $\Delta H_{rxn}^\circ$ .

91. Top fuel dragsters and funny cars burn nitromethane as fuel according to the balanced combustion equation:



The enthalpy of combustion for nitromethane is  $-709.2 \text{ kJ/mol}$ . Calculate the standard enthalpy of formation ( $\Delta H_f^\circ$ ) for nitromethane.

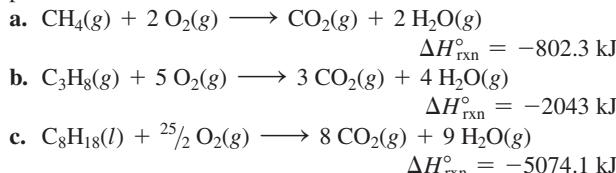
92. The explosive nitroglycerin ( $\text{C}_3\text{H}_5\text{N}_3\text{O}_9$ ) decomposes rapidly upon ignition or sudden impact according to the balanced equation:



Calculate the standard enthalpy of formation ( $\Delta H_f^\circ$ ) for nitroglycerin.

### Energy Use and the Environment

93. Determine the mass of  $\text{CO}_2$  produced by burning enough of each of the following fuels to produce  $1.00 \times 10^2 \text{ kJ}$  of heat. Which fuel contributes least to global warming per kJ of heat produced?



94. Methanol ( $\text{CH}_3\text{OH}$ ) has been suggested as a fuel to replace gasoline. Write a balanced equation for the combustion of methanol, find  $\Delta H_{rxn}^\circ$ , and determine the mass of carbon dioxide emitted per kJ of heat produced. Use the information from the previous exercise to calculate the same quantity for octane,  $\text{C}_8\text{H}_{18}$ . How does methanol compare to octane with respect to global warming?

95. The citizens of the world burn the fossil fuel equivalent of  $7 \times 10^{12} \text{ kg}$  of petroleum per year. Assume that all of this petroleum is in the form of octane ( $\text{C}_8\text{H}_{18}$ ) and calculate how much  $\text{CO}_2$  (in kg) is produced by world fossil fuel combustion per year. (Hint: Begin by writing a balanced equation for the combustion of octane.) If the atmosphere currently contains approximately  $3 \times 10^{15} \text{ kg}$  of  $\text{CO}_2$ , how long will it take for the world's fossil fuel combustion to double the amount of atmospheric carbon dioxide?

96. In a sunny location, sunlight has a power density of about  $1 \text{ kW/m}^2$ . Photovoltaic solar cells can convert this power into electricity with 15% efficiency. If a typical home uses 385 kWh of electricity per month, how many square meters of solar cells would be required to meet its energy requirements? Assume that electricity can be generated from the sunlight for 8 hours per day.



▲ What area of solar cells do you need to power a home?

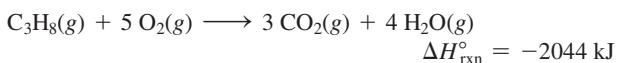
## Cumulative Problems

- 97.** The kinetic energy of a rolling billiard ball is given by  $KE = \frac{1}{2}mv^2$ . Suppose a 0.17 kg billiard ball is rolling down a pool table with an initial speed of 4.5 m/s. As it travels, it loses some of its energy as heat. The ball slows down to 3.8 m/s and then collides head-on with a second billiard ball of equal mass. The first billiard ball completely stops and the second one rolls away with a velocity of 3.8 m/s. Assume the first billiard ball is the system and calculate  $w$ ,  $q$ , and  $\Delta E$  for the process.
- 98.** A 100 W lightbulb is placed in a cylinder equipped with a moveable piston. The lightbulb is turned on for 0.015 hour, and the assembly expands from an initial volume of 0.85 L to a final volume of 5.88 L against an external pressure of 1.0 atm. Use the wattage of the lightbulb and the time it is on to calculate  $\Delta E$  in joules (assume that the cylinder and lightbulb assembly is the system and assume two significant figures). Calculate  $w$  and  $q$ .
- 99.** Evaporating sweat cools the body because evaporation is an endothermic process:



Estimate the mass of water that must evaporate from the skin to cool the body by 0.50 °C. Assume a body mass of 95 kg and assume that the specific heat capacity of the body is 4.0 J/g · °C.

- 100.** LP gas burns according to the exothermic reaction:



What mass of LP gas is necessary to heat 1.5 L of water from room temperature (25.0 °C) to boiling (100.0 °C)? Assume that during heating, 15% of the heat emitted by the LP gas combustion goes to heat the water. The rest is lost as heat to the surroundings.

- 101.** Use standard enthalpies of formation to calculate the standard change in enthalpy for the melting of ice. (The  $\Delta H_f^{\circ}$  for  $\text{H}_2\text{O}(s)$  is -291.8 kJ/mol.) Use this value to calculate the mass of ice required to cool 355 mL of a beverage from room temperature (25.0 °C) to 0.0 °C. Assume that the specific heat capacity and density of the beverage are the same as those of water.

- 102.** Dry ice is solid carbon dioxide. Instead of melting, solid carbon dioxide sublimes according to the equation:



When carbon dioxide sublimes, the gaseous  $\text{CO}_2$  is cold enough to cause water vapor in the air to condense, forming fog.

When dry ice is added to warm water, heat from the water causes the dry ice to sublime more quickly. The evaporating carbon dioxide produces a dense fog often used to create special effects. In a simple dry ice fog machine, dry ice is added to warm water in a Styrofoam cooler. The dry ice produces fog until it evaporates away, or until the water gets too cold to sublime the dry ice quickly enough. Suppose that a small Styrofoam cooler holds 15.0 liters of water heated to 85 °C. Use standard enthalpies of formation to calculate the change in enthalpy for dry ice sublimation, and calculate the mass of dry ice that should be added to the water so that the dry ice completely sublimes away when the water reaches 25 °C. Assume no heat loss to the surroundings. [The  $\Delta H_f^{\circ}$  for  $\text{CO}_2(s)$  is -427.4 kJ/mol.]

- 103.** A 25.5 g aluminum block is warmed to 65.4 °C and plunged into an insulated beaker containing 55.2 g water initially at 22.2 °C. The aluminum and the water are allowed to come to thermal equilibrium. Assuming that no heat is lost, what is the final temperature of the water and aluminum?
- 104.** If 50.0 mL of ethanol (density = 0.789 g/mL) initially at 7.0 °C is mixed with 50.0 mL of water (density = 1.0 g/mL) initially at 28.4 °C in an insulated beaker, and assuming that no heat is lost, what is the final temperature of the mixture?
- 105.** Palmitic acid ( $\text{C}_{16}\text{H}_{32}\text{O}_2$ ) is a dietary fat found in beef and butter. The caloric content of palmitic acid is typical of fats in general. Write a balanced equation for the complete combustion of palmitic acid and calculate the standard enthalpy of combustion. What is the caloric content of palmitic acid in Cal/g? Do the same calculation for table sugar (sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ). Which dietary substance (sugar or fat) contains more Calories per gram? The standard enthalpy of formation of palmitic acid is -208 kJ/mol and that of sucrose is -2226.1 kJ/mol. [Use  $\text{H}_2\text{O}(l)$  in the balanced chemical equations because the metabolism of these compounds produces liquid water.]
- 106.** Hydrogen and methanol have both been proposed as alternatives to hydrocarbon fuels. Write balanced reactions for the complete combustion of hydrogen and methanol and use standard enthalpies of formation to calculate the amount of heat released per kilogram of the fuel. Which fuel contains the most energy in the least mass? How does the energy of these fuels compare to that of octane ( $\text{C}_8\text{H}_{18}$ )?
- 107.** Derive a relationship between  $\Delta H$  and  $\Delta E$  for a process in which the temperature of a fixed amount of an ideal gas changes.
- 108.** Under certain nonstandard conditions, oxidation by  $\text{O}_2(g)$  of 1 mol of  $\text{SO}_2(g)$  to  $\text{SO}_3(g)$  absorbs 89.5 kJ. The enthalpy of formation of  $\text{SO}_3(g)$  is -204.2 kJ under these conditions. Find the enthalpy of formation of  $\text{SO}_2(g)$ .
- 109.** One tablespoon of peanut butter has a mass of 16 g. It is combusted in a calorimeter whose heat capacity is 120.0 kJ/°C. The temperature of the calorimeter rises from 22.2 °C to 25.4 °C. Find the food caloric content of peanut butter.
- 110.** A mixture of 2.0 mol of  $\text{H}_2(g)$  and 1.0 mol of  $\text{O}_2(g)$  is placed in a sealed evacuated container made of a perfect insulating material at 25 °C. The mixture is ignited with a spark and reacts to form liquid water. Determine the temperature of the water.
- 111.** A 20.0 L volume of an ideal gas in a cylinder with a piston is at a pressure of 3.0 atm. Enough weight is suddenly removed from the piston to lower the external pressure to 1.5 atm. The gas then expands at constant temperature until its pressure is 1.5 atm. Find  $\Delta E$ ,  $\Delta H$ ,  $q$ , and  $w$  for this change in state.

- 112.** When 10.00 g of phosphorus is burned in  $O_2(g)$  to form  $P_4O_{10}(s)$ , enough heat is generated to raise the temperature of 2950 g of water from 18.0 °C to 38.0 °C. Calculate the enthalpy of formation of  $P_4O_{10}(s)$  under these conditions.
- 113.** The  $\Delta H$  for the oxidation of S in the gas phase to  $SO_3$  is –204 kJ/mol and for the oxidation of  $SO_2$  to  $SO_3$  is 89.5 kJ/mol. Find the enthalpy of formation of  $SO_2$  under these conditions.
- 114.** The  $\Delta H_f^\circ$  of  $TiI_3(s)$  is –328 kJ/mol and the  $\Delta H^\circ$  for the reaction  $2\ Ti(s) + 3\ I_2(g) \longrightarrow 2\ TiI_3(s)$  is –839 kJ. Calculate the  $\Delta H$  of sublimation of  $I_2(s)$ , which is a solid at 25 °C.
- 115.** A gaseous fuel mixture contains 25.3% methane ( $CH_4$ ), 38.2% ethane ( $C_2H_6$ ), and the rest propane ( $C_3H_8$ ) by volume. When the fuel mixture contained in a 1.55 L tank, stored at 755 mmHg and 298 K, undergoes complete combustion, how much heat is emitted? (Assume that the water produced by the combustion is in the gaseous state.)
- 116.** A gaseous fuel mixture stored at 745 mmHg and 298 K contains only methane ( $CH_4$ ) and propane ( $C_3H_8$ ). When 11.7 L of this fuel mixture is burned, it produces 769 kJ of heat. What is the mole fraction of methane in the mixture? (Assume that the water produced by the combustion is in the gaseous state.)
- 117.** A copper cube measuring 1.55 cm on edge and an aluminum cube measuring 1.62 cm on edge are both heated to 55.0 °C and submerged in 100.0 mL of water at 22.2 °C. What is the final temperature of the water when equilibrium is reached? (Assume a density of 0.998 g/mL for water.)
- 118.** A pure gold ring and a pure silver ring have a total mass of 14.9 g. The two rings are heated to 62.0 °C and dropped into 15.0 mL of water at 23.5 °C. When equilibrium is reached, the temperature of the water is 25.0 °C. What is the mass of each ring? (Assume a density of 0.998 g/mL for water.)

## Challenge Problems

- 119.** A typical frostless refrigerator uses 655 kWh of energy per year in the form of electricity. Suppose that all of this electricity is generated at a power plant that burns coal containing 3.2% sulfur by mass and that all of the sulfur is emitted as  $SO_2$  when the coal is burned. If all of the  $SO_2$  goes on to react with rainwater to form  $H_2SO_4$ , what mass of  $H_2SO_4$  does the annual operation of the refrigerator produce? (Hint: Assume that the remaining percentage of the coal is carbon and begin by calculating  $\Delta H_{rxn}^\circ$  for the combustion of carbon.)
- 120.** A large sport utility vehicle has a mass of  $2.5 \times 10^3$  kg. Calculate the mass of  $CO_2$  emitted into the atmosphere upon accelerating the SUV from 0.0 mph to 65.0 mph. Assume that the required energy comes from the combustion of octane with 30% efficiency. (Hint: Use  $KE = \frac{1}{2}mv^2$  to calculate the kinetic energy required for the acceleration.)
- 121.** Combustion of natural gas (primarily methane) occurs in most household heaters. The heat given off in this reaction is used to raise the temperature of the air in the house. Assuming that all the energy given off in the reaction goes to heating up only the air in the house, determine the mass of methane required to heat the air in a house by 10.0 °C. Assume that the house dimensions are 30.0 m × 30.0 m × 3.0 m, specific heat capacity of air is 30 J/K · mol, and 1.00 mol of air occupies 22.4 L for all temperatures concerned.
- 122.** When backpacking in the wilderness, hikers often boil water to sterilize it for drinking. Suppose that you are planning a backpacking trip and will need to boil 35 L of water for your group. What volume of fuel should you bring? Assume that the fuel has an average formula of  $C_7H_{16}$ , 15% of the heat generated from combustion goes to heat the water (the rest is lost to the surroundings), the density of the fuel is 0.78 g/mL, the initial temperature of the water is 25.0 °C, and the standard enthalpy of formation of  $C_7H_{16}$  is –224.4 kJ/mol.
- 123.** An ice cube of mass 9.0 g is added to a cup of coffee. The coffee's initial temperature is 90.0 °C and the cup contains 120.0 g of liquid. Assume the specific heat capacity of the coffee is the same as that of water. The heat of fusion of ice (the heat associated with ice melting) is 6.0 kJ/mol. Find the temperature of the coffee after the ice melts.
- 124.** Find  $\Delta H$ ,  $\Delta E$ ,  $q$ , and  $w$  for the freezing of water at –10.0 °C. The specific heat capacity of ice is 2.04 J/g · °C and its heat of fusion (the quantity of heat associated with melting) is –332 J/g.
- 125.** Starting from the relationship between temperature and kinetic energy for an ideal gas, find the value of the molar heat capacity of an ideal gas when its temperature is changed at constant volume. Find its molar heat capacity when its temperature is changed at constant pressure.
- 126.** An amount of an ideal gas expands from 12.0 L to 24.0 L at a constant pressure of 1.0 atm. Then the gas is cooled at a constant volume of 24.0 L back to its original temperature. Then it contracts back to its original volume. Find the total heat flow for the entire process.
- 127.** The heat of vaporization of water at 373 K is 40.7 kJ/mol. Find  $q$ ,  $w$ ,  $\Delta E$ , and  $\Delta H$  for the evaporation of 454 g of water at this temperature at 1 atm.
- 128.** Find  $\Delta E$ ,  $\Delta H$ ,  $q$ , and  $w$  for the change in state of 1.0 mol  $H_2O(l)$  at 80 °C to  $H_2O(g)$  at 110 °C. The heat capacity of  $H_2O(l) = 75.3\text{ J/mol K}$ , heat capacity of  $H_2O(g) = 25.0\text{ J/mol K}$ , and the heat of vaporization of  $H_2O$  is  $40.7 \times 10^3\text{ J/mol}$  at 100 °C.
- 129.** The heat of combustion of liquid octane ( $C_8H_{18}$ ) to carbon dioxide and liquid water at 298 K is –1303 kJ/mol. Find  $\Delta E$  for this reaction.
- 130.** Find  $\Delta H$  for the combustion of ethanol ( $C_2H_6O$ ) to carbon dioxide and liquid water from the following data. The heat capacity of the bomb calorimeter is 34.65 kJ/K and the combustion of 1.765 g of ethanol raises the temperature of the calorimeter from 294.33 K to 295.84 K.

## Conceptual Problems

- 131.** Which statement is true of the internal energy of the system and its surroundings following a process in which  $\Delta E_{\text{sys}} = +65 \text{ kJ}$ ? Explain.
- The system and the surroundings both lose 65 kJ of energy.
  - The system and the surroundings both gain 65 kJ of energy.
  - The system loses 65 kJ of energy and the surroundings gain 65 kJ of energy.
  - The system gains 65 kJ of energy and the surroundings lose 65 kJ of energy.
- 132.** The internal energy of an ideal gas depends only on its temperature. Which statement is true of an isothermal (constant-temperature) expansion of an ideal gas against a constant external pressure? Explain.
- $\Delta E$  is positive
  - $w$  is positive
  - $q$  is positive
  - $\Delta E$  is negative
- 133.** Which expression describes the heat evolved in a chemical reaction when the reaction is carried out at constant pressure? Explain.
- $\Delta E - w$
  - $\Delta E$
  - $\Delta E - q$
- 134.** Two identical refrigerators are plugged in for the first time. Refrigerator A is empty (except for air) and refrigerator B is filled with jugs of water. The compressors of both refrigerators immediately turn on and begin cooling the interiors of the refrigerators. After 2 hours, the compressor of refrigerator A turns off while the compressor of refrigerator B continues to run. The next day, the compressor of refrigerator A can be heard turning on and off every few minutes, while the compressor of refrigerator B turns off and on every hour or so (and stays on longer each time). Explain these observations.
- 135.** A 1 kg cylinder of aluminum and 1 kg jug of water, both at room temperature, are put into a refrigerator. After 1 hour, the temperature of each object is measured. One of the objects is much cooler than the other. Which one is cooler and why?
- 136.** Two substances A and B, initially at different temperatures, are thermally isolated from their surroundings and allowed to come into thermal contact. The mass of substance A is twice the mass of substance B, but the specific heat capacity of substance B is four times the specific heat capacity of substance A. Which substance will undergo a larger change in temperature?
- 137.** When 1 mol of a gas burns at constant pressure, it produces 2418 J of heat and does 5 J of work. Determine  $\Delta E$ ,  $\Delta H$ ,  $q$ , and  $w$  for the process.
- 138.** In an exothermic reaction, the reactants lose energy and the reaction feels hot to the touch. Explain why the reaction feels hot even though the reactants are losing energy. Where does the energy come from?
- 139.** Which statement is true of a reaction in which  $\Delta V$  is positive? Explain.
- $\Delta H = \Delta E$
  - $\Delta H > \Delta E$
  - $\Delta H < \Delta E$

## Answers to Conceptual Connections

### System and Surroundings

**6.1** The correct answer is (a). When  $\Delta E_{\text{sys}}$  is negative, energy flows out of the system and into the surroundings. The energy increase in the surroundings must exactly match the decrease in the system.

### Heat and Work

**6.2** (a) heat, sign is positive (b) work, sign is positive (c) heat, sign is negative

### The Heat Capacity of Water

**6.3** Bring the water; it has the higher heat capacity and will therefore release more heat as it cools.

### Thermal Energy Transfer

**6.4** (c) The specific heat capacity of substance B is twice that of A, but since the mass of B is half that of A, the quantity  $m \times C_s$  will be identical for both substances so that the final temperature is exactly midway between the two initial temperatures.

### The Difference between $\Delta H$ and $\Delta E$

**6.5**  $\Delta H$  represents only the heat exchanged; therefore,  $\Delta H = -2658 \text{ kJ}$ .  $\Delta E$  represents the heat *and work* exchanged; therefore,  $\Delta E = -2661 \text{ kJ}$ . The signs of both  $\Delta H$  and  $\Delta E$

are negative because heat and work are flowing out of the system and into the surroundings. Notice that the values of  $\Delta H$  and  $\Delta E$  are similar in magnitude, as is the case in many chemical reactions.

### Exothermic and Endothermic Reactions

**6.6** An endothermic reaction feels cold to the touch because the reaction (acting here as the system) absorbs heat from the surroundings. When you touch the vessel in which the reaction occurs, you, being part of the surroundings, lose heat to the system (the reaction), which makes you feel cold. The heat absorbed by the reaction (from your body, in this case) does not increase its temperature, but rather becomes potential energy stored in chemical bonds.

### Constant-Pressure versus Constant-Volume Calorimetry

**6.7** The value of  $q_{\text{rxn}}$  with the greater magnitude ( $-12.5 \text{ kJ}$ ) must have come from the bomb calorimeter. Recall that  $\Delta E_{\text{rxn}} = q_{\text{rxn}} + w_{\text{rxn}}$ . In a bomb calorimeter, the energy change that occurs in the course of the reaction all takes the form of heat ( $q$ ). In a coffee-cup calorimeter, the amount of energy released as heat may be smaller because some of the energy may be used to do work ( $w$ ).

# 7

# The Quantum-Mechanical Model of the Atom

*Anyone who is not shocked by quantum mechanics has not understood it.*

—Niels Bohr (1885–1962)

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**T**HE EARLY PART OF THE TWENTIETH century brought changes that revolutionized how we think about physical reality, especially in the atomic realm. Before that time, all descriptions of the behavior of matter had been deterministic—the present set of conditions completely determining the future. Quantum mechanics changed that. This new theory suggested that for subatomic particles—electrons, neutrons, and protons—the present does NOT completely determine the future. For example, if you shoot one electron down a path and measure where it lands, a second electron shot down the same path under the same conditions will most likely land in a different place! Quantum-mechanical theory was developed by several unusually gifted scientists including Albert Einstein, Niels Bohr, Louis de Broglie, Max Planck, Werner Heisenberg, P. A. M. Dirac, and Erwin Schrödinger. These scientists did not necessarily feel comfortable with their own theory. Bohr said, “Anyone who is not shocked by quantum mechanics has not understood it.” Schrödinger wrote, “I don’t like it, and I’m sorry I ever had anything to do with it.” Albert Einstein disbelieved the very theory he helped create, stating, “God does not play dice with the universe.” In fact, Einstein attempted to disprove quantum mechanics—without success—until he died. But quantum mechanics is able to account for fundamental observations, including the very stability of atoms, which could not be understood within the framework of classical physics. Today, quantum mechanics forms the foundation of chemistry—explaining the periodic table and the behavior of the elements in chemical bonding—as well as providing the practical basis for lasers, computers, and countless other applications.



## 7.1 Schrödinger's Cat

Atoms and the particles that compose them are unimaginably small. Electrons have a mass of less than a trillionth of a trillionth of a gram, and a size so small that it is immeasurable. A single speck of dust contains more electrons than the number of people that have existed on Earth over all the centuries of time. Electrons are *small* in the absolute sense of the word—they are among the smallest particles that make up matter. And yet, as we have seen, an atom’s electrons determine many of its chemical and physical properties. If we are to understand these properties, we must try to understand electrons.

In the early twentieth century, scientists discovered that the *absolutely small* (or *quantum*) world of the electron behaves differently than the *large* (or *macroscopic*) world that we are used to observing. Chief among these differences is the idea that, when unobserved, *absolutely small particles like electrons can be in two different states at the same time*. For example, through a process called radioactive decay (see Chapter 19) an atom can emit small (that is, *absolutely small*) energetic particles from its nucleus. In the macroscopic world, something either emits an energetic particle or it doesn’t. In the quantum world, however, the unobserved atom can be in a state in which it is doing both—emitting the particle and not emitting the particle—simultaneously. At first, this seems absurd.

*The thought experiment known as Schrödinger's cat is intended to show that the strangeness of the quantum world does not transfer to the macroscopic world.*

The absurdity resolves itself, however, upon observation. When we set out to measure the emitted particle, the act of measurement actually forces the atom into one state or other.

Early twentieth century physicists struggled with this idea. Austrian physicist Erwin Schrödinger (1887–1961), in an attempt to demonstrate that this quantum strangeness could never transfer itself to the macroscopic world, published a paper in 1935 that contained a thought experiment about a cat, now known as Schrödinger's cat. In the thought experiment, the cat is put into a steel chamber that contains radioactive atoms such as the atom described in the previous paragraph. The chamber is equipped with a mechanism that, upon the emission of an energetic particle by one of the radioactive atoms, causes a hammer to break a flask of hydrocyanic acid, a poison. If the flask breaks, the poison is released and the cat dies.

Now here comes the absurdity: if the steel chamber is closed, the whole system remains unobserved, and the radioactive atom is in a state in which it has emitted the particle and not emitted the particle (with equal probability). Therefore, the cat is both dead and undead. Schrödinger put it this way: “[the steel chamber would have] *in it the living and dead cat (pardon the expression) mixed or smeared out in equal parts.*” When the chamber is opened, the act of observation forces the entire system into one state or the other: the cat is either dead or alive, not both. However, while unobserved, the cat is both dead and alive. The absurdity of the both dead and undead cat in Schrödinger's thought experiment was meant to demonstrate how quantum strangeness does not transfer to the macroscopic world.

In this chapter, we examine the **quantum-mechanical model** of the atom, a model that explains the strange behavior of electrons. In particular, we focus on how the model describes electrons as they exist within atoms, and how those electrons determine the chemical and physical properties of elements. You have already learned much about those properties. You know, for example, that some elements are metals and that others are nonmetals. You know that the noble gases are chemically inert and that the alkali metals are chemically reactive. You know that sodium tends to form  $1+$  ions and that fluorine tends to form  $1-$  ions. But we have not explored *why*. The quantum-mechanical model explains why. In doing so, it explains the modern periodic table and provides the basis for our understanding of chemical bonding.

## 7.2 The Nature of Light

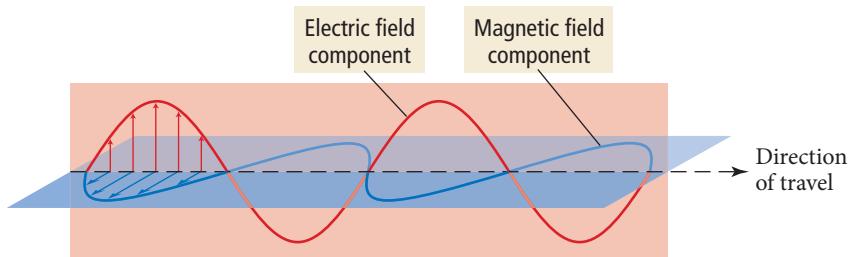
Before we explore electrons and their behavior within the atom, we must understand some of the properties of light. As quantum mechanics developed, light was (surprisingly) found to have many characteristics in common with electrons. Chief among these is the *wave-particle duality* of light. Certain properties of light are best described by thinking of it as a wave, while other properties are best described by thinking of it as a particle. In this section, we will first explore the wave behavior of light, and then its particle behavior. We will then turn to electrons to see how they also display the same wave–particle duality.

### The Wave Nature of Light

Light is **electromagnetic radiation**, a type of energy embodied in oscillating electric and magnetic fields. A *magnetic field* is a region of space where a magnetic particle experiences a force (think of the space around a magnet). An *electric field* is a region of space where an electrically charged particle experiences a force. A proton, for example, has an electric field around it. If you bring another charged particle into that field, that particle will experience a force.

Electromagnetic radiation can be described as a wave composed of oscillating, mutually perpendicular electric and magnetic fields propagating through space, as shown in Figure 7.1 ►. In a vacuum, these waves move at a constant speed of  $3.00 \times 10^8$  m/s (186,000 mi/s)—fast enough to circle the Earth in one-seventh of a second. This great speed is the reason for the delay between the moment when you see a firework in the sky and the moment when you hear the sound of its explosion. The light from the exploding firework reaches your eye almost instantaneously. The sound, traveling much more slowly

## Electromagnetic Radiation



(340 m/s), takes longer. The same thing happens in a thunderstorm—you see the flash of lightning immediately, but the sound of thunder takes a few seconds to reach you (The sound of thunder is delayed by 5 seconds for each mile between you and its origin.)

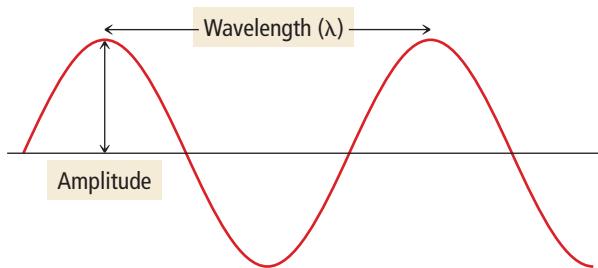


We can characterize a wave by its *amplitude* and its *wavelength*. In the graphical representation shown below, the **amplitude** of the wave is the vertical height of a crest (or depth of a trough). The amplitude of the electric and magnetic field waves in light determines the light's *intensity* or brightness—the greater the amplitude, the greater the intensity. The **wavelength** ( $\lambda$ ) of the wave is the distance between adjacent crests (or any two analogous points) and is measured in units such as meters, micrometers, or nanometers.

### ◀ FIGURE 7.1 Electromagnetic Radiation

**Radiation** Electromagnetic radiation can be described as a wave composed of oscillating electric and magnetic fields. The fields oscillate in perpendicular planes.

◀ Because light travels nearly a million times faster than sound, the flash of lightning reaches your eyes before the roll of thunder reaches your ears.

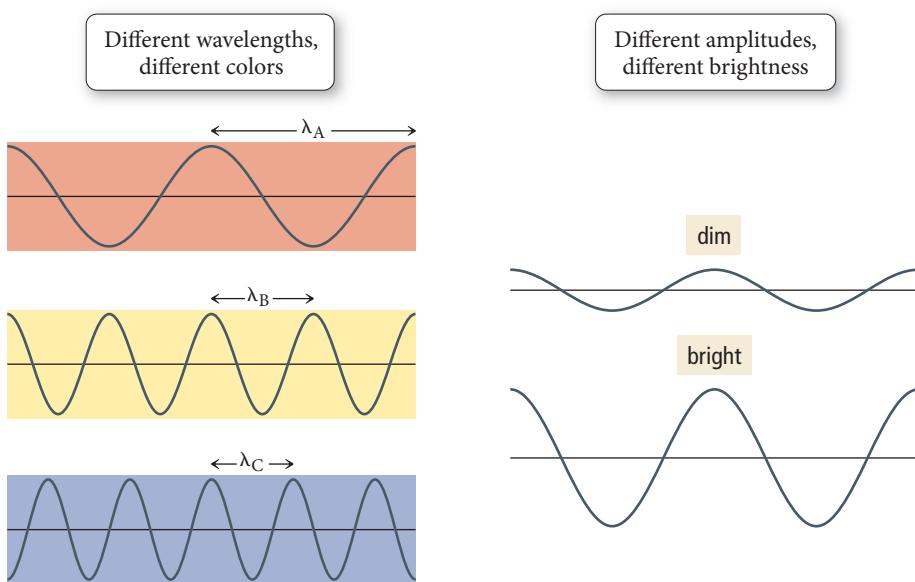


Wavelength and amplitude are both related to the quantity of energy carried by a wave. Imagine trying to swim out from a shore pounded by waves. Waves of greater amplitude (higher waves) or shorter wavelength (more closely spaced, and thus steeper, waves) will make the swim more difficult. Notice also that amplitude and wavelength

The symbol  $\lambda$  is the Greek letter lambda, pronounced “lamb-duh.”

► **FIGURE 7.2 Wavelength and Amplitude**

Wavelength and amplitude are independent properties. The wavelength of light determines its color. The amplitude, or intensity, determines its brightness.



can vary independently of one another, as shown in Figure 7.2 ▲. A wave can have a large amplitude and a long wavelength, or a small amplitude and a short wavelength. The most energetic waves have large amplitudes and short wavelengths.

Like all waves, light is also characterized by its **frequency** ( $\nu$ ), the number of cycles (or wave crests) that pass through a stationary point in a given period of time. The units of frequency are cycles per second (cycle/s) or simply  $s^{-1}$ . An equivalent unit of frequency is the hertz (Hz), defined as 1 cycle/s. The frequency of a wave is directly proportional to the speed at which the wave is traveling—the faster the wave, the more crests will pass a fixed location per unit time. Frequency is also *inversely* proportional to the wavelength ( $\lambda$ )—the farther apart the crests, the fewer that will pass a fixed location per unit time. For light, therefore, we can write the equation:

$$\nu = \frac{c}{\lambda} \quad [7.1]$$

where the speed of light,  $c$ , and the wavelength,  $\lambda$ , are both expressed in the same unit of distance. Wavelength and frequency represent different ways of specifying the same information—if we know one, we can readily calculate the other.

For *visible light*—light that can be seen by the human eye—wavelength (or, alternatively, frequency) determines color. White light, produced by the sun or by a lightbulb, contains a spectrum of wavelengths and therefore a spectrum of colors. We can see these colors—red, orange, yellow, green, blue, indigo, and violet—in a rainbow or when white light is passed through a prism (Figure 7.3 ▼). Red light, with a wavelength of about 750 nanometers (nm), has the longest wavelength of visible light; violet light, with a wavelength of about 400 nm, has the shortest. The presence of a variety of wavelengths in white light is responsible for the way we perceive colors in objects. When a substance absorbs some colors while reflecting others, it appears colored. For example, a red shirt appears red because it reflects predominantly red light while absorbing most other colors (Figure 7.4 ▼). Our eyes see only the reflected light, making the shirt appear red.

| nano =  $10^{-9}$

► **FIGURE 7.3 Components of White Light**

We can pass white light through a prism and decompose it into its constituent colors, each with a different wavelength. The array of colors makes up the spectrum of visible light.



► **FIGURE 7.4 The Color of an Object**

A red shirt is red because it reflects predominantly red light while absorbing most other colors.

### EXAMPLE 7.1 Wavelength and Frequency

Calculate the wavelength (in nm) of the red light emitted by a barcode scanner that has a frequency of  $4.62 \times 10^{14} \text{ s}^{-1}$ .

#### SOLUTION

You are given the frequency of the light and asked to find its wavelength. Use Equation 7.1, which relates frequency to wavelength. You can convert the wavelength from meters to nanometers by using the conversion factor between the two ( $1 \text{ nm} = 10^{-9} \text{ m}$ ).

$$\begin{aligned} v &= \frac{c}{\lambda} \\ \lambda &= \frac{c}{v} = \frac{3.00 \times 10^8 \text{ m/s}}{4.62 \times 10^{14} \text{ s}} \\ &= 6.49 \times 10^{-7} \text{ m} \\ &= 6.49 \times 10^{-7} \text{ m} \times \frac{1 \text{ nm}}{10^{-9} \text{ m}} = 649 \text{ nm} \end{aligned}$$

#### FOR PRACTICE 7.1

A laser dazzles the audience in a rock concert by emitting green light with a wavelength of 515 nm. Calculate the frequency of the light.

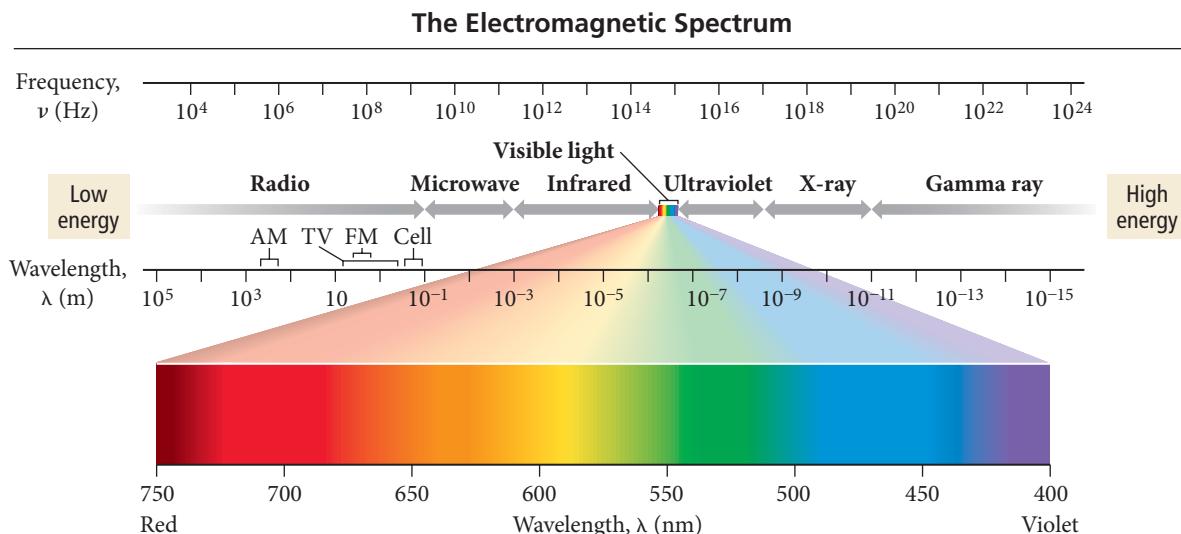
## The Electromagnetic Spectrum

Visible light makes up only a tiny portion of the entire **electromagnetic spectrum**, which includes all wavelengths of electromagnetic radiation. Figure 7.5 ▼ shows the main regions of the electromagnetic spectrum, ranging in wavelength from  $10^{-15} \text{ m}$  (gamma rays) to  $10^5 \text{ m}$  (radio waves). In Figure 7.5, short-wavelength, high-frequency radiation is on the right and long-wavelength, low-frequency radiation is on the left. As you can see, visible light constitutes only a small region in the middle.

Recall that short-wavelength light inherently has greater energy than long-wavelength light. The most energetic forms of electromagnetic radiation have the shortest wavelengths. The form of electromagnetic radiation with the shortest wavelength is the **gamma ( $\gamma$ ) ray**. Gamma rays are produced by the sun, other stars, and certain unstable atomic nuclei on Earth. Excessive exposure to gamma rays is dangerous to humans because the high energy of gamma rays can damage biological molecules.

Next on the electromagnetic spectrum, with longer wavelengths than gamma rays, are **X-rays**, familiar to us from their medical use. X-rays pass through many substances that

We will discuss gamma rays in more detail in Chapter 19.



▲ FIGURE 7.5 The Electromagnetic Spectrum The right side of the spectrum consists of high-energy, high-frequency, short-wavelength radiation. The left side consists of low-energy, low-frequency, long-wavelength radiation. Visible light constitutes a small segment in the middle.



▲ To produce a medical X-ray, the patient is exposed to short-wavelength electromagnetic radiation that can pass through the skin to create an image of bones and internal organs.

block visible light and are therefore used to image bones and internal organs. Like gamma rays, X-rays are sufficiently energetic to damage biological molecules. While several annual exposures to X-rays are relatively harmless, too much exposure to X-rays increases cancer risk.

Sandwiched between X-rays and visible light in the electromagnetic spectrum is **ultraviolet (UV) radiation**, most familiar to us as the component of sunlight that produces a sunburn or suntan. While not as energetic as gamma rays or X-rays, ultraviolet light still carries enough energy to damage biological molecules. Excessive exposure to ultraviolet light increases the risk of skin cancer and cataracts and causes premature wrinkling of the skin.

Next on the spectrum is **visible light**, ranging from violet (shorter wavelength, higher energy) to red (longer wavelength, lower energy). Visible light—at low to moderate intensity—does not carry enough energy to damage biological molecules. It does, however, cause certain molecules in our eyes to change their shape, sending a signal to our brains that results in our ability to see.

Beyond visible light lies **infrared (IR) radiation**. The heat you feel when you place your hand near a hot object is infrared radiation. All warm objects, including human bodies, emit infrared light. Although infrared light is invisible to our eyes, infrared sensors can detect it and are often employed in night vision technology to help people “see” in the dark.



## Chemistry and Medicine

### Radiation Treatment for Cancer

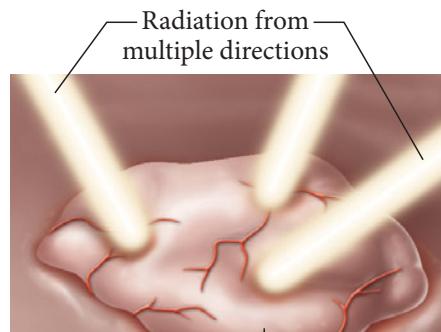
X-rays and gamma rays are sometimes called ionizing radiation because their short wavelengths correspond to high energies that can ionize atoms and molecules. When ionizing radiation interacts with biological molecules, it can permanently change or even destroy them. Consequently, we normally try to limit our exposure to ionizing radiation. However, doctors use ionizing radiation to destroy molecules within unwanted cells such as cancer cells.

In radiation therapy (also called radiotherapy) doctors aim X-ray or gamma-ray beams at cancerous tumors (groups of cells that divide uncontrollably and invade surrounding healthy tissue). The ionizing radiation damages the molecules within the tumor’s cells that carry genetic information—information necessary for the cell to grow and divide. Consequently, the cell dies or stops dividing. Ionizing radiation also damages molecules in healthy cells, but cancerous cells divide more quickly than normal cells, making them more susceptible to genetic damage. Nonetheless, harm to healthy tissues during treatments can result in side effects such as fatigue, skin lesions, hair loss, and organ damage. Medical workers try to reduce such effects by appropriate shielding (of healthy tissue) and by targeting the tumor from multiple directions, minimizing the exposure of healthy cells while maximizing the exposure of cancerous cells.

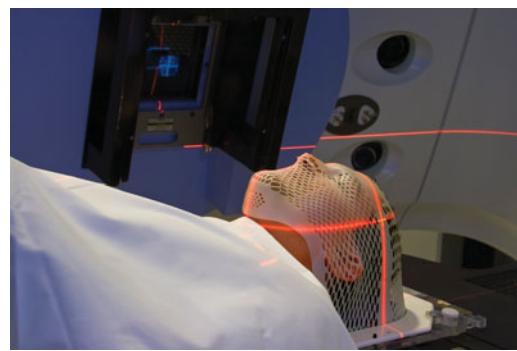
Another side effect of exposing healthy cells to radiation is that they too may become cancerous. If a treatment for cancer may cause cancer, why do we continue to use it? In radiation therapy, as in most other disease therapies, there is an associated risk. We take risks all the time, many of them for lesser reasons. For example, every time we fly in an airplane or drive in a car, we risk injury or even death. Why? Because we perceive the benefit—the convenience of being able to travel a significant distance in a short time—to be worth the relatively small risk. The situation is similar in cancer therapy, or any other medical therapy for that matter. The benefit of cancer therapy (possibly curing a cancer that might otherwise kill you) is worth the risk (a slight increase in the chance of developing a future cancer).

### Question

Why is visible light (by itself) not used to destroy cancerous tumors?

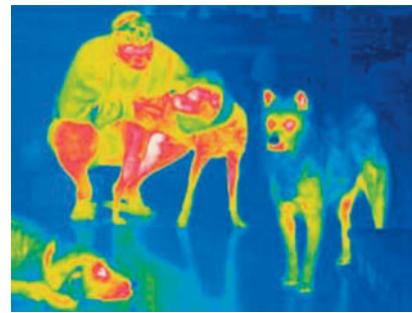


▲ During radiation therapy, a tumor is targeted from multiple directions in order to minimize the exposure of healthy cells while maximizing the exposure of cancerous cells.



▲ In radiation therapy, highly energetic gamma rays are aimed at cancerous tumors.

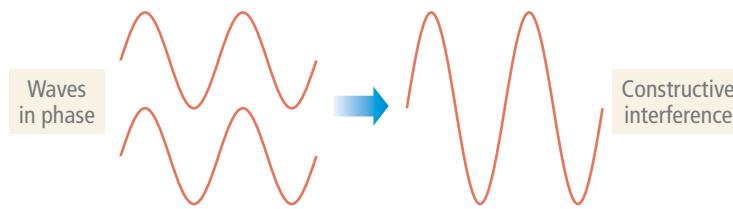
Beyond infrared light, at longer wavelengths still, are **microwaves**, used for radar and in microwave ovens. Although microwave radiation has longer wavelengths and therefore lower energies than visible or infrared light, it is efficiently absorbed by water and can therefore heat substances that contain water. The longest wavelengths are those of **radio waves**, which are used to transmit the signals responsible for AM and FM radio, cellular telephone, television, and other forms of communication.



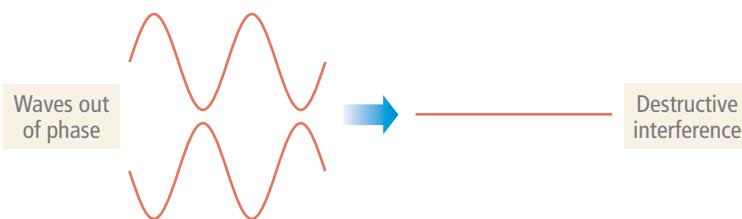
▲ Warm objects emit infrared light, which is invisible to the eye but can be captured on film or by detectors to produce an infrared photograph.

## Interference and Diffraction

Waves, including electromagnetic waves, interact with each other in a characteristic way called **interference**: they cancel each other out or build each other up, depending on their alignment upon interaction. For example, if two waves of equal amplitude are *in phase* when they interact—that is, they align with overlapping crests—a wave with twice the amplitude results. This is called **constructive interference**.



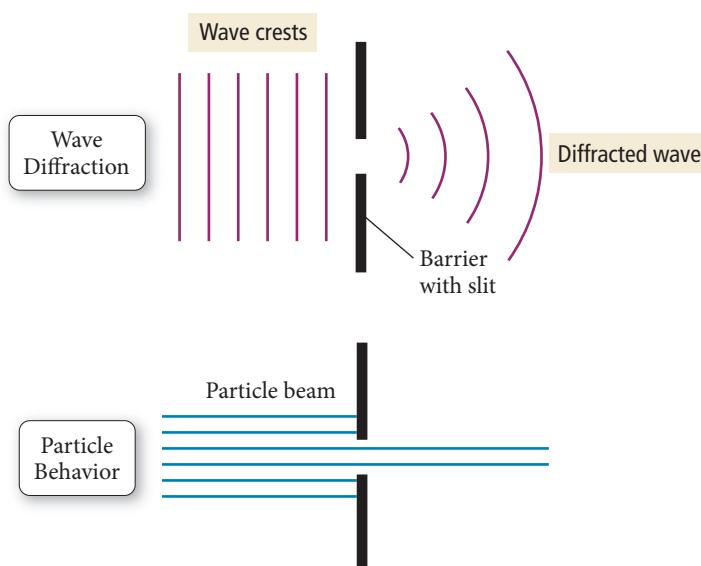
On the other hand, if two waves are completely *out of phase* when they interact—that is, they align so that the crest from one source overlaps with the trough from the other source—the waves cancel by **destructive interference**.



Understanding interference in waves is critical to understanding the wave nature of the electron, as we will soon see.

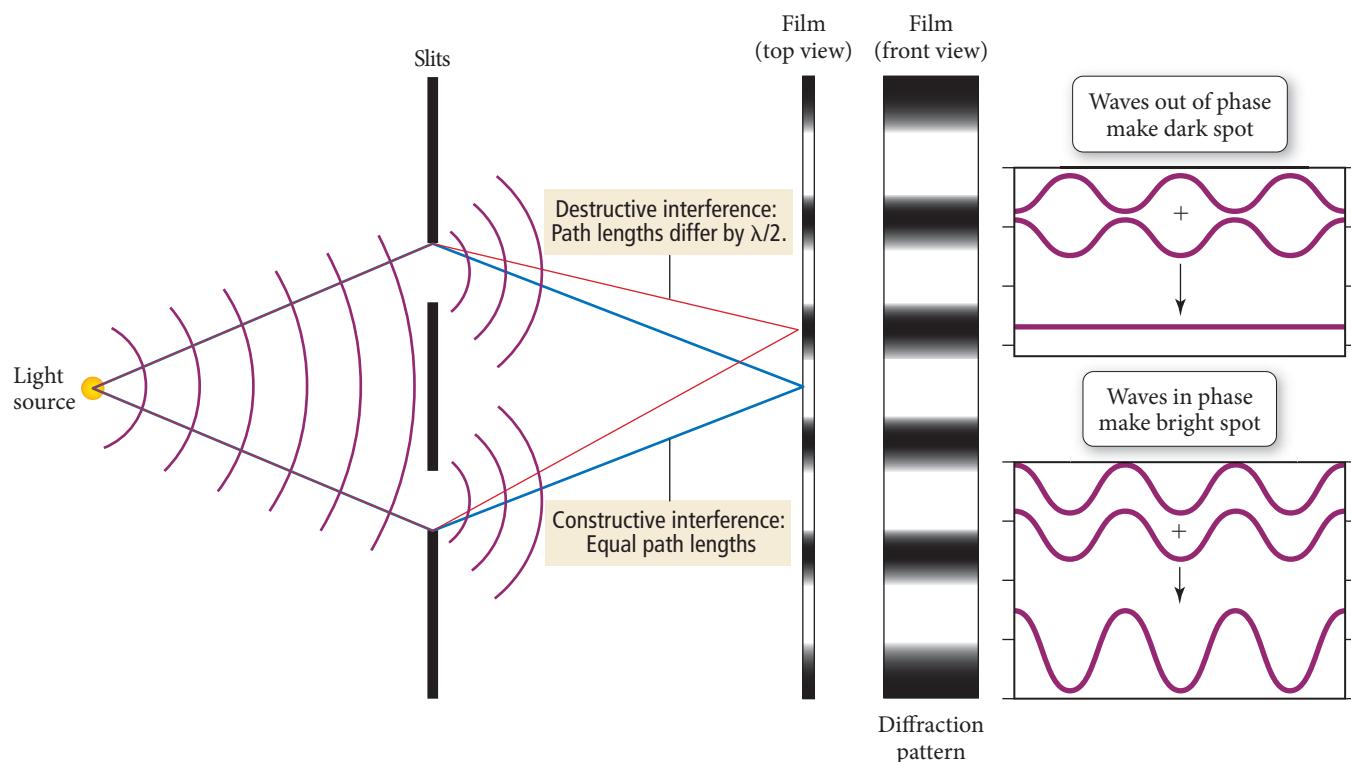


▲ When a reflected wave meets an incoming wave near the shore, the two waves interfere constructively for an instant, producing a large amplitude spike.



◀ FIGURE 7.6 Diffraction In this view from above, we can see how waves bend, or diffract, when they encounter an obstacle or slit with a size comparable to their wavelength. When a wave passes through a small opening, it spreads out. Particles, by contrast, do not diffract; they simply pass through the opening.

### Interference from Two Slits



**▲ FIGURE 7.7** Interference from Two Slits

**Slits** When a beam of light passes through two small slits, the two resulting waves interfere with each other. Whether the interference is constructive or destructive at any given point depends on the difference in the path lengths traveled by the waves. The resulting interference pattern appears as a series of bright and dark lines on a screen.

an *interference pattern*, as shown in Figure 7.7 ▲. Each slit acts as a new wave source, and the two new waves interfere with each other. The resulting pattern is a series of bright and dark lines that can be viewed on a screen (or recorded on a film) placed a short distance behind the slits. At the center of the screen, the two waves travel equal distances and interfere constructively to produce a bright line. A small distance away from the center in either direction, the two waves travel slightly different distances, so they are out of phase. At the point where the difference in distance is one-half of one wavelength, the interference is destructive and a dark line appears on the screen. Moving a bit further away from the center produces constructive interference again because the difference between the paths is one whole wavelength. The end result is the interference pattern shown by the light and dark bars in Figure 7.7. Notice that interference results from the ability of a wave to diffract through two slits—an inherent property of waves.

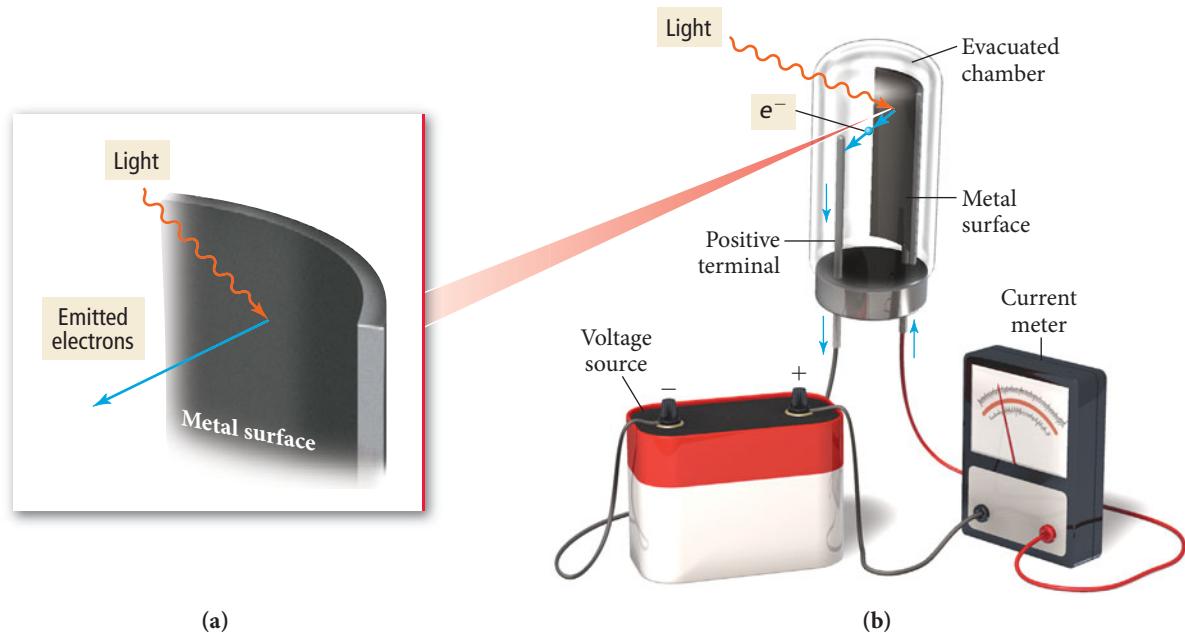
### The Particle Nature of Light

Prior to the early 1900s, and especially after the discovery of the diffraction of light, light was thought to be purely a wave phenomenon. Its behavior was described adequately by classical electromagnetic theory, which treated the electric and magnetic fields that constitute light as waves propagating through space. However, a number of discoveries brought the classical view into question. Chief among these was the *photoelectric effect*.

The **photoelectric effect** is the observation that many metals emit electrons when light shines upon them, as shown in Figure 7.8 ▷. Classical electromagnetic theory attributed this effect to the transfer of energy from the light to an electron in the metal, which resulted in the dislodgment of the electron. According to this explanation, only the amplitude (intensity) of the light affects the emission of electrons, not the wavelength. In other words, according to the classical description, the rate at which electrons leave the metal due to the photoelectric effect increases with increasing intensity of the light. A dim light was expected to result in a *lag time* between the initial shining of the light and the subsequent emission of an electron.

The term *classical*, as in classical electromagnetic theory or classical mechanics, refers to descriptions of matter and energy before the advent of quantum mechanics.

## The Photoelectric Effect



**▲ FIGURE 7.8 The Photoelectric Effect** (a) When sufficiently energetic light shines on a metal surface, the surface emits electrons. (b) The emitted electrons can be measured as an electrical current.

The lag time would be the minimum amount of time required for the dim light to transfer sufficient energy to the electron to dislodge it.

The experimental results, however, did not support the classical prediction. Scientists found that a high-frequency, low-intensity light produces electrons *without* the predicted lag time. Furthermore, the light used to dislodge electrons in the photoelectric effect exhibits a *threshold frequency*, below which no electrons are emitted from the metal, no matter how long the light shines on the metal. Figure 7.9 ► is a graph of the rate of electron ejection from the metal versus the frequency of light used. Notice that increasing the intensity of the light does not change the threshold frequency. In other words, low-frequency (long-wavelength) light *does not* eject electrons from a metal regardless of its intensity or its duration. But high-frequency (short-wavelength) light *does* eject electrons, even if its intensity is low. What could explain this odd behavior?

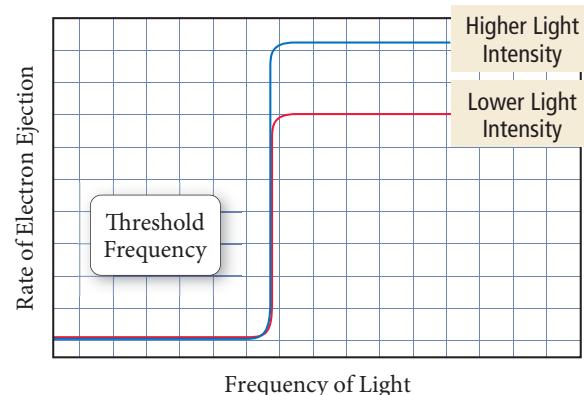
In 1905, Albert Einstein proposed a bold explanation for the photoelectric effect: *light energy must come in packets*. According to Einstein, the amount of energy ( $E$ ) in a light packet depends on its frequency ( $\nu$ ) according to the following equation:

$$E = h\nu \quad [7.2]$$

where  $h$ , called *Planck's constant*, has the value  $h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$ . A *packet* of light is called a **photon** or a **quantum** of light. Since  $\nu = c/\lambda$ , the energy of a photon can also be expressed in terms of wavelength as follows:

$$E = \frac{hc}{\lambda} \quad [7.3]$$

Unlike classical electromagnetic theory, in which light was viewed purely as a wave whose intensity was *continuously variable*, Einstein suggested that light was *lumpy*. From this perspective, a beam of light is *not* a wave propagating through space, but a shower of particles (photons), each with energy  $h\nu$ .



**▲ FIGURE 7.9 The Photoelectric Effect** A plot of the electron ejection rate versus frequency of light for the photoelectric effect. Electrons are only ejected when the energy of a photon exceeds the energy with which an electron is held to the metal. The frequency at which this occurs is called the *threshold frequency*.

Einstein was not the first to suggest that energy was quantized. Max Planck used the idea in 1900 to account for certain characteristics of radiation from hot bodies. However, he did not suggest that light actually traveled in discrete packets.

The energy of a photon is directly proportional to its frequency and inversely proportional to its wavelength.

**EXAMPLE 7.2** Photon Energy

A nitrogen gas laser pulse with a wavelength of 337 nm contains 3.83 mJ of energy. How many photons does it contain?

**SORT** You are given the wavelength and total energy of a light pulse and asked to find the number of photons it contains.

**STRATEGIZE** In the first part of the conceptual plan, calculate the energy of an individual photon from its wavelength.

In the second part, divide the total energy of the pulse by the energy of a photon to get the number of photons in the pulse.

**SOLVE** To execute the first part of the conceptual plan, convert the wavelength to meters and substitute it into the equation to calculate the energy of a 337 nm photon.

To execute the second part of the conceptual plan, convert the energy of the pulse from mJ to J. Then divide the energy of the pulse by the energy of a photon to obtain the number of photons.

**GIVEN:**  $E_{\text{pulse}} = 3.83 \text{ mJ}$   
 $\lambda = 337 \text{ nm}$

**FIND:** number of photons

**CONCEPTUAL PLAN**

$$\lambda \rightarrow E_{\text{photon}}$$

$$E = \frac{hc}{\lambda}$$

$$\frac{E_{\text{pulse}}}{E_{\text{photon}}} = \text{number of photons}$$

**RELATIONSHIPS USED**  $E = hc/\lambda$  (Equation 7.3)

**SOLUTION**

$$\lambda = 337 \text{ nm} \times \frac{10^{-9} \text{ m}}{1 \text{ nm}} = 3.37 \times 10^{-7} \text{ m}$$

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s}) \left( 3.00 \times 10^8 \frac{\text{m}}{\text{s}} \right)}{3.37 \times 10^{-7} \text{ m}}$$

$$= 5.8985 \times 10^{-19} \text{ J}$$

$$3.83 \text{ mJ} \times \frac{10^{-3} \text{ J}}{1 \text{ mJ}} = 3.83 \times 10^{-3} \text{ J}$$

$$\text{number of photons} = \frac{E_{\text{pulse}}}{E_{\text{photon}}} = \frac{3.83 \times 10^{-3} \text{ J}}{5.8985 \times 10^{-19} \text{ J}}$$

$$= 6.49 \times 10^{15} \text{ photons}$$

**CHECK** The units of the answer, photons, are correct. The magnitude of the answer ( $10^{15}$ ) is reasonable. Photons are small particles and any macroscopic collection should contain a large number of them.

**FOR PRACTICE 7.2**

A 100-watt lightbulb radiates energy at a rate of 100 J/s (The watt, a unit of power, or energy over time, is defined as 1 J/s.) If all of the light emitted has a wavelength of 525 nm, how many photons are emitted per second? (Assume three significant figures in this calculation.)

**FOR MORE PRACTICE 7.2**

The energy required to dislodge electrons from sodium metal via the photoelectric effect is 275 kJ/mol. What wavelength in nm of light has sufficient energy per photon to dislodge an electron from the surface of sodium?

### EXAMPLE 7.3 Wavelength, Energy, and Frequency

Arrange the three types of electromagnetic radiation—visible light, X-rays, and microwaves—in order of increasing

- (a) wavelength.      (b) frequency.      (c) energy per photon.

#### SOLUTION:

Examine Figure 7.5 and note that X-rays have the shortest wavelength, followed by visible light and then microwaves.

(a) wavelength  
X rays < visible < microwaves

Since frequency and wavelength are inversely proportional—the longer the wavelength the shorter the frequency—the ordering with respect to frequency is the reverse of the ordering with respect to wavelength.

(b) frequency  
microwaves < visible < X rays

Energy per photon decreases with increasing wavelength but increases with increasing frequency; therefore, the ordering with respect to energy per photon is the same as for frequency.

(c) energy per photon  
microwaves < visible < X rays

#### FOR PRACTICE 7.3

Arrange these three colors of visible light—green, red, and blue—in order of increasing

- (a) wavelength.      (b) frequency.      (c) energy per photon.

Einstein's idea that light is quantized elegantly explains the photoelectric effect. The emission of electrons from the metal depends on whether or not a single photon has sufficient energy (as given by  $h\nu$ ) to dislodge a single electron. For an electron bound to the metal with binding energy  $\phi$ , the threshold frequency is reached when the energy of the photon is equal to  $\phi$ .

The symbol  $\phi$  is the Greek letter phi, pronounced "fi."

#### Threshold frequency condition

$$h\nu = \phi$$

Energy of      Binding energy of  
photon            emitted electron

Low-frequency light does not eject electrons because no single photon has the minimum energy necessary to dislodge the electron. We can draw an analogy between a photon ejecting an electron from a metal surface and a ball breaking a glass window. In this analogy, low-frequency photons are like ping-pong balls—a ping-pong ball thrown at glass window does not break it (just as a low-frequency photon does not eject an electron). Increasing the *intensity* of low-frequency light is like increasing the number of ping-pong balls thrown at the window—doing so simply increases the number of low-energy photons but does not produce any single photon with sufficient energy. In contrast, increasing the *frequency* of the light, even at low intensity, *increases the energy of each photon*. In our analogy, a high-frequency photon is like a baseball—a baseball thrown at a glass window breaks it (just as a high frequency photon dislodges an electron with no lag time).

As the frequency of the light is increased past the threshold frequency, the excess energy of the photon (beyond what is needed to dislodge the electron) is transferred to the electron in the form of kinetic energy. The kinetic energy (KE) of the ejected electron, therefore, is the difference between the energy of the photon ( $h\nu$ ) and the binding energy of the electron, as given by the equation:

$$KE = h\nu - \phi$$

Although the quantization of light explained the photoelectric effect, the wave explanation of light continued to have explanatory power as well, depending on the circumstances of the particular observation. So the principle that slowly emerged (albeit with some measure of resistance) is what we now call the *wave-particle duality of light*. Sometimes light appears to behave like a wave, at other times like a particle. Which behavior you observe depends on the particular experiment.

### Conceptual Connection 7.1 The Photoelectric Effect

Light of three different wavelengths—325 nm, 455 nm, and 632 nm—is shined on a metal surface. The observations for each wavelength, labeled A, B, and C, is as follows:

Observation A: No photoelectrons were observed.

Observation B: Photoelectrons with a kinetic energy of 155 kJ/mol were observed.

Observation C: Photoelectrons with a kinetic energy of 51 kJ/mol were observed.

Which observation corresponds to which wavelength of light?

## 7.3 Atomic Spectroscopy and the Bohr Model

The discovery of the particle nature of light began to break down the division that existed in nineteenth-century physics between electromagnetic radiation, which was thought of as a wave phenomenon, and the small particles (protons, neutrons, and electrons) that compose atoms, which were thought to follow Newton's laws of motion. Just as the photoelectric effect suggested the particle nature of light, so certain observations about atoms began to suggest a wave nature for particles. The most important of these came from *atomic spectroscopy*, the study of the electromagnetic radiation absorbed and emitted by atoms.

When an atom absorbs energy—in the form of heat, light, or electricity—it often re-emits that energy as light. For example, a neon sign is composed of one or more glass tubes filled with neon gas. When an electric current is passed through the tube, the neon atoms absorb some of the electrical energy and re-emit it as the familiar red light of a neon sign. If the atoms in the tube are different (that is, not neon), they emit light of a different color. In other words, atoms of each element emit light of a characteristic color. Mercury atoms, for example, emit light that appears blue, helium atoms emit light that appears violet, and hydrogen atoms emit light that appears reddish (Figure 7.10 ▲).

Remember that the color of visible light is determined by its wavelength. Closer inspection of the light emitted by various atoms reveals that it contains several distinct wavelengths. We can separate the light emitted by a single element in a glass tube into its constituent wavelengths by passing it through a prism (just like we separate the white light from a lightbulb), as shown in Figure 7.11 ▶. The result is a series of bright lines called an **emission spectrum**. The emission spectrum of a particular element is always the same—it consists of the same bright lines at the same characteristic wavelengths—and can be used to identify the element. For example, light arriving from a distant star contains the emission spectra of the elements that compose the star. Analysis of the light allows us to identify the elements present in the star.

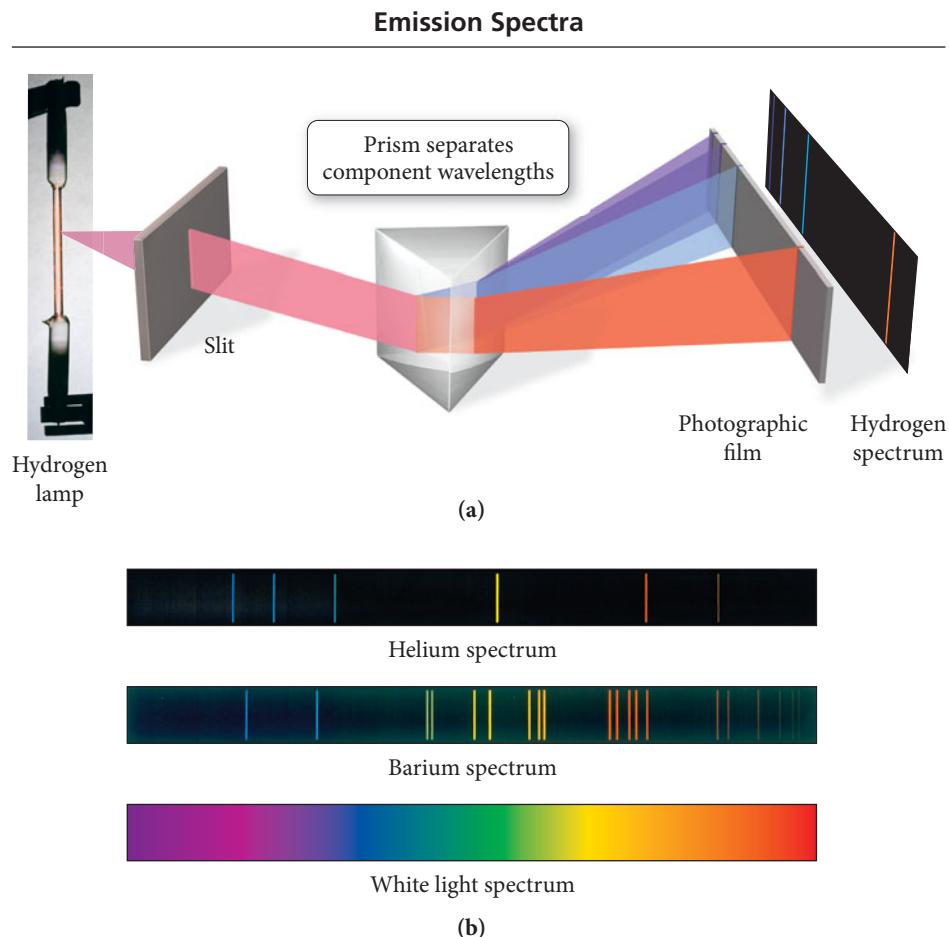
Notice the differences between a white light spectrum and the emission spectra of hydrogen, helium, and barium (shown in Figure 7.11). The white light spectrum is *continuous*, meaning that there are no sudden interruptions in the intensity of the light as a function of wavelength—the spectrum consists of light of all wavelengths. The emission spectra of hydrogen, helium, and barium, however, are not continuous—they consist of bright lines at specific wavelengths, with complete darkness in between. That is, only certain discrete wavelengths of light are present. Classical physics could not explain why these spectra consisted of discrete lines. In fact, according to classical physics, an atom composed of an electron orbiting a nucleus should emit a continuous white light spectrum. Even more problematic, the electron should lose energy as it emits the light and spiral into the nucleus. According to classical physics, an atom should not even be stable.



▲ The familiar red light from a neon sign is emitted by neon atoms that have absorbed electrical energy, which they re-emit as visible radiation.



▲ FIGURE 7.10 Mercury, Helium, and Hydrogen Each element emits a characteristic color.



◀ **FIGURE 7.11** Emission Spectra

(a) The light emitted from a hydrogen, helium, or barium lamp consists of specific wavelengths that can be separated by passing the light through a prism. (b) The resulting bright lines constitute an emission spectrum characteristic of the element that produced it.

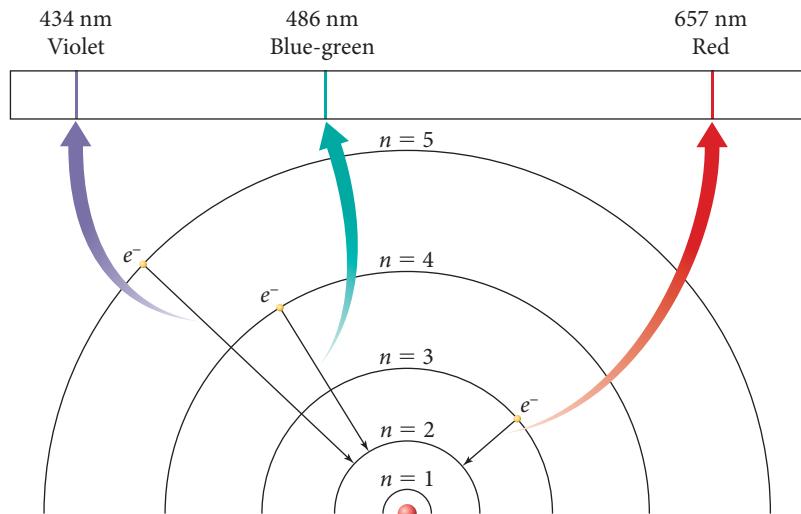
Johannes Rydberg, a Swedish mathematician, analyzed many atomic spectra and developed an equation that predicts the wavelengths of the hydrogen emission spectrum. However, his equation (shown in the margin) gives little insight into *why* atomic spectra are discrete, *why* atoms are stable, or *why* his equation works.

The Danish physicist Niels Bohr (1885–1962) attempted to develop a model for the atom that explained atomic spectra. In his model, electrons travel around the nucleus in circular orbits (analogous to those of the planets around the sun). However, in contrast to planetary orbits—which can theoretically exist at any distance from the sun—Bohr’s orbits exist only at specific, fixed distances from the nucleus. The energy of each Bohr orbit is also fixed, or *quantized*. Bohr called these orbits *stationary states* and suggested that, although they obey the laws of classical mechanics, they also possess “a peculiar, mechanically unexplainable, stability.” We now know that the stationary states were really manifestations of the wave nature of the electron, which we will expand upon shortly. Bohr further proposed that, in contradiction to classical electromagnetic theory, no radiation is emitted by an electron orbiting the nucleus in a stationary state. It is only when an electron jumps, or makes a *transition*, from one stationary state to another that radiation is emitted or absorbed (Figure 7.12 ▶).

The transitions between stationary states in a hydrogen atom are quite unlike any transitions

The Rydberg equation is  $1/\lambda = R(1/m^2 - 1/n^2)$ , where  $R$  is the Rydberg constant ( $1.097 \times 10^7 \text{ m}^{-1}$ ), and  $m$  and  $n$  are integers.

### The Bohr Model and Emission Spectra



▲ **FIGURE 7.12** The Bohr Model and Emission Spectra According to the Bohr model, each spectral line is produced when an electron falls from one stable orbit, or stationary state, to another of lower energy.



## Chemistry in Your Day

### Atomic Spectroscopy, a Bar Code for Atoms

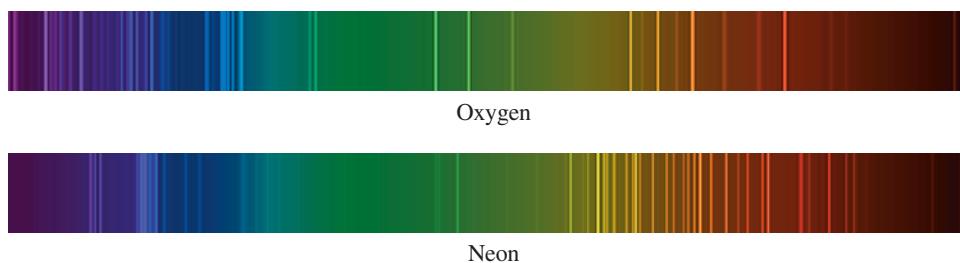
When you check out of the grocery store, a laser scanner reads the bar code on the items that you buy. Each item has a unique code that identifies the item and its price. Similarly, each element in the periodic table has a spectrum unlike that of any other element. For example, Figure 7.13 ▶ shows the emission spectra of oxygen and neon. (In Figure 7.11, we saw the emission spectra of hydrogen, helium, and barium.) Notice that each spectrum is unique and, as such, can be used to identify the substance.

The presence of intense lines in the spectra of a number of metals is the basis for *flame tests*, simple tests used to identify elements in ionic compounds in the absence of a precise analysis of a compound's spectrum. For example, the emission spectrum of sodium features two closely spaced, bright yellow lines. When a crystal of a sodium salt (or a drop of a solution containing a sodium salt) is put into a flame, the flame glows bright yellow (Figure 7.14 ►). As Figure 7.14 shows, other metals exhibit similarly characteristic colors in flame tests. Each color represents an especially bright spectral emission line (or a combination of two or more such lines). Similar emissions form the basis of the colors seen in fireworks.

Although the *emission* of light from elements is easier to detect, the *absorption* of light by elements is even more commonly used for purposes of identification. Whereas emission spectra consist of bright lines on a dark background, absorption spectra consist of dark lines on a bright background (Figure 7.15 ►). An absorption spectrum is measured by passing white light through a



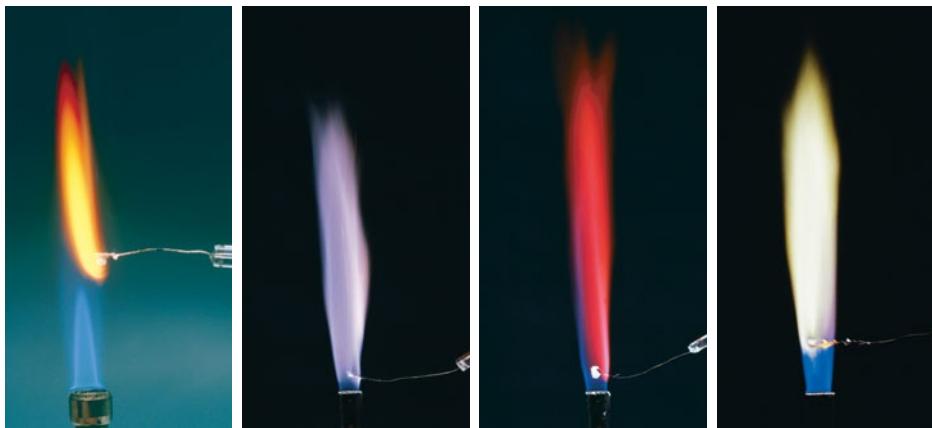
▲ Fireworks typically contain the salts of such metals as sodium, calcium, strontium, barium, and copper. Emissions from these elements produce the brilliant colors of pyrotechnic displays.



▲ FIGURE 7.13 Emission Spectra of Oxygen and Neon The emission spectrum of each element is unique and we can use it to identify the element.

that you might be familiar with in the macroscopic world. The electron is *never* observed between states; it is observed only in one state or another. The emission spectrum of an atom consists of discrete lines because the stationary states exist only at specific, fixed energies. The energy of the photon emitted when an electron makes a transition from one stationary state to another is the energy difference between the two stationary states. Transitions between stationary states that are closer together, therefore, produce light of lower energy (longer wavelength) than transitions between stationary states that are farther apart.

In spite of its initial success in explaining the line spectrum of hydrogen, the Bohr model left many unanswered questions. It did, however, serve as an intermediate model between a classical view of the electron and a fully quantum-mechanical view, and therefore has great historical and conceptual importance. Nonetheless, it was ultimately replaced by a more complete quantum-mechanical theory that fully incorporated the wave nature of the electron.



**◀ FIGURE 7.14** Flame Tests (from left to right) for Sodium, Potassium, Lithium, and Barium We can identify elements by the characteristic color of the light they produce when heated. The colors derive from especially bright lines in their emission spectra.

sample and observing what wavelengths are *missing* due to absorption by the sample. Notice that, in the spectrum of mercury shown in Figure 7.15, the absorption lines are at the same wavelengths as the emission lines. This is because the processes that produce them are mirror images. In emission, an electron makes a transition from a higher energy level to a lower energy one. In absorption, the transition is between the same two energy levels, but from the lower level to the higher one.

Absorption spectrometers, found in most chemistry laboratories, typically plot the intensity of absorption as a function of wavelength. Such plots are useful both for identifying substances (qualitative analysis) and for determining the concentration of substances (quantitative analysis). Quantitative analysis is possible because the amount of light absorbed by a sample depends on the concentration of the absorbing substance within the sample. For example, the concentration of  $\text{Ca}^{2+}$  in a hard water sample can be determined by measuring the quantity of light absorbed by the calcium ion at its characteristic wavelength.



**◀ FIGURE 7.15** Emission and Absorption Spectrum of Mercury Elements absorb light of the same wavelengths that they radiate when heated. When these wavelengths are subtracted from a beam of white light, the result is a pattern of dark lines corresponding to an absorption spectrum.

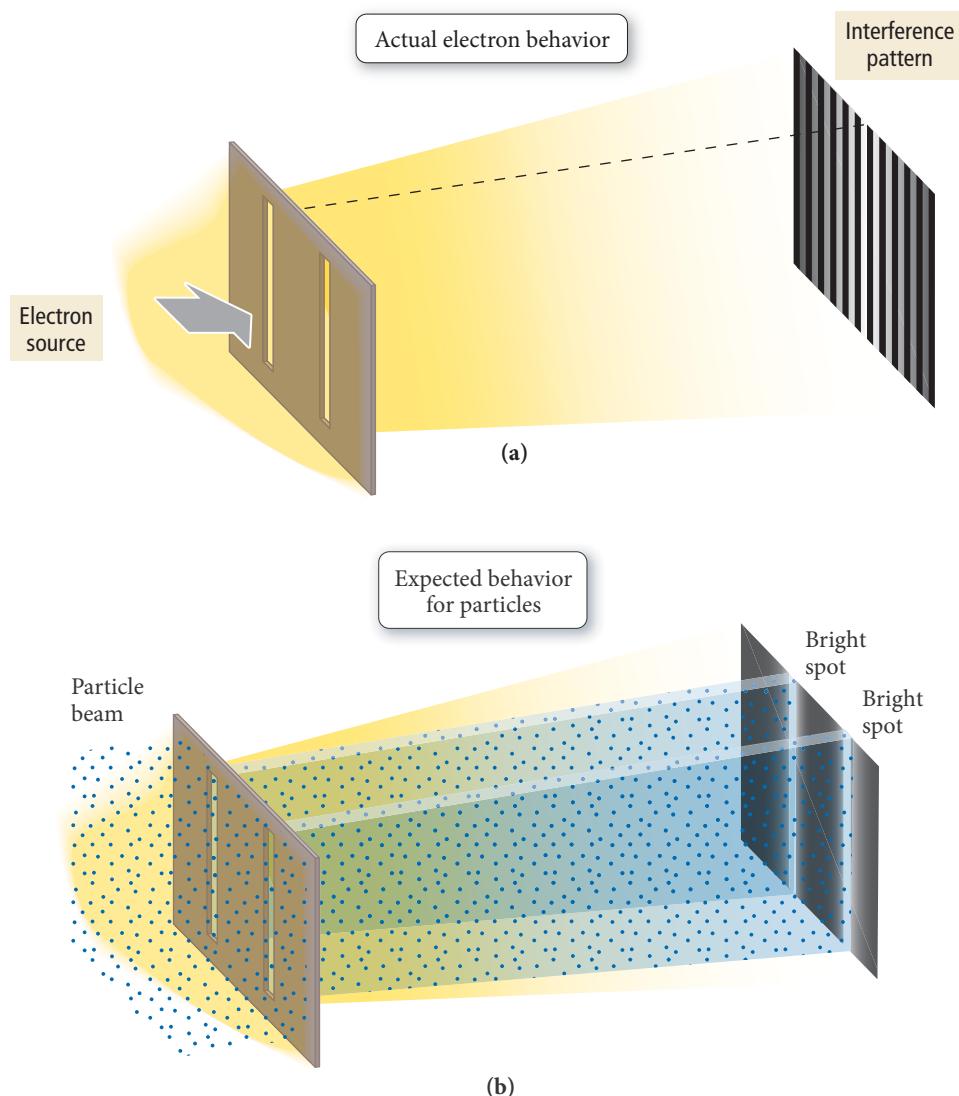
## 7.4 The Wave Nature of Matter: The de Broglie Wavelength, the Uncertainty Principle, and Indeterminacy

The heart of the quantum-mechanical theory that replaced Bohr's model is the wave nature of the electron, first proposed by Louis de Broglie (1892–1987) in 1924 and later confirmed by experiments in 1927. It seemed incredible at the time, but electrons—which were then thought of only as particles and known to have mass—also have a wave nature. The wave nature of the electron is seen most clearly in its diffraction. If an electron beam is aimed at two closely spaced slits, and a series (or array) of detectors is arranged to detect the electrons after they pass through the slits, an interference pattern similar to that observed for light is recorded behind the slits (Figure 7.16(a) ▶). The detectors at the center of the array (midway between the two slits) detect a large number of electrons—exactly the opposite of what you would expect for particles (Figure 7.16(b) ▶). Moving outward from this center spot, the detectors alternately detect small numbers of electrons and then large numbers again and so on, forming an interference pattern characteristic of waves.

The first evidence of electron wave properties was provided by the Davisson-Germer experiment of 1927, in which electrons were observed to undergo diffraction by a metal crystal.

**► FIGURE 7.16** Electron Diffraction

When a beam of electrons goes through two closely spaced slits (a), an interference pattern is created, as if the electrons were waves. By contrast, a beam of particles passing through two slits (b) produces two smaller beams of particles. Notice that particle beams produce two bright stripes with darkness in between but waves produce the brightest strip directly in the center of the screen.



For interference to occur, the spacing of the slits has to be on the order of atomic dimensions.

Counter to what might be our initial intuition about electron interference, the interference pattern is *not caused by pairs of electrons interfering with each other, but rather by single electrons interfering with themselves*. If the electron source is turned down to a very low level, so that electrons come out only one at a time, *the interference pattern remains*. In other words, we can design an experiment in which electrons come out of the source singly. We can then record where each electron strikes the detector after it has passed through the slits. If we record the positions of thousands of electrons over a long period of time, we find the same interference pattern shown in Figure 7.16(a). This leads us to an important conclusion: *the wave nature of the electron is an inherent property of individual electrons*. Recall from Section 7.1 that unobserved electrons can simultaneously occupy two different states. In this case, the unobserved electron goes through both slits—it exists in two states simultaneously, just like Schrödinger's cat—and interferes with itself. As it turns out, this wave nature explains the existence of stationary states (in the Bohr model) and prevents the electrons in an atom from crashing into the nucleus as predicted by classical physics. We now turn to three important manifestations of the electron's wave nature: the de Broglie wavelength, the uncertainty principle, and indeterminacy.

## The de Broglie Wavelength

As we have seen, a single electron traveling through space has a wave nature; its wavelength is related to its kinetic energy (the energy associated with its motion). The faster the electron is moving, the higher its kinetic energy and the shorter its wavelength.

The wavelength ( $\lambda$ ) of an electron of mass  $m$  moving at velocity  $v$  is given by the **de Broglie relation**:

$$\lambda = \frac{h}{mv} \quad \text{de Broglie relation} \quad [7.4]$$

where  $h$  is Planck's constant. Notice that the velocity of a moving electron is related to its wavelength—knowing one is equivalent to knowing the other.

The mass of an object ( $m$ ) times its velocity ( $v$ ) is its momentum. Therefore, the wavelength of an electron is inversely proportional to its momentum.

### EXAMPLE 7.4 De Broglie Wavelength

Calculate the wavelength of an electron traveling with a speed of  $2.65 \times 10^6$  m/s.

**SORT** You are given the speed of an electron and asked to calculate its wavelength.

**STRATEGIZE** The conceptual plan shows how the de Broglie relation relates the wavelength of an electron to its mass and velocity.

**SOLVE** Substitute the velocity, Planck's constant, and the mass of an electron to calculate the electron's wavelength. To correctly cancel the units, break down the J in Planck's constant into its SI base units ( $1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2/\text{s}^2$ ).

**GIVEN:**  $v = 2.65 \times 10^6$  m/s

**FIND:**  $\lambda$

#### CONCEPTUAL PLAN

$$\lambda = \frac{h}{mv}$$

#### RELATIONSHIPS USED

$$\lambda = h/mv \text{ (de Broglie relation, Equation 7.4)}$$

#### SOLUTION

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2}}{(9.11 \times 10^{-31} \text{ kg}) \left( 2.65 \times 10^6 \frac{\text{m}}{\text{s}} \right)} = 2.74 \times 10^{-10} \text{ m}$$

**CHECK** The units of the answer (m) are correct. The magnitude of the answer is very small, as expected for the wavelength of an electron.

#### FOR PRACTICE 7.4

What is the velocity of an electron that has a de Broglie wavelength approximately the length of a chemical bond? Assume this length to be  $1.2 \times 10^{-10}$  m.

### Conceptual Connection 7.2 The de Broglie Wavelength of Macroscopic Objects

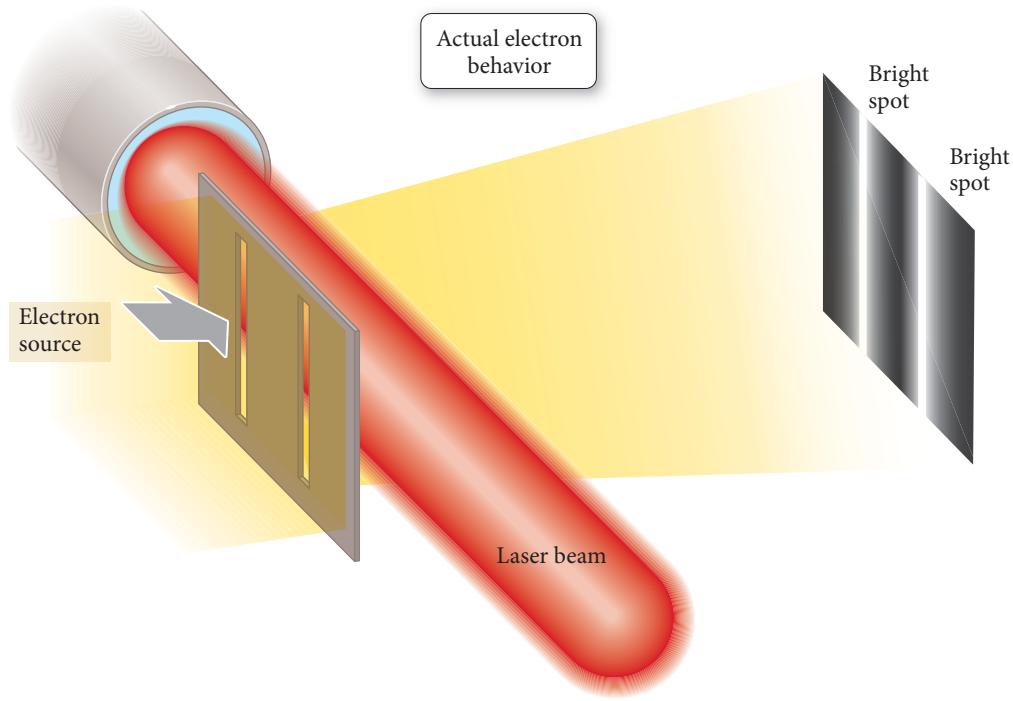
Since quantum-mechanical theory is universal, it applies to all objects, regardless of size. Therefore, according to the de Broglie relation, a thrown baseball should also exhibit wave properties. Why don't we observe such properties at the ballpark?

### The Uncertainty Principle

The wave nature of the electron is difficult to reconcile with its particle nature. How can a single entity behave as both a wave and a particle? We can begin to address this question by returning to the single-electron diffraction experiment. How does a single electron aimed at a double slit produce an interference pattern? We saw previously that the electron travels through both slits and interferes with itself. This idea is testable. We simply have to observe the single electron as it travels through both of the slits.

If it travels through both slits simultaneously, our hypothesis is correct. But here is where nature gets tricky.

Any experiment designed to observe the electron as it travels through the slits results in the detection of an electron “particle” traveling through a single slit and no interference pattern. Recall from Section 7.1 that an *unobserved* electron can occupy two different states; however, the act of observation forces it into one state or the other. Similarly, the act of observing the electron as it travels through both slits forces it to go through only one slit. The following electron diffraction experiment is designed to observe which slit the electron travels through by using a laser beam placed directly behind the slits.



An electron that crosses the laser beam produces a tiny “flash” when a single photon is scattered at the point of crossing. If a flash shows up behind a particular slit, that indicates an electron is passing through that slit. When the experiment is performed, the flash always originates either from one slit *or* the other, but *never* from both at once. Furthermore, the interference pattern, which was present without the laser, is now absent. With the laser on, the electrons hit positions directly behind each slit, as if they were ordinary particles; their wavelike behavior is no longer manifested.

As it turns out, no matter how hard we try or whatever method we set up, *we can never both see the interference pattern and simultaneously determine which hole the electron goes through*. It has never been done, and most scientists agree that it never will. In the words of P. A. M. Dirac,

There is a limit to the fineness of our powers of observation and the smallness of the accompanying disturbance—a limit which is inherent in the nature of things and can never be surpassed by improved technique or increased skill on the part of the observer.

The single electron diffraction experiment demonstrates that we cannot simultaneously observe both the wave nature and the particle nature of the electron. When we try to observe which hole the electron goes through (associated with the particle nature of the electron) we lose the interference pattern (associated with the wave nature of the electron). When we try to observe the interference pattern, we cannot determine which hole the electron goes through. The wave nature and particle nature of the electron are

said to be **complementary properties**. Complementary properties exclude one another—the more we know about one, the less we know about the other. Which of two complementary properties we observe depends on the experiment we perform—in quantum mechanics, the observation of an event affects its outcome.

As we just saw in the de Broglie relation, the *velocity* of an electron is related to its *wave nature*. The *position* of an electron, however, is related to its *particle nature*. (Particles have well-defined position, but waves do not.) Consequently, our inability to observe the electron simultaneously as both a particle and a wave means that *we cannot simultaneously measure its position and its velocity*. Werner Heisenberg formalized this idea with the equation:

$$\Delta x \times m \Delta v \geq \frac{h}{4\pi} \text{ Heisenberg's uncertainty principle} \quad [7.5]$$

where  $\Delta x$  is the uncertainty in the position,  $\Delta v$  is the uncertainty in the velocity,  $m$  is the mass of the particle, and  $h$  is Planck's constant. **Heisenberg's uncertainty principle** states that the product of  $\Delta x$  and  $m\Delta v$  must be greater than or equal to a finite number ( $h/4\pi$ ). In other words, the more accurately you know the position of an electron (the smaller  $\Delta x$ ) the less accurately you can know its velocity (the bigger  $\Delta v$ ) and vice versa. The complementarity of the wave nature and particle nature of the electron results in the complementarity of velocity and position.

Although Heisenberg's uncertainty principle may seem puzzling, it actually solves a great puzzle. Without the uncertainty principle, we are left with a paradox: how can something be *both* a particle and a wave? Saying that an object is both a particle and a wave is like saying that an object is both a circle and a square, a contradiction. Heisenberg solved the contradiction by introducing complementarity—an electron is observed as *either* a particle or a wave, but never both at once. This idea was captured by Schrodinger's thought experiment about the cat: when observed, the cat is either dead or alive, not both.



▲ Werner Heisenberg (1901–1976)

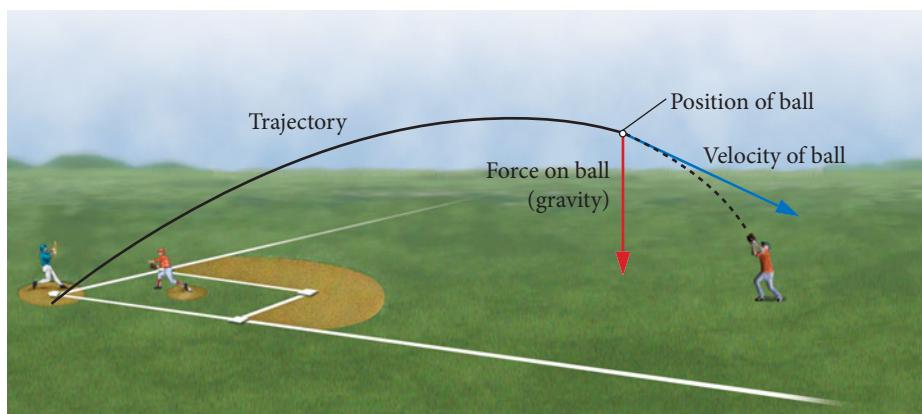
## Indeterminacy and Probability Distribution Maps

According to classical physics, and in particular Newton's laws of motion, particles move in a *trajectory* (or path) that is determined by the particle's velocity (the speed and direction of travel), its position, and the forces acting on it. Even if you are not familiar with Newton's laws, you probably have an intuitive sense of them. For example, when you chase a baseball in the outfield, you visually predict where the ball will land by observing its path. You do this by noting its initial position and velocity, watching how these are affected by the forces acting on it (gravity, air resistance, wind), and then inferring its trajectory, as shown in Figure 7.17 ▶. If you knew only the ball's velocity, or only its position (imagine a still photo of the baseball in the air), you could not predict its landing spot. In classical mechanics, both position and velocity are required to predict a trajectory.

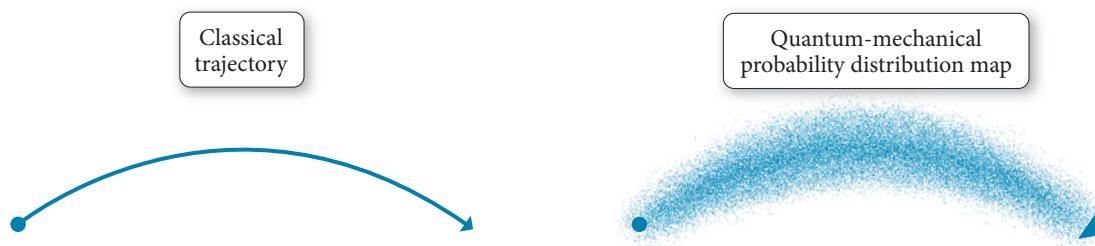
Newton's laws of motion are **deterministic**—the present *determines* the future. This means that if two baseballs are hit consecutively with the same velocity from the same

Remember that velocity includes speed as well as direction of travel.

### The Classical Concept of Trajectory



◀ **FIGURE 7.17** The Concept of Trajectory  
In classical mechanics, the position and velocity of a particle determine its future trajectory, or path. Thus, an outfielder can catch a baseball by observing its position and velocity, allowing for the effects of forces acting on it, such as gravity, and estimating its trajectory. (For simplicity, air resistance and wind are not shown.)

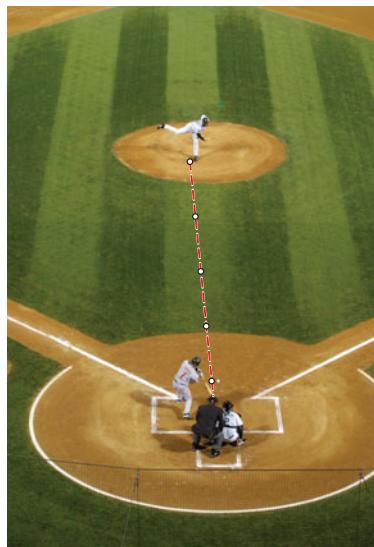


**▲ FIGURE 7.18 Trajectory versus Probability** In quantum mechanics, we cannot calculate deterministic trajectories. Instead, it is necessary to think in terms of probability maps: statistical pictures of where a quantum-mechanical particle, such as an electron, is most likely to be found. In this hypothetical map, darker shading indicates greater probability.

position under identical conditions, they will land in exactly the same place. The same is not true of electrons. We have just seen that we cannot simultaneously know the position and velocity of an electron; therefore, we cannot know its trajectory. In quantum mechanics, trajectories are replaced with *probability distribution maps*, as shown in Figure 7.18 ▲. A probability distribution map is a statistical map that shows where an electron is likely to be found under a given set of conditions.

To understand the concept of a probability distribution map, let us return to baseball. Imagine a baseball thrown from the pitcher's mound to a catcher behind home plate (Figure 7.19 ◀.) The catcher can watch the baseball's path, predict exactly where it will cross home plate, and place his mitt in the correct place to catch it. As we have seen, the same predictions cannot be made for an electron. If an electron were thrown from the pitcher's mound to home plate, it would land in a different place every time, even if it were thrown in exactly the same way. This behavior is called **indeterminacy**. Unlike a baseball, whose future path is *determined* by its position and velocity when it leaves the pitcher's hand, the future path of an electron is indeterminate, and can only be described statistically.

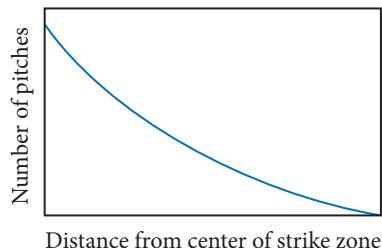
In the quantum-mechanical world of the electron, the catcher cannot know exactly where the electron will cross the plate for any given throw. However, if he were to record hundreds of identical electron throws, the catcher would observe a reproducible, *statistical pattern* of where the electron crosses the plate. He could even draw a map of the strike zone showing the probability of an electron crossing a certain area, as shown in Figure 7.20 ▼. This would be a probability distribution map. In the sections that follow, we discuss quantum-mechanical electron *orbitals*, which are essentially probability distribution maps for electrons as they exist within atoms.



**▲ FIGURE 7.19 Trajectory of a Macroscopic Object** A baseball follows a well-defined trajectory from the hand of the pitcher to the mitt of the catcher.



The Quantum-Mechanical Strike Zone



**▲ FIGURE 7.20 The Quantum-Mechanical Strike Zone** An electron does not have a well-defined trajectory. However, we can construct a probability distribution map to show the relative probability of it crossing home plate at different points.

## 7.5 Quantum Mechanics and the Atom

As we have seen, the position and velocity of the electron are complementary properties—if we know one accurately, the other becomes indeterminate. Since velocity is directly related to energy (recall that kinetic energy equals  $\frac{1}{2}mv^2$ ), position and *energy* are also complementary properties—the more we know about one, the less we know about the other. Many of the properties of an element, however, depend on the energies of its electrons. For example, whether an electron is transferred from one atom to another to form an ionic bond depends in part on the relative energies of the electron in the two atoms. In the following paragraphs, we describe the probability distribution maps for electron states in which the electron has well-defined energy, but not well-defined position. In other words, for each of these states, we can specify the *energy* of the electron precisely, but not its location at a given instant. Instead, the electron's position is described in terms of an **orbital**, a probability distribution map showing where the electron is likely to be found. Since chemical bonding often involves the sharing of electrons between atoms to form covalent bonds, the spatial distribution of atomic electrons is important to bonding.

The mathematical derivation of energies and orbitals for electrons in atoms comes from solving the *Schrödinger* equation for the atom of interest. The general form of the Schrödinger equation is:

$$\mathcal{H}\psi = E\psi \quad [7.6]$$

The symbol  $\mathcal{H}$  stands for the Hamiltonian operator, a set of mathematical operations that represent the total energy (kinetic and potential) of the electron within the atom. The symbol  $E$  is the actual energy of the electron. The symbol  $\psi$  is the **wave function**, a mathematical function that describes the wavelike nature of the electron. A plot of the wave function squared ( $\psi^2$ ) represents an orbital, a position probability distribution map of the electron.

These states are known as *energy eigenstates*.

An operator is different from a normal algebraic entity. In general, an operator transforms a mathematical function into another mathematical function. For example,  $d/dx$  is an operator that means “take the derivative of.” When  $d/dx$  operates on a function (such as  $x^2$ ) it returns another function ( $2x$ ).

The symbol  $\psi$  is the Greek letter psi, pronounced “sigh.”

### Solutions to the Schrödinger Equation for the Hydrogen Atom

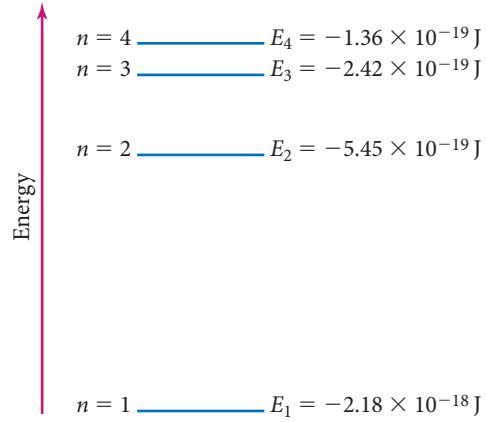
When the Schrödinger equation is solved, it yields many solutions—many possible wave functions. The wave functions themselves are fairly complicated mathematical functions, and we do not examine them in detail in this book. Instead, we will introduce graphical representations (or plots) of the orbitals that correspond to the wave functions. Each orbital is specified by three interrelated **quantum numbers**:  $n$ , the **principal quantum number**;  $l$ , the **angular momentum quantum number** (sometimes called the *azimuthal quantum number*); and  $m_l$ , the **magnetic quantum number**. These quantum numbers all have integer values, as had been hinted at by both the Rydberg equation and Bohr's model. A fourth quantum number,  $m_s$ , the **spin quantum number**, specifies the orientation of the spin of the electron. We examine each of these quantum numbers individually.

**The Principal Quantum Number ( $n$ )** The principal quantum number is an integer that determines the overall size and energy of an orbital. Its possible values are  $n = 1, 2, 3, \dots$  and so on. For the hydrogen atom, the energy of an electron in an orbital with quantum number  $n$  is given by the equation:

$$E_n = -2.18 \times 10^{-18} \text{ J} \left( \frac{1}{n^2} \right) \quad (n = 1, 2, 3, \dots) \quad [7.7]$$

The energy is negative because the electron's energy is lowered (made more negative) by its interaction with the nucleus (see the description of Coulomb's law in Section 8.3). The constant,  $2.18 \times 10^{-18} \text{ J}$ , is known as the Rydberg constant for hydrogen ( $R_H$ ). Notice that orbitals with higher values of  $n$  have greater (less negative) energies, as shown in the energy level diagram at right. Notice also that, as  $n$  increases, the spacing between the energy levels becomes smaller.

**The Angular Momentum Quantum Number ( $l$ )** The angular momentum quantum number is an integer that determines the shape of the orbital. We will consider these shapes in Section 7.6. The possible values of  $l$  are  $0, 1, 2, \dots, (n - 1)$ . In other words, for a given value of  $n$ ,  $l$  can be any integer (including 0) up to  $n - 1$ .



For example, if  $n = 1$ , then the only possible value of  $l$  is 0; if  $n = 2$ , the possible values of  $l$  are 0 and 1. To avoid confusion between  $n$  and  $l$ , values of  $l$  are often assigned letters as follows:

The values of  $l$  beyond 3 are designated with letters in alphabetical order so that  $l = 4$  is designated  $g$ ,  $l = 5$  is designated  $h$ , and so on.

Value of $l$	Letter Designation
$l = 0$	$s$
$l = 1$	$p$
$l = 2$	$d$
$l = 3$	$f$

### Conceptual Connection 7.3 The Relationship between $n$ and $l$ .

What values of  $l$  are possible for  $n = 3$ ?

- (a) 0 (or  $s$ )
- (b) 0 and 1 (or  $s$  and  $p$ )
- (c) 0, 1, and 2 (or  $s$ ,  $p$ , and  $d$ )
- (d) 0, 1, 2, and 3 (or  $s$ ,  $p$ ,  $d$ , and  $f$ )

**The Magnetic Quantum Number ( $m_l$ )** The magnetic quantum number is an integer that specifies the orientation of the orbital. We will consider these orientations in Section 7.6. The possible values of  $m_l$  are the integer values (including zero) ranging from  $-l$  to  $+l$ . For example, if  $l = 0$  then the only possible value of  $m_l$  is 0; if  $l = 1$ , the possible values of  $m_l$  are  $-1$ , 0, and  $+1$ .

### Conceptual Connection 7.4 The Relationship between $l$ and $m_l$ .

What values of  $m_l$  are possible for  $l = 2$ ?

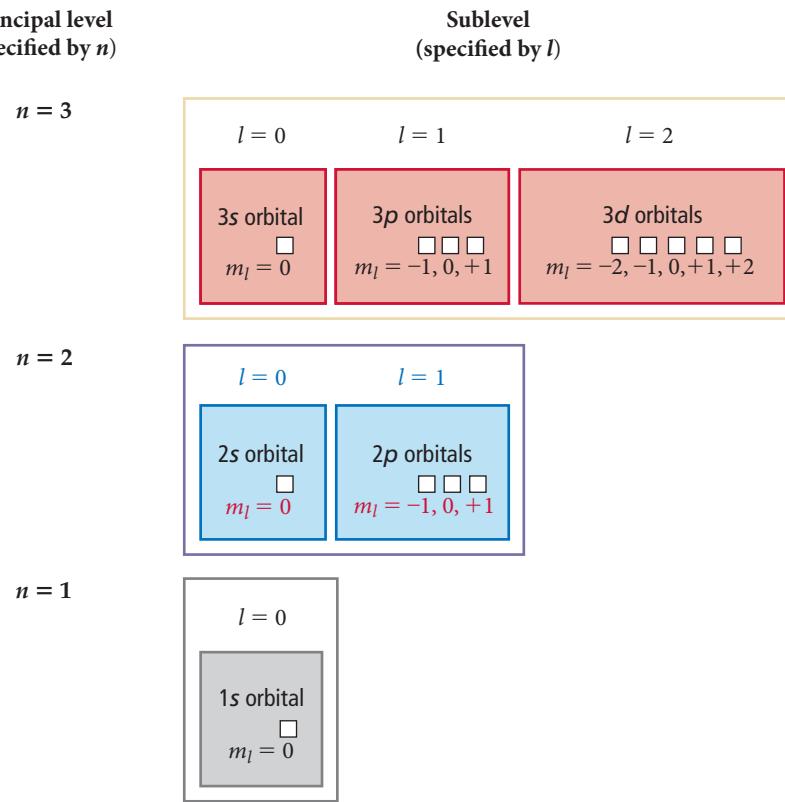
- (a) 0, 1, and 2
- (b) 0
- (c)  $-1$ , 0 and  $+1$
- (d)  $-2$ ,  $-1$ , 0,  $+1$ , and  $+2$

The idea of a “spinning” electron is something of a metaphor. A more correct way to express the same idea is to say that an electron has inherent angular momentum.

**The Spin Quantum Number ( $m_s$ )** The spin quantum number specifies the orientation of the *spin* of the electron. Electron spin is a fundamental property of an electron (like its negative charge). One electron does not have more or less spin than another—all electrons have the same amount of spin. The orientation of the electron’s spin is quantized, with only two possibilities: that we can call spin up ( $m_s = +1/2$ ) and spin down ( $m_s = -1/2$ ). The spin quantum number becomes important in Section 8.3 when we begin to consider how electrons occupy orbitals. For now, we will focus on the first three quantum numbers.

Each specific combination of the first three quantum numbers ( $n$ ,  $l$ , and  $m_l$ ) specifies one atomic orbital. For example, the orbital with  $n = 1$ ,  $l = 0$ , and  $m_l = 0$  is known as the  $1s$  orbital. The 1 in  $1s$  is the value of  $n$  and the  $s$  specifies that  $l = 0$ . There is only one  $1s$  orbital in an atom, and its  $m_l$  value is zero. Orbitals with the same value of  $n$  are said to be in the same **principal level (or principal shell)**. Orbitals with the same value of  $n$  and  $l$  are said to be in the same **sublevel (or subshell)**.

The following diagram shows all of the orbitals (each represented by a small square) in the first three principal levels.



For example, the  $n = 2$  level contains the  $l = 0$  and  $l = 1$  sublevels. Within the  $n = 2$  level, the  $l = 0$  sublevel—called the  $2s$  sublevel—contains only one orbital (the  $2s$  orbital), with  $m_l = 0$ . The  $l = 1$  sublevel—called the  $2p$  sublevel—contains three  $2p$  orbitals, with  $m_l = -1, 0, +1$ .

In general, notice the following:

- The number of sublevels in any level is equal to  $n$ , the principal quantum number. Therefore, the  $n = 1$  level has one sublevel, the  $n = 2$  level has two sublevels, etc.
- The number of orbitals in any sublevel is equal to  $2l + 1$ . Therefore, the  $s$  sublevel ( $l = 0$ ) has one orbital, the  $p$  sublevel ( $l = 1$ ) has three orbitals, the  $d$  sublevel ( $l = 2$ ) has five orbitals, etc.
- The number of orbitals in a level is equal to  $n^2$ . Therefore, the  $n = 1$  level has one orbital, the  $n = 2$  level has four orbitals, the  $n = 3$  level has nine orbitals, etc.

### EXAMPLE 7.5 Quantum Numbers I

What are the quantum numbers and names (for example,  $2s$ ,  $2p$ ) of the orbitals in the  $n = 4$  principal level? How many  $n = 4$  orbitals exist?

#### SOLUTION

First determine the possible values of  $l$  (from the given value of  $n$ ). For a given value of  $n$ , the possible values of  $l$  are  $0, 1, 2, \dots, (n - 1)$ .

$n = 4$ ; therefore,  $l = 0, 1, 2$ , and  $3$

Next, determine the the possible values of  $m_l$  for each value of  $l$ . For a given value of  $l$ , the possible values of  $m_l$  are the integer values including zero ranging from  $-l$  to  $+l$ . The name of an orbital is its principal quantum number ( $n$ ) followed by the letter corresponding to the value  $l$ . The total number of orbitals is given by  $n^2$ .

$l$	Possible $m_l$ Values	Orbital name
0	0	$4s$ (1 orbital)
1	$-1, 0, +1$	$4p$ (3 orbitals)
2	$-2, -1, 0, +1, +2$	$4d$ (5 orbitals)
3	$-3, -2, -1, 0, +1, +2, +3$	$4f$ (7 orbitals)
Total number of orbitals = $4^2 = 16$		

#### FOR PRACTICE 7.5

List the quantum numbers associated with all of the  $5d$  orbitals. How many  $5d$  orbitals exist?

#### EXAMPLE 7.6 Quantum Numbers II

These sets of quantum numbers are each supposed to specify an orbital. One set, however, is erroneous. Which one and why?

- |                             |                              |
|-----------------------------|------------------------------|
| (a) $n = 3; l = 0; m_l = 0$ | (b) $n = 2; l = 1; m_l = -1$ |
| (c) $n = 1; l = 0; m_l = 0$ | (d) $n = 4; l = 1; m_l = -2$ |

#### SOLUTION

Choice (d) is erroneous because for  $l = 1$ , the possible values of  $m_l$  are only  $-1, 0$ , and  $+1$ .

#### FOR PRACTICE 7.6

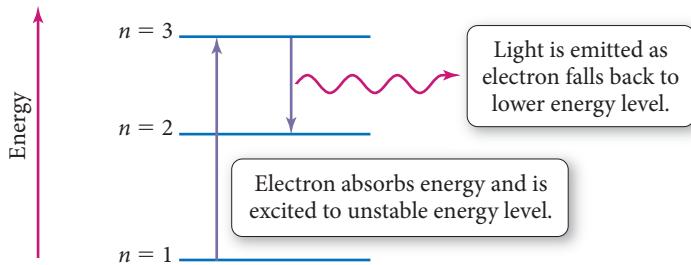
Each set of quantum numbers is supposed to specify an orbital. However, each set contains one quantum number that is not allowed. Replace the quantum number that is not allowed with one that is allowed.

- |                              |
|------------------------------|
| (a) $n = 3; l = 3; m_l = +2$ |
| (b) $n = 2; l = 1; m_l = -2$ |
| (c) $n = 1; l = 1; m_l = 0$  |

### Atomic Spectroscopy Explained

Quantum theory explains the atomic spectra of atoms discussed in Section 7.3. Each wavelength in the emission spectrum of an atom corresponds to an electron *transition* between quantum-mechanical orbitals. When an atom absorbs energy, an electron in a lower energy orbital is *excited* or promoted to a higher energy orbital, as shown in Figure 7.21 ▶. In this new configuration, however, the atom is unstable, and the

#### Excitation and Radiation



#### ► FIGURE 7.21 Excitation and Radiation

When an atom absorbs energy, an electron can be excited from an orbital in a lower energy level to an orbital in a higher energy level. The electron in this “excited state” is unstable, however, and relaxes to a lower energy level, releasing energy in the form of electromagnetic radiation.

electron quickly falls back or *relaxes* to a lower energy orbital. As it does so, it releases a photon of light containing an amount of energy precisely equal to the energy difference between the two energy levels. We saw previously (see Equation 7.7) that the energy of an orbital in a hydrogen atom with principal quantum number  $n$  is given by  $E_n = -2.18 \times 10^{-18} \text{ J}(1/n^2)$ , where  $n = 1, 2, 3, \dots$ . Therefore, the *difference* in energy between two levels  $n_{\text{initial}}$  and  $n_{\text{final}}$  is given by  $\Delta E = E_{\text{final}} - E_{\text{initial}}$ . If we substitute the expression for  $E_n$  into the expression for  $\Delta E$ , we get the following important expression for the change in energy that occurs in a hydrogen atom when an electron changes energy levels:

$$\begin{aligned}\Delta E &= E_{\text{final}} - E_{\text{initial}} \\ &= -2.18 \times 10^{-18} \text{ J}\left(\frac{1}{n_f^2}\right) - \left[-2.18 \times 10^{-18} \text{ J}\left(\frac{1}{n_i^2}\right)\right] \\ \Delta E &= -2.18 \times 10^{-18} \text{ J}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)\end{aligned}\quad [7.8]$$

For example, suppose that an electron in a hydrogen atom relaxes from an orbital in the  $n = 3$  level to an orbital in the  $n = 2$  level. Then  $\Delta E$ , the energy difference corresponding to the transition from  $n = 3$  to  $n = 2$ , is determined as follows:

$$\begin{aligned}\Delta E_{\text{atom}} &= E_2 - E_3 \\ &= -2.18 \times 10^{-18} \text{ J}\left(\frac{1}{2^2}\right) - \left[-2.18 \times 10^{-18} \text{ J}\left(\frac{1}{3^2}\right)\right] \\ &= -2.18 \times 10^{-18} \text{ J}\left(\frac{1}{2^2} - \frac{1}{3^2}\right) \\ &= -3.03 \times 10^{-19} \text{ J}\end{aligned}$$

The energy carries a negative sign because the atom *emits* the energy as it relaxes from  $n = 3$  to  $n = 2$ . Since energy must be conserved, the exact amount of energy emitted by the atom is carried away by the photon:

$$\Delta E_{\text{atom}} = -E_{\text{photon}}$$

This energy then determines the frequency and wavelength of the photon. Since the wavelength of the photon is related to its energy as  $E = hc/\lambda$ , we calculate the wavelength of the photon as:

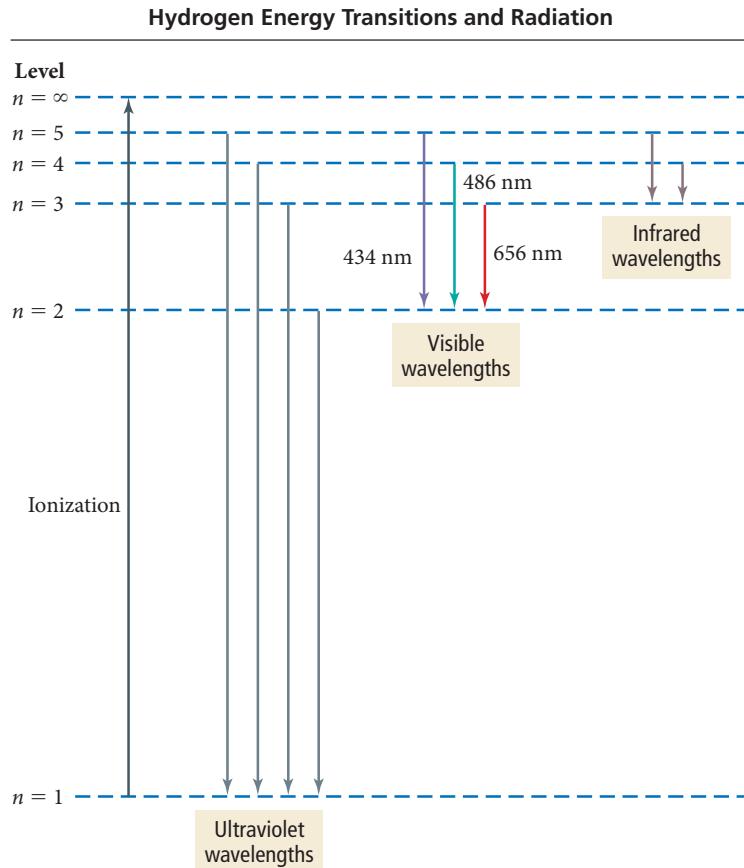
$$\begin{aligned}\lambda &= \frac{hc}{E} \\ &= \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{3.03 \times 10^{-19} \text{ J}} \\ &= 6.56 \times 10^{-7} \text{ m or } 656 \text{ nm}\end{aligned}$$

Consequently, the light emitted by an excited hydrogen atom as it relaxes from an orbital in the  $n = 3$  level to an orbital in the  $n = 2$  level has a wavelength of 656 nm (red). Similarly, we can calculate the light emitted due to a transition from  $n = 4$  to  $n = 2$  to be 486 nm (green). Notice that transitions between orbitals that are further apart in energy produce light that is higher in energy, and therefore shorter in wavelength, than transitions between orbitals that are closer together. Figure 7.22 ► shows several of the transitions in the hydrogen atom and their corresponding wavelengths.

**The Rydberg equation,**  
 $1/\lambda = R(1/m^2 - 1/n^2)$ , can be  
 derived from the relationships just covered.  
 We leave this derivation to an exercise  
 (see Problem 7.96).

**► FIGURE 7.22** Hydrogen Energy

**Transitions and Radiation** An atomic energy level diagram for hydrogen, showing some possible electron transitions between levels and the corresponding wavelengths of emitted light.



### Conceptual Connection 7.5 Emission Spectra

Which transition results in emitted light with the shortest wavelength?

- (a)  $n = 5 \longrightarrow n = 4$     (b)  $n = 4 \longrightarrow n = 3$     (c)  $n = 3 \longrightarrow n = 2$

### EXAMPLE 7.7 Wavelength of Light for a Transition in the Hydrogen Atom

Determine the wavelength of light emitted when an electron in a hydrogen atom makes a transition from an orbital in  $n = 6$  to an orbital in  $n = 5$ .

**SORT** You are given the energy levels of an atomic transition and asked to find the wavelength of emitted light.

**STRATEGIZE** In the first part of the conceptual plan, calculate the energy of the electron in the  $n = 6$  and  $n = 5$  orbitals using Equation 7.7 and subtract to find  $\Delta E_{\text{atom}}$ .

In the second part, find  $E_{\text{photon}}$  by taking the negative of  $\Delta E_{\text{atom}}$  and then calculate the wavelength corresponding to a photon of this energy using Equation 7.3. (The difference in sign between  $E_{\text{photon}}$  and  $\Delta E_{\text{atom}}$  applies only to emission. *The energy of a photon must always be positive.*)

**GIVEN:**  $n = 6 \longrightarrow n = 5$

**FIND:**  $\lambda$

#### CONCEPTUAL PLAN

$$\begin{array}{ccc} n = 5, n = 6 & \xrightarrow{\hspace{1cm}} & \Delta E_{\text{atom}} \\ & & \Delta E = E_5 - E_6 \end{array}$$

$$\begin{array}{ccccc} \Delta E_{\text{atom}} & \xrightarrow{\hspace{1cm}} & E_{\text{photon}} & \xrightarrow{\hspace{1cm}} & \lambda \\ \Delta E_{\text{atom}} = -E_{\text{photon}} & & & & E = \frac{hc}{\lambda} \end{array}$$

#### RELATIONSHIPS USED

$$E_n = -2.18 \times 10^{-18} \text{ J} (1/n^2)$$

$$E = hc/\lambda$$

**SOLVE** Follow the conceptual plan. Begin by calculating  $\Delta E_{\text{atom}}$ .

**SOLUTION**

$$\begin{aligned}\Delta E_{\text{atom}} &= E_5 - E_6 \\ &= -2.18 \times 10^{-18} \text{ J} \left( \frac{1}{5^2} \right) - \left[ -2.18 \times 10^{-18} \text{ J} \left( \frac{1}{6^2} \right) \right] \\ &= -2.18 \times 10^{-18} \text{ J} \left( \frac{1}{5^2} - \frac{1}{6^2} \right) \\ &= -2.6644 \times 10^{-20} \text{ J}\end{aligned}$$

Calculate  $E_{\text{photon}}$  by changing the sign of  $\Delta E_{\text{atom}}$ .

$$E_{\text{photon}} = -\Delta E_{\text{atom}} = +2.6644 \times 10^{-20} \text{ J}$$

Solve the equation relating the energy of a photon to its wavelength for  $\lambda$ . Substitute the energy of the photon and calculate  $\lambda$ .

$$\begin{aligned}E &= \frac{hc}{\lambda} \\ \lambda &= \frac{hc}{E} \\ &= \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{2.6644 \times 10^{-20} \text{ J}} \\ &= 7.46 \times 10^{-6} \text{ m or } 7460 \text{ nm}\end{aligned}$$

**CHECK** The units of the answer (m) are correct for wavelength. The magnitude is reasonable because  $10^{-6}$  m is in the infrared region of the electromagnetic spectrum. We know that transitions from  $n = 3$  or  $n = 4$  to  $n = 2$  lie in the visible region, so it makes sense that a transition between levels of higher  $n$  value (which are energetically closer to one another) would result in light of longer wavelength.

**FOR PRACTICE 7.7**

Determine the wavelength of the light absorbed when an electron in a hydrogen atom makes a transition from an orbital in which  $n = 2$  to an orbital in which  $n = 7$ .

**FOR MORE PRACTICE 7.7**

An electron in the  $n = 6$  level of the hydrogen atom relaxes to a lower energy level, emitting light of  $\lambda = 93.8$  nm. Find the principal level to which the electron relaxed.

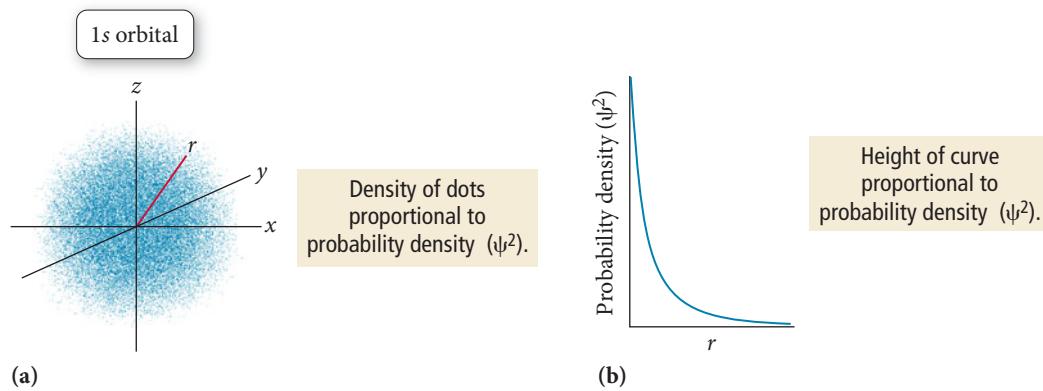
## 7.6 The Shapes of Atomic Orbitals

As we noted previously, the shapes of atomic orbitals are important because covalent chemical bonds depend on the sharing of the electrons that occupy these orbitals. In one model of chemical bonding, for example, a bond consists of the overlap of atomic orbitals on adjacent atoms. The shapes of the overlapping orbitals determine the shape of the molecule. Although we limit ourselves in this chapter to the orbitals of the hydrogen atom, we will see in Chapter 8 that the orbitals of all atoms can be approximated as being hydrogen-like and therefore having very similar shapes to those of hydrogen.

The shape of an atomic orbital is determined primarily by  $l$ , the angular momentum quantum number. Recall that each value of  $l$  is assigned a letter that corresponds to particular orbitals. For example, the orbitals with  $l = 0$  are called  $s$  orbitals; those with  $l = 1$ ,  $p$  orbitals; those with  $l = 2$ ,  $d$  orbitals, etc. We now examine the shape of each of these orbitals.

### s Orbitals ( $l = 0$ )

The lowest energy orbital is the spherically symmetrical  $1s$  orbital shown in Figure 7.23(a) ►. This image is actually a three-dimensional plot of the wave function



▲ FIGURE 7.23 The 1s Orbital: Two Representations In (a) the dot density is proportional to the electron probability density. In (b), the height of the curve is proportional to the electron probability density. The  $x$ -axis is  $r$ , the distance from the nucleus.

squared ( $\psi^2$ ), which represents **probability density**, the probability (per unit volume) of finding the electron at a point in space.

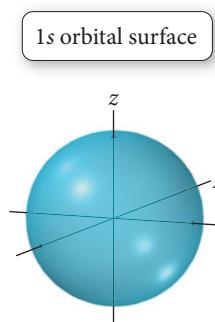
$$\psi^2 = \text{probability density} = \frac{\text{probability}}{\text{unit volume}}$$

The magnitude of  $\psi^2$  in this plot is proportional to the density of the dots shown in the image. The high dot density near the nucleus (at the very center of the plot) indicates a higher probability density for the electron there. As you move away from the nucleus, the probability density decreases. Figure 7.23(b) ▲ shows a plot of probability density ( $\psi^2$ ) versus  $r$ , the distance from the nucleus. The plot represents a slice through the three-dimensional plot of  $\psi^2$  and shows how the probability density decreases as  $r$  increases.

We can understand probability density with the help of a thought experiment. Imagine an electron in the 1s orbital located within the volume surrounding the nucleus. Imagine also taking a photograph of the electron every second for 10 or 15 minutes. In one photograph, the electron is very close to the nucleus, in another it is farther away, and so on. Each photo has a dot showing the electron's position relative to the nucleus when the photo was taken. Remember that you can never predict where the electron will be for any one photo. However, if you took hundreds of photos and superimposed all of them, you would have a plot similar to Figure 7.23(a)—a statistical representation of how likely the electron is to be found at each point.

The thought experiment we just examined can result in a possible misunderstanding: that the electron is moving around (like a moth near a flame) between photographs. However, in the quantum-mechanical model, that is not the case. Between photographs, the location of the electron is uncertain—in a sense its location is spread out over the entire volume of the orbital. Only when the photograph is taken (that is, when a measurement of its location is made) does the location of the electron become localized to one spot. Between measurements, the electron has no single location. Recall from Section 7.1 that the measurement affects the outcome of any quantum system.

An atomic orbital can also be represented by a geometrical shape that encompasses the volume where the electron is likely to be found most frequently—typically, 90% of the time. For example, the 1s orbital can be represented as the three-dimensional sphere shown in Figure 7.24 ◀. If we were to superimpose the dot-density representation of the 1s orbital on the shape representation, 90% of the dots would be within the sphere, meaning that when the electron is in the 1s orbital it has a 90% chance of being found within the sphere.



▲ FIGURE 7.24 The 1s Orbital Surface

In this representation, the surface of the sphere encompasses the volume where the electron is found 90% of the time when the electron is in the 1s orbital.

The plots we have just seen represent probability *density*. However, they are a bit misleading because they seem to imply that the electron is most likely to be found *at the nucleus*. To get a better idea of where the electron is most likely to be found, we can use a plot called the **radial distribution function**, shown in Figure 7.25 ► for the 1s orbital. The radial distribution function represents the *total probability of finding the electron within a thin spherical shell at a distance r from the nucleus*.

$$\text{Total radial probability (at a given } r) = \frac{\text{probability}}{\text{unit volume}} \times \text{volume of shell at } r$$

The radial distribution function represents, not probability density *at a point r*, but total probability *at a radius r*. In contrast to probability density, which has a maximum at the nucleus, the radial distribution function has a value of *zero* at the nucleus. It increases to a maximum at 52.9 pm and then decreases again with increasing *r*.

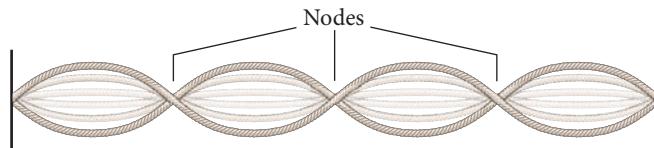
The shape of the radial distribution function is the result of multiplying together two functions with opposite trends in *r*:

1. The probability density function ( $\psi^2$ ), which is the probability per unit volume, has a maximum at the nucleus, and decreases with increasing *r*.
2. The volume of the thin shell, which is zero at the nucleus and increases with increasing *r*.

At the nucleus (*r* = 0), for example, the probability *density* is at a maximum; however, the volume of a thin spherical shell is zero, so the radial distribution function is zero. As *r* increases, the volume of the thin spherical shell increases. We can understand this by making an analogy to an onion. A spherical shell at a distance *r* from the nucleus is like a layer in an onion at a distance *r* from its center. If the layers of the onion all have the same thickness, then the volume of any one layer—think of this as the total amount of onion in the layer—is greater as *r* increases. Similarly, the volume of any one spherical shell in the radial distribution function increases with increasing distance from the nucleus, resulting in a greater total probability of finding the electron within that shell. Close to the nucleus, this increase in volume with increasing *r* outpaces the decrease in probability density, producing a maximum at 52.9 pm. Farther out, however, the density tapers off faster than the volume increases.

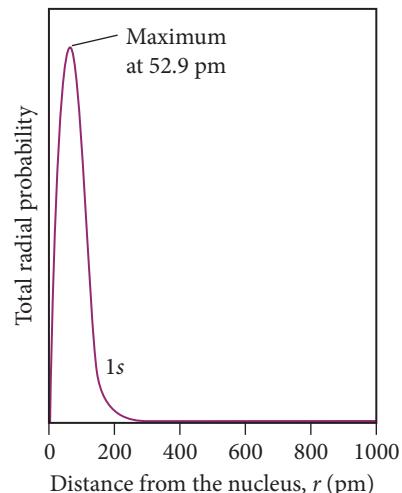
The maximum in the radial distribution function, 52.9 pm, turns out to be the very same radius that Bohr had predicted for the innermost orbit of the hydrogen atom. However, there is a significant conceptual difference between the two radii. In the Bohr model, every time you probe the atom (in its lowest energy state), you would find the electron at a radius of 52.9 pm. In the quantum-mechanical model, you would generally find the electron at various radii, with 52.9 pm having the greatest probability.

The probability densities and radial distribution functions for the 2s and 3s orbitals are shown in Figure 7.26 ►. Like the 1s orbital, these orbitals are spherically symmetric. These orbitals are larger in size than the 1s orbital, and, unlike the 1s orbital, they contain at least one **node**. A **node** is a point where the wave function ( $\psi$ ), and therefore the probability density ( $\psi^2$ ) and radial distribution function, all go through zero. A node in a wave function is much like a node in a standing wave on a vibrating string. We can see nodes in an orbital most clearly by looking at a slice through the orbital. Plots of probability density and the radial distribution function as a function of *r* both reveal the presence of nodes. The probability of finding the electron at a node is zero.



▲ The nodes in quantum-mechanical atomic orbitals are three-dimensional analogs of the nodes on a vibrating string.

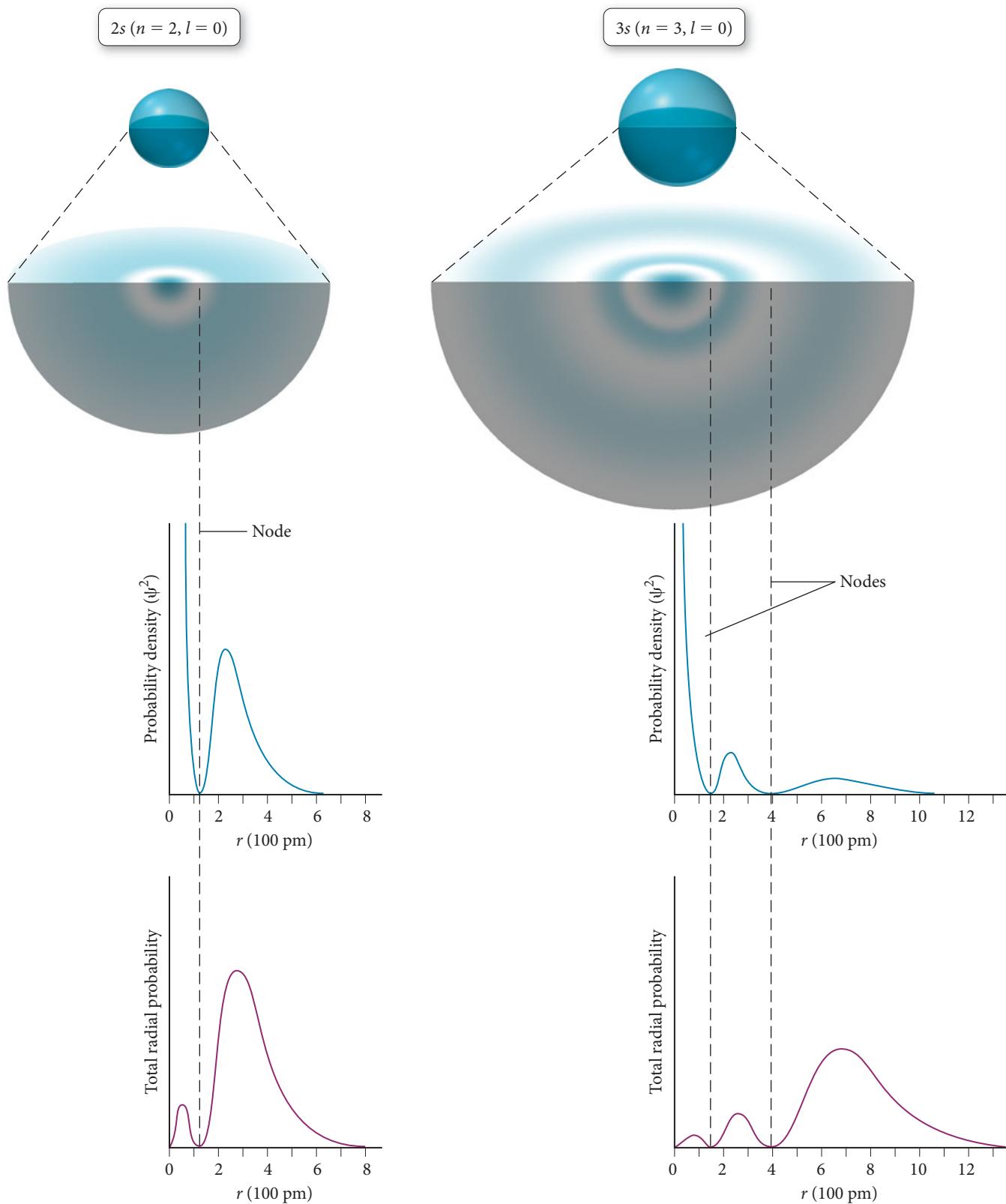
### 1s Radial Distribution Function



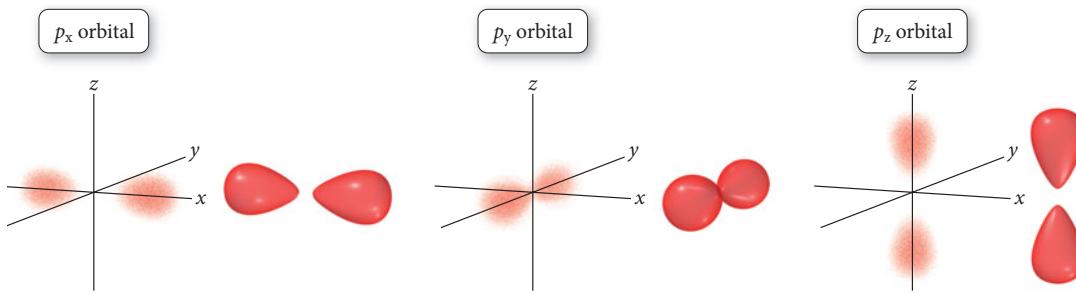
▲ FIGURE 7.25 The Radial Distribution Function for the 1s Orbital The curve shows the total probability of finding the electron within a thin shell at a distance *r* from the nucleus.

| 1 pm =  $10^{-12}$  m

### The 2s and 3s Orbitals

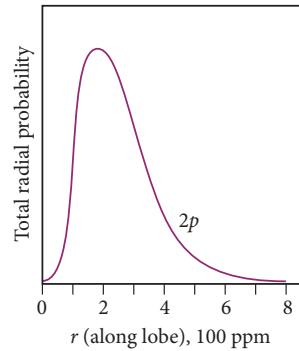


▲ FIGURE 7.26 Probability Densities and Radial Distribution Functions for the 2s and 3s Orbitals.



**▲ FIGURE 7.27** The  $2p$  Orbitals and Their Radial Distribution Function The radial distribution function is the same for all three  $2p$  orbitals when the  $x$ -axis of the graph is taken as the axis containing the lobes of the orbital.

Radial Distribution Function



## p Orbitals ( $l = 1$ )

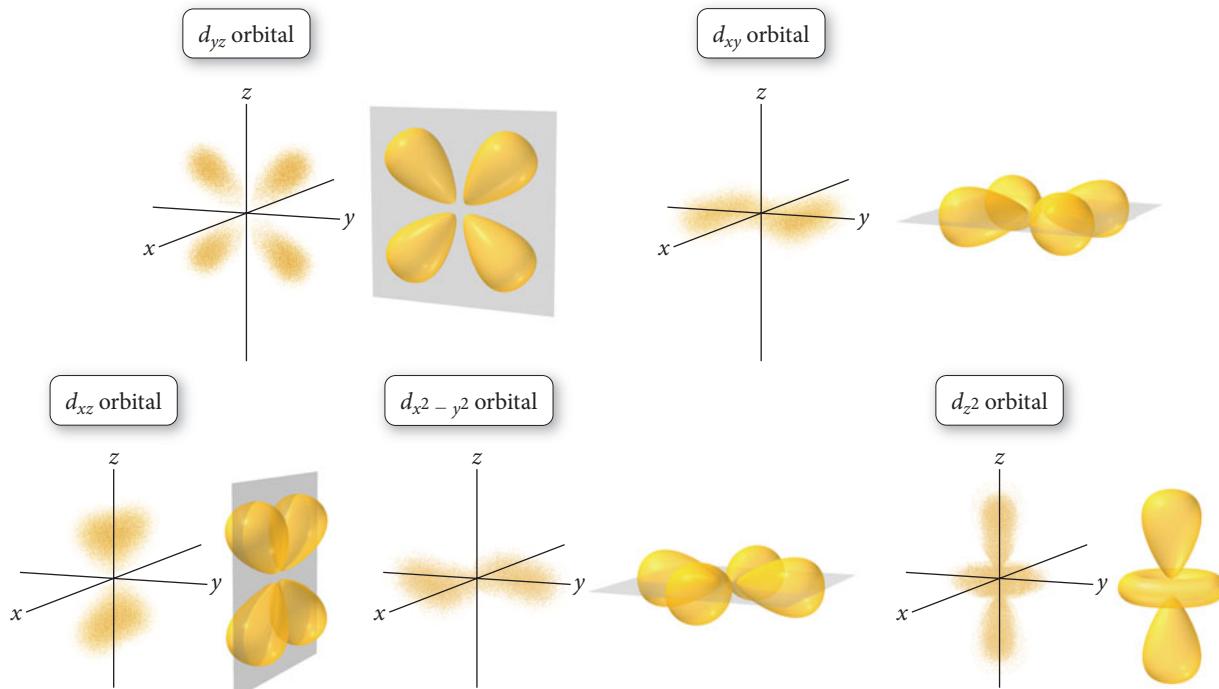
Each principal level with  $n = 2$  or greater contains three  $p$  orbitals ( $m_l = -1, 0, +1$ ). The three  $2p$  orbitals and their radial distribution functions are shown in Figure 7.27 ▲. The  $p$  orbitals are not spherically symmetric like the  $s$  orbitals, but they have two *lobes* of electron density on either side of the nucleus and a node located at the nucleus. The three  $p$  orbitals differ only in their orientation and are orthogonal (mutually perpendicular) to one another. It is convenient to define an  $x$ ,  $y$ , and  $z$  axis system and then label each  $p$  orbital as  $p_x$ ,  $p_y$  and  $p_z$ . The  $3p$ ,  $4p$ ,  $5p$ , and higher  $p$  orbitals are all similar in shape to the  $2p$  orbitals, but they contain additional nodes (like the higher  $s$  orbitals) and are progressively larger in size.

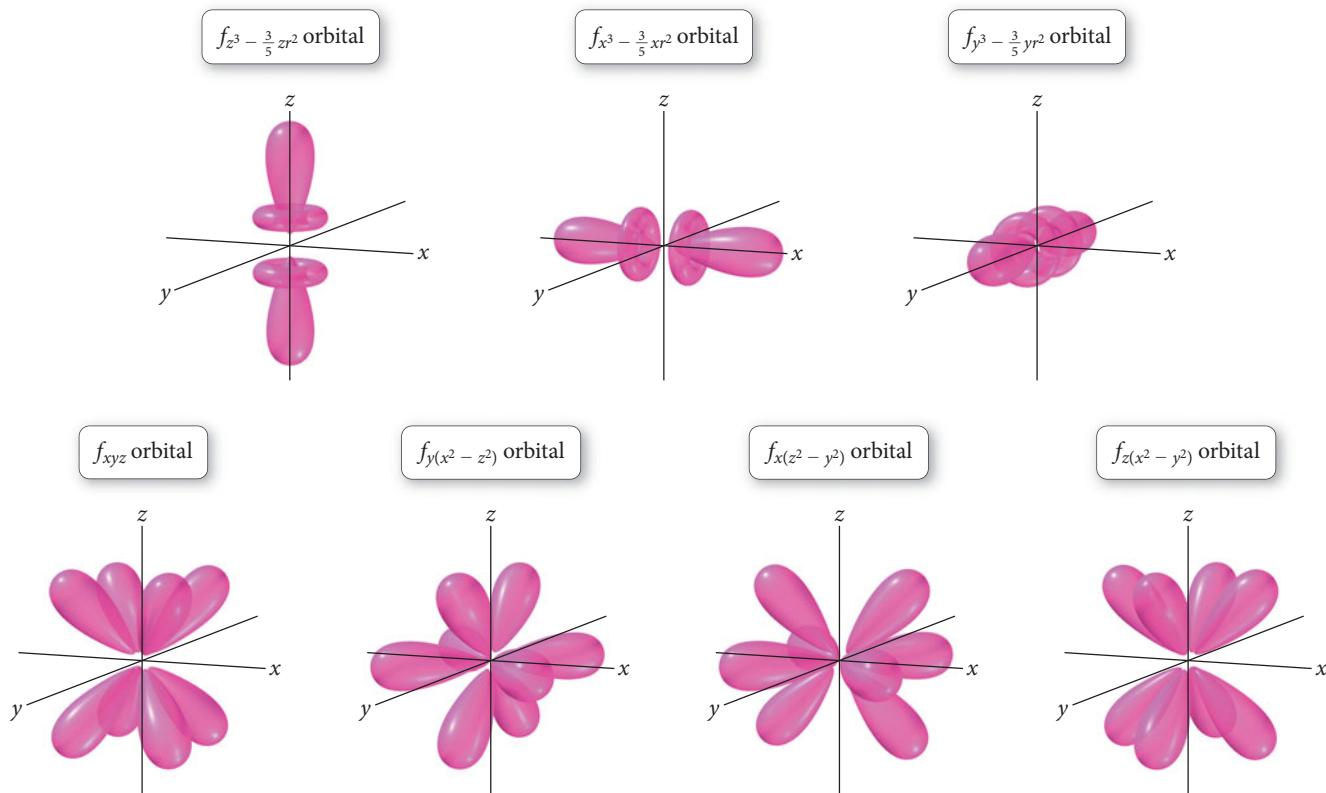
## d Orbitals ( $l = 2$ )

Each principal level with  $n = 3$  or greater contains five  $d$  orbitals ( $m_l = -2, -1, 0, +1, +2$ ). The five  $3d$  orbitals are shown in Figure 7.28 ▼. Four of these orbitals have a cloverleaf shape, with four lobes of electron density around the nucleus and two perpendicular nodal planes. The  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals are oriented along the  $xy$ ,  $xz$ , and  $yz$  planes, respectively, and their lobes are oriented *between* the corresponding axes. The four lobes of the  $d_{x^2-y^2}$  orbital are oriented along the  $x$ - and  $y$ -axes. The  $d_{z^2}$  orbital is different in shape from the other four, having two lobes oriented along the  $z$ -axis and a donut-shaped ring along the  $xy$  plane. The  $4d$ ,  $5d$ ,  $6d$ , etc., orbitals are all similar in shape to the  $3d$  orbitals, but they contain additional nodes and are progressively larger in size.

A nodal plane is a plane where the electron probability density is zero. For example, in the  $d_{xy}$  orbitals, the nodal planes lie in the  $xz$  and  $yz$  planes.

**▼ FIGURE 7.28** The  $3d$  Orbitals.





▲ FIGURE 7.29 The 4f Orbitals.

### f Orbitals ( $l = 3$ )

Each principal level with  $n = 4$  or greater contains seven  $f$  orbitals ( $m_l = -3, -2, -1, 0, +1, +2, +3$ ), as shown in Figure 7.29 ▲. These  $f$  orbitals have more lobes and nodes than  $d$  orbitals.

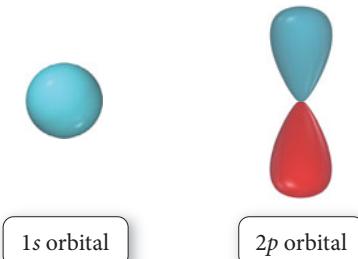
### The Phase of Orbitals

The orbitals we have just shown are three-dimensional waves. We can understand an important property of these orbitals by analogy to one-dimensional waves. Consider the following one-dimensional waves:



The wave on the left has a positive amplitude over its entire length, while the wave on the right has a positive amplitude over half of its length and a negative amplitude over the other half. The sign of the amplitude of a wave—positive or negative—is known as its **phase**. In these images, blue indicates positive phase and red indicates negative phase. The phase of a wave determines how it interferes with another wave as we saw in Section 7.2.

Just as a one-dimensional wave has a phase, so does a three-dimensional wave. We often represent the phase of a quantum-mechanical orbital with color. For example, the phase of a 1s and 2p orbital can be represented as follows:



In these depictions, blue represents positive phase and red represents negative phase. The  $1s$  orbital is all one phase, while the  $2p$  orbital exhibits two different phases. The phase of quantum-mechanical orbitals is important in bonding, as we shall see in Chapter 10.

## The Shape of Atoms

If some orbitals are shaped like dumbbells and three-dimensional cloverleafs, and if most of the volume of an atom is empty space diffusely occupied by electrons in these orbitals, then why do we often depict atoms as spheres? Atoms are usually drawn as spheres because most atoms contain many electrons occupying a number of different orbitals. Therefore, the shape of an atom is obtained by superimposing all of its orbitals. If we superimpose the  $s$ ,  $p$ , and  $d$  orbitals we get a roughly spherical shape, as shown in Figure 7.30 ▶.

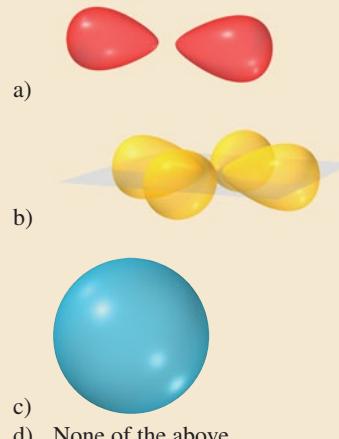


**▲ FIGURE 7.30 Why Atoms Are Spherical**  
Atoms are depicted as roughly spherical because all the orbitals together make up a roughly spherical shape.

## CHAPTER IN REVIEW

### Self Assessment Quiz

- Q1.** Which wavelength of light has the highest frequency?
- 10 nm
  - 10 mm
  - 1 nm
  - 1 mm
- Q2.** Which kind of electromagnetic radiation contains the greatest energy per photon?
- microwaves
  - gamma rays
  - X-rays
  - visible light
- Q3.** How much energy (in J) is contained in 1.00 mole of 552 nm photons?
- $3.60 \times 10^{-19}$  J
  - $2.17 \times 10^5$  J
  - $3.60 \times 10^{-28}$  J
  - $5.98 \times 10^{-43}$  J
- Q4.** Light from three different lasers (A, B, and C), each with a different wavelength, was shined onto the same metal surface. Laser A produced no photoelectrons. Lasers B and C both produced photoelectrons, but the photoelectrons produced by laser B had a greater velocity than those produced by laser C. Arrange the lasers in order of increasing wavelength.
- $A < B < C$
  - $B < C < A$
  - $C < B < A$
  - $A < C < B$
- Q5.** Calculate the wavelength of an electron traveling at  $1.85 \times 10^7$  m/s.
- $2.54 \times 10^{13}$  m
  - $3.93 \times 10^{-14}$  m
  - $2.54 \times 10^{10}$  m
  - $3.93 \times 10^{-11}$  m
- Q6.** Which set of three quantum numbers *does not* specify an orbital in the hydrogen atom?
- $n = 2; l = 1; m_l = -1$
  - $n = 3; l = 3; m_l = -2$
  - $n = 2; l = 0; m_l = 0$
  - $n = 3; l = 2; m_l = 2$
- Q7.** Calculate the wavelength of light emitted when an electron in the hydrogen atom makes a transition from an orbital with  $n = 5$  to an orbital with  $n = 3$ .
- $1.28 \times 10^{-6}$  m
  - $6.04 \times 10^{-7}$  m
  - $2.28 \times 10^{-6}$  m
  - $1.55 \times 10^{-19}$  m
- Q8.** Which electron transition produces light of the highest frequency in the hydrogen atom?
- $5p \longrightarrow 1s$
  - $4p \longrightarrow 1s$
  - $3p \longrightarrow 1s$
  - $2p \longrightarrow 1s$
- Q9.** How much time (in seconds) does it take light to travel 1.00 billion km?
- $3.00 \times 10^{17}$  s
  - 3.33 s
  - $3.33 \times 10^3$  s
  - $3.00 \times 10^{20}$  s
- Q10.** Which orbital is a  $d$  orbital?



- c) None of the above

## Key Terms

### Section 7.1

quantum-mechanical model (296)

### Section 7.2

electromagnetic radiation (296)  
amplitude (297)  
wavelength ( $\lambda$ ) (297)  
frequency ( $\nu$ ) (298)  
electromagnetic spectrum (299)  
gamma rays (299)  
X-rays (299)  
ultraviolet (UV) radiation (300)  
visible light (300)  
infrared (IR) radiation (300)

microwaves (301)

radio waves (301)

interference (301)

constructive interference (301)

destructive interference (301)

diffraction (301)

photoelectric effect (302)

photon (quantum) (303)

### Section 7.3

emission spectrum (306)

### Section 7.4

de Broglie relation (311)  
complementary properties (313)

Heisenberg's uncertainty principle (313)

deterministic (313)

indeterminacy (314)

### Section 7.5

orbital (315)

wave function (315)

quantum number (315)

principal quantum number ( $n$ ) (315)

angular momentum quantum number ( $l$ ) (315)

magnetic quantum number ( $m_l$ ) (315)

spin quantum number ( $m_s$ ) (315)

principal level (shell) (316)  
sublevel (subshell) (316)

### Section 7.6

probability density (322)  
radial distribution function (323)  
node (323)  
phase (326)

## Key Concepts

### The Realm of Quantum Mechanics (7.1)

- The theory of quantum mechanics explains the behavior of particles, such as photons (particles of light) and electrons, in the atomic and subatomic realms.
- Since the electrons of an atom determine many of its chemical and physical properties, quantum mechanics is foundational to understanding chemistry.

### The Nature of Light (7.2)

- Light is a type of electromagnetic radiation—a form of energy embodied in oscillating electric and magnetic fields that travels through space at  $3.00 \times 10^8$  m/s.
- The wave nature of light is characterized by its wavelength—the distance between wave crests—and its ability to experience interference (constructive or destructive) and diffraction.
- The particle nature of light is characterized by the specific quantity of energy carried in each photon.
- The electromagnetic spectrum includes all wavelengths of electromagnetic radiation from gamma rays (high energy per photon, short wavelength) to radio waves (low energy per photon, long wavelength). Visible light is a tiny sliver in the middle of the electromagnetic spectrum.

### Atomic Spectroscopy (7.3)

- Atomic spectroscopy is the study of the light absorbed and emitted by atoms when an electron makes a transition from one energy level to another.
- The wavelengths absorbed or emitted depend on the energy differences between the levels involved in the transition; large energy differences result in short wavelengths and small energy differences result in long wavelengths.

### The Wave Nature of Matter (7.4)

- Electrons have a wave nature with an associated wavelength, as quantified by the de Broglie relation.

- The wave nature and particle nature of matter are complementary—the more we know of one, the less we know of the other.
- The wave-particle duality of electrons is quantified in Heisenberg's uncertainty principle, which states that there is a limit to how well we can know both the position of an electron (associated with the electron's particle nature) and the velocity times the mass of an electron (associated with the electron's wave nature)—the more accurately one is measured, the greater the uncertainty in measurement of the other.
- The inability to simultaneously know both the position and the velocity of an electron results in indeterminacy, the inability to predict a trajectory for an electron. Consequently, electron behavior is described differently than the behavior of everyday-sized particles.
- The trajectory we normally associate with macroscopic objects is replaced, for electrons, with statistical descriptions that show not the electron's path, but the region where it is most likely to be found.

### The Quantum-Mechanical Model of the Atom (7.5, 7.6)

- The most common way to describe electrons in atoms according to quantum mechanics is to solve the Schrödinger equation for the energy states of the electrons within the atom. When the electron is in these states, its energy is well-defined but its position is not. The position of an electron is described by a probability distribution map called an orbital.
- The solutions to the Schrödinger equation (including the energies and orbitals) are characterized by four quantum numbers:  $n$ ,  $l$ ,  $m_l$ , and  $m_s$ .
- The principal quantum number ( $n$ ) determines the energy of the electron and the size of the orbital, the angular momentum quantum number ( $l$ ) determines the shape of the orbital, the magnetic quantum number ( $m_l$ ) determines the orientation of the orbital, and the spin quantum number ( $m_s$ ) specifies the orientation of the spin of the electron.

## Key Equations and Relationships

Relationship between Frequency ( $\nu$ ), Wavelength ( $\lambda$ ), and the Speed of Light (c) (7.2)

$$\nu = \frac{c}{\lambda}$$

Relationship between Energy ( $E$ ), Frequency ( $\nu$ ), Wavelength ( $\lambda$ ), and Planck's Constant ( $h$ ) (7.2)

$$E = h\nu$$

$$E = \frac{hc}{\lambda}$$

De Broglie Relation: Relationship between Wavelength ( $\lambda$ ), Mass ( $m$ ), and Velocity ( $v$ ) of a Particle (7.4)

$$\lambda = \frac{h}{mv}$$

Heisenberg's Uncertainty Principle: Relationship between a Particle's Uncertainty in Position ( $\Delta x$ ) and Uncertainty in Velocity ( $\Delta v$ ) (7.4)

$$\Delta x \times m\Delta v \geq \frac{h}{4\pi}$$

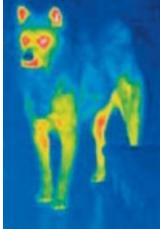
Energy of an Electron in an Orbital with Quantum Number  $n$  in a Hydrogen Atom (7.5)

$$E_n = -2.18 \times 10^{-18} \text{ J} \left( \frac{1}{n^2} \right) \quad (n = 1, 2, 3, \dots)$$

Change in Energy That Occurs in an Atom When It Undergoes a Transition between Levels  $n_{\text{initial}}$  and  $n_{\text{final}}$  (7.5)

$$\Delta E = -2.18 \times 10^{-18} \text{ J} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

## Key Learning Outcomes

Chapter Objectives	Assessment
Calculating the Wavelength and Frequency of Light (7.2)	Example 7.1 For Practice 7.1 Exercises 39, 40
	
Calculating the Energy of a Photon (7.2)	Example 7.2 For Practice 7.2 For More Practice 7.4 Exercises 41–46
Relating Wavelength, Energy, and Frequency to the Electromagnetic Spectrum (7.2)	Example 7.3 For Practice 7.3 Exercises 37, 42
Using the de Broglie Relation to Calculate Wavelength (7.4)	Example 7.4 For Practice 7.4 Exercises 49–54
Relating Quantum Numbers to One Another and to Their Corresponding Orbitals (7.5)	Examples 7.5, 7.6 For Practice 7.5, 7.6 Exercises 59–62
Relating the Wavelength of Light to Transitions in the Hydrogen Atom (7.5)	Example 7.7 For Practice 7.7 For More Practice 7.7 Exercises 69–72

## EXERCISES

### Review Questions

- Why is the quantum-mechanical model of the atom important for understanding chemistry?
- What is light? How fast does it travel in a vacuum?
- Define the wavelength and amplitude of a wave. How are these related to the energy of the wave?
- Define the frequency of electromagnetic radiation. How is frequency related to wavelength?
- What determines the color of light? Describe the difference between red light and blue light.
- What determines the color of a colored object? Explain why grass appears green.
- Give an approximate range of wavelengths for each type of electromagnetic radiation and summarize the characteristics and/or the uses of each.
  - gamma rays
  - X-rays
  - ultraviolet radiation
  - visible light
  - infrared radiation
  - microwave radiation
  - radio waves

8. Explain the wave behavior known as interference. Explain the difference between constructive and destructive interference.
9. Explain the wave behavior known as diffraction. Draw the diffraction pattern that occurs when light travels through two slits comparable in size and separation to the light's wavelength.
10. Describe the photoelectric effect. How did experimental observations of this phenomenon differ from the predictions of classical electromagnetic theory?
11. How did the photoelectric effect lead Einstein to propose that light is quantized?
12. What is a photon? How is the energy of a photon related to its wavelength? Its frequency?
13. What is an emission spectrum? How does an emission spectrum of a gas in a discharge tube differ from a white light spectrum?
14. Describe the Bohr model for the atom. How did the Bohr model account for the emission spectra of atoms?
15. Explain electron diffraction.
16. What is the de Broglie wavelength of an electron? What determines the value of the de Broglie wavelength for an electron?
17. What are complementary properties? How does electron diffraction demonstrate the complementarity of the wave nature and particle nature of the electron?
18. Explain Heisenberg's uncertainty principle. What paradox is at least partially solved by the uncertainty principle?
19. What is a trajectory? What kind of information do you need to predict the trajectory of a particle?
20. Why does the uncertainty principle make it impossible to predict a trajectory for the electron?
21. Newton's laws of motion are *deterministic*. Explain this statement.
22. An electron behaves in ways that are at least partially indeterminate. Explain this statement.
23. What is a probability distribution map?
24. For each solution to the Schrödinger equation, what can be precisely specified: the electron's energy or its position? Explain.
25. What is a quantum-mechanical orbital?
26. What is the Schrödinger equation? What is a wave function? How is a wave function related to an orbital?
27. What are the possible values of the principal quantum number  $n$ ? What does the principal quantum number determine?
28. What are the possible values of the angular momentum quantum number  $l$ ? What does the angular momentum quantum number determine?
29. What are the possible values of the magnetic quantum number  $m_l$ ? What does the magnetic quantum number determine?
30. List all the orbitals in each principal level. Specify the three quantum numbers for each orbital.
 

<b>a.</b> $n = 1$	<b>b.</b> $n = 2$
<b>c.</b> $n = 3$	<b>d.</b> $n = 4$
31. Explain the difference between a plot showing the probability density for an orbital and one showing the radial distribution function.
32. Make sketches of the general shapes of the  $s$ ,  $p$ , and  $d$  orbitals.
33. List the four different sublevels. Given that only a maximum of two electrons can occupy an orbital, determine the maximum number of electrons that can exist in each sublevel.
34. Why are atoms usually portrayed as spheres when most orbitals are not spherically shaped?

## Problems by Topic

### Electromagnetic Radiation

35. The distance from the sun to Earth is  $1.496 \times 10^8$  km. How long does it take light to travel from the sun to Earth?
36. The nearest star to our sun is Proxima Centauri, at a distance of 4.3 light-years from the sun. A light-year is the distance that light travels in one year (365 days). How far away, in km, is Proxima Centauri from the sun?
37. List these types of electromagnetic radiation in order of (i) increasing wavelength and (ii) increasing energy per photon:
 

<b>a.</b> radio waves	<b>b.</b> microwaves
<b>c.</b> infrared radiation	<b>d.</b> ultraviolet radiation
38. List these types of electromagnetic radiation in order of (i) increasing frequency and (ii) decreasing energy per photon:
 

<b>a.</b> gamma rays	<b>b.</b> radio waves
<b>c.</b> microwaves	<b>d.</b> visible light
39. Calculate the frequency of each wavelength of electromagnetic radiation:
  - a.** 632.8 nm (wavelength of red light from helium–neon laser)
  - b.** 503 nm (wavelength of maximum solar radiation)
  - c.** 0.052 nm (a wavelength contained in medical X-rays)
40. Calculate the wavelength of each frequency of electromagnetic radiation:
  - a.** 100.2 MHz (typical frequency for FM radio broadcasting)
  - b.** 1070 kHz (typical frequency for AM radio broadcasting) (assume four significant figures)
  - c.** 835.6 MHz (common frequency used for cell phone communication)

41. Calculate the energy of a photon of electromagnetic radiation at each of the wavelengths indicated in Problem 39.
42. Calculate the energy of a photon of electromagnetic radiation at each of the frequencies indicated in Problem 40.
43. A laser pulse with wavelength 532 nm contains 3.85 mJ of energy. How many photons are in the laser pulse?
44. A heat lamp produces 32.8 watts of power at a wavelength of  $6.5\text{ }\mu\text{m}$ . How many photons are emitted per second? (1 watt = 1 J/s)
45. Determine the energy of 1 mol of photons for each kind of light. (Assume three significant figures.)
 

<b>a.</b> infrared radiation (1500 nm)	<b>b.</b> visible light (500 nm)
<b>c.</b> ultraviolet radiation (150 nm)	
46. How much energy is contained in 1 mol of each?
 

<b>a.</b> X-ray photons with a wavelength of 0.135 nm	<b>b.</b> $\gamma$ -ray photons with a wavelength of $2.15 \times 10^{-5}$ nm.
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### The Wave Nature of Matter and the Uncertainty Principle

47. Sketch the interference pattern that results from the diffraction of electrons passing through two closely spaced slits.
48. What happens to the interference pattern described in Problem 47 if the rate of electrons going through the slits is decreased to one electron per hour? What happens to the pattern if we try to determine which slit the electron goes through by using a laser placed directly behind the slits?

- 49.** The resolution limit of a microscope is roughly equal to the wavelength of light used in producing the image. Electron microscopes use an electron beam (in place of photons) to produce much higher resolution images, about 0.20 nm in modern instruments. Assuming that the resolution of an electron microscope is equal to the de Broglie wavelength of the electrons used, to what speed must the electrons be accelerated to obtain a resolution of 0.20 nm?
- 50.** The smallest atoms can themselves exhibit quantum-mechanical behavior. Calculate the de Broglie wavelength (in pm) of a hydrogen atom traveling at 475 m/s.
- 51.** What is the de Broglie wavelength of an electron traveling at  $1.35 \times 10^5$  m/s?
- 52.** A proton in a linear accelerator has a de Broglie wavelength of 122 pm. What is the speed of the proton?
- 53.** Calculate the de Broglie wavelength of a 143 g baseball traveling at 95 mph. Why is the wave nature of matter not important for a baseball?
- 54.** A 0.22-caliber handgun fires a 27 g bullet at a velocity of 765 m/s. Calculate the de Broglie wavelength of the bullet. Is the wave nature of matter significant for bullets?
- 55.** An electron has an uncertainty in its position of 552 pm. What is the uncertainty in its velocity?
- 56.** An electron traveling at  $3.7 \times 10^5$  m/s has an uncertainty in its velocity of  $1.88 \times 10^5$  m/s. What is the uncertainty in its position?

### Orbitals and Quantum Numbers

- 57.** Which electron is, on average, closer to the nucleus: an electron in a  $2s$  orbital or an electron in a  $3s$  orbital?
- 58.** Which electron is, on average, further from the nucleus: an electron in a  $3p$  orbital or an electron in a  $4p$  orbital?
- 59.** What are the possible values of  $l$  for each value of  $n$ ?
- 1
  - 2
  - 3
  - 4
- 60.** What are the possible values of  $m_l$  for each value of  $l$ ?
- 0
  - 1
  - 2
  - 3
- 61.** Which set of quantum numbers *cannot* occur together to specify an orbital?
- $n = 2, l = 1, m_l = -1$
  - $n = 3, l = 2, m_l = 0$
  - $n = 3, l = 3, m_l = 2$
  - $n = 4, l = 3, m_l = 0$

### Cumulative Problems

- 73.** Ultraviolet radiation and radiation of shorter wavelengths can damage biological molecules because they carry enough energy to break bonds within the molecules. A typical carbon–carbon bond requires 348 kJ/mol to break. What is the longest wavelength of radiation with enough energy to break carbon–carbon bonds?
- 74.** The human eye contains a molecule called 11-*cis*-retinal that changes shape when struck with light of sufficient energy. The change in shape triggers a series of events that results in an electrical signal being sent to the brain. The minimum energy required to change the conformation of 11-*cis*-retinal within the eye is about 164 kJ/mol. Calculate the longest wavelength visible to the human eye.
- 75.** An argon ion laser puts out 5.0 W of continuous power at a wavelength of 532 nm. The diameter of the laser beam is 5.5 mm. If the laser is pointed toward a pinhole with a diameter

- 62.** Which combinations of  $n$  and  $l$  represent real orbitals and which do not exist?
- $1s$
  - $2p$
  - $4s$
  - $2d$
- 63.** Sketch the  $1s$  and  $2p$  orbitals. How would the  $2s$  and  $3p$  orbitals differ from the  $1s$  and  $2p$  orbitals?
- 64.** Sketch the  $3d$  orbitals. How would the  $4d$  orbitals differ from the  $3d$  orbitals?

### Atomic Spectroscopy

- 65.** An electron in a hydrogen atom is excited with electrical energy to an excited state with  $n = 2$ . The atom then emits a photon. What is the value of  $n$  for the electron following the emission?
- 66.** Determine whether each transition in the hydrogen atom corresponds to absorption or emission of energy.
- $n = 3 \longrightarrow n = 1$
  - $n = 2 \longrightarrow n = 4$
  - $n = 4 \longrightarrow n = 3$
- 67.** According to the quantum-mechanical model for the hydrogen atom, which electron transitions would produce light with the longer wavelength:  $2p \longrightarrow 1s$  or  $3p \longrightarrow 1s$ ?
- 68.** According to the quantum-mechanical model for the hydrogen atom, which electron transition would produce light with the longer wavelength:  $3p \longrightarrow 2s$  or  $4p \longrightarrow 3p$ ?
- 69.** Calculate the wavelength of the light emitted when an electron in a hydrogen atom makes each transition and indicate the region of the electromagnetic spectrum (infrared, visible, ultraviolet, etc.) where the light is found.
- $n = 2 \longrightarrow n = 1$
  - $n = 3 \longrightarrow n = 1$
  - $n = 4 \longrightarrow n = 2$
  - $n = 5 \longrightarrow n = 2$
- 70.** Calculate the frequency of the light emitted when an electron in a hydrogen atom makes each transition:
- $n = 4 \longrightarrow n = 3$
  - $n = 5 \longrightarrow n = 1$
  - $n = 5 \longrightarrow n = 4$
  - $n = 6 \longrightarrow n = 5$
- 71.** An electron in the  $n = 7$  level of the hydrogen atom relaxes to a lower energy level, emitting light of 397 nm. What is the value of  $n$  for the level to which the electron relaxed?
- 72.** An electron in a hydrogen atom relaxes to the  $n = 4$  level, emitting light of 114 THz. What is the value of  $n$  for the level in which the electron originated?

of 1.2 mm, how many photons will travel through the pinhole per second? Assume that the light intensity is equally distributed throughout the entire cross-sectional area of the beam. (1 W = 1 J/s)

- 76.** A green leaf has a surface area of  $2.50 \text{ cm}^2$ . If solar radiation is  $1000 \text{ W/m}^2$ , how many photons strike the leaf every second? Assume three significant figures and an average wavelength of 504 nm for solar radiation.
- 77.** In a technique used for surface analysis called Auger electron spectroscopy (AES), electrons are accelerated toward a metal surface. These electrons cause the emissions of secondary electrons—called auger electrons—from the metal surface. The kinetic energy of the auger electrons depends on the composition of the surface. The presence of oxygen atoms on the surface results in

- auger electrons with a kinetic energy of approximately 506 eV. What is the de Broglie wavelength of one of these electrons?
- [ $KE = \frac{1}{2}mv^2$ ; 1 electron volt (eV) =  $1.602 \times 10^{-19}$  J]
78. An X-ray photon of wavelength 0.989 nm strikes a surface. The emitted electron has a kinetic energy of 969 eV. What is the binding energy of the electron in kJ/mol?
- [ $KE = \frac{1}{2}mv^2$ ; 1 electron volt (eV) =  $1.602 \times 10^{-19}$  J]
79. Ionization involves completely removing an electron from an atom. How much energy is required to ionize a hydrogen atom in its ground (or lowest energy) state? What wavelength of light contains enough energy in a single photon to ionize a hydrogen atom?
80. The energy required to ionize sodium is 496 kJ/mol. What minimum frequency of light is required to ionize sodium?
81. Suppose that in an alternate universe, the possible values of  $l$  were the integer values from 0 to  $n$  (instead of 0 to  $n - 1$ ). Assuming no other differences between this imaginary universe and ours, how many orbitals would exist in each level?
- a.  $n = 1$       b.  $n = 2$       c.  $n = 3$
82. Suppose that, in an alternate universe, the possible values of  $m_l$  are the integer values including 0 ranging from  $-l - 1$  to  $l + 1$  (instead of simply  $-l$  to  $+l$ ). How many orbitals exist in each sublevel?
- a.  $s$  sublevel      b.  $p$  sublevel      c.  $d$  sublevel
83. An atomic emission spectrum of hydrogen shows three wavelengths: 1875 nm, 1282 nm, and 1093 nm. Assign these wavelengths to transitions in the hydrogen atom.
84. An atomic emission spectrum of hydrogen shows three wavelengths: 121.5 nm, 102.6 nm, and 97.23 nm. Assign these wavelengths to transitions in the hydrogen atom.
85. The binding energy of electrons in a metal is 193 kJ/mol. Find the threshold frequency of the metal.
86. In order for a thermonuclear fusion reaction of two deuterons ( ${}^2_1H^+$ ) to take place, the deuterons must collide each with a velocity of about  $1 \times 10^6$  m/s. Find the wavelength of such a deuteron.
87. The speed of sound in air is 344 m/s at room temperature. The lowest frequency of a large organ pipe is  $30\text{ s}^{-1}$  and the highest frequency of a piccolo is  $1.5 \times 10^4\text{ s}^{-1}$ . Find the difference in wavelength between these two sounds.
88. The distance from Earth to the sun is  $1.5 \times 10^8$  km. Find the number of crests in a light wave of frequency  $1.0 \times 10^{14}\text{ s}^{-1}$  traveling from the sun to the Earth.
89. The iodine molecule can be photodissociated into iodine atoms in the gas phase with light of wavelengths shorter than about 792 nm. A 100.0 mL glass tube contains 55.7 mtorr of gaseous iodine at  $25.0^\circ\text{C}$ . What minimum amount of light energy must be absorbed by the iodine in the tube to dissociate 15.0% of the molecules?
90. A 5.00 mL ampule of a 0.100 M solution of naphthalene in hexane is excited with a flash of light. The naphthalene emits 15.5 J of energy at an average wavelength of 349 nm. What percentage of the naphthalene molecules emitted a photon?
91. A laser produces 20.0 mW of red light. In 1.00 hr, the laser emits  $2.29 \times 10^{20}$  photons. What is the wavelength of the laser?
92. A particular laser consumes 150.0 watts of electrical power and produces a stream of  $1.33 \times 10^{19}$  1064 nm photons per second. What is the percent efficiency of the laser in converting electrical power to light?

## Challenge Problems

93. An electron confined to a one-dimensional box has energy levels given by the equation
- $$E_n = n^2 h^2 / 8 mL^2$$
- where  $n$  is a quantum number with possible values of 1, 2, 3, ...,  $m$  is the mass of the particle, and  $L$  is the length of the box.
- a. Calculate the energies of the  $n = 1$ ,  $n = 2$ , and  $n = 3$  levels for an electron in a box with a length of 155 pm.
- b. Calculate the wavelength of light required to make a transition from  $n = 1 \longrightarrow n = 2$  and from  $n = 2 \longrightarrow n = 3$ . In what region of the electromagnetic spectrum do these wavelengths lie?
94. The energy of a vibrating molecule is quantized much like the energy of an electron in the hydrogen atom. The energy levels of a vibrating molecule are given by the equation

$$E_n = \left(n + \frac{1}{2}\right)h\nu$$

where  $n$  is a quantum number with possible values of 1, 2, ..., and  $\nu$  is the frequency of vibration. The vibration frequency of HCl is approximately  $8.85 \times 10^{13}\text{ s}^{-1}$ . What minimum energy is required to excite a vibration in HCl? What wavelength of light is required to excite this vibration?

95. The wave functions for the 1s and 2s orbitals are as follows:
- $$1s \quad \psi = (1/\pi)^{1/2} (1/a_0^{3/2}) \exp(-r/a_0)$$
- $$2s \quad \psi = (1/32\pi)^{1/2} (1/a_0^{3/2}) (2-r/a_0) \exp(-r/a_0)$$
- where  $a_0$  is a constant ( $a_0 = 53$  pm) and  $r$  is the distance from the nucleus. Use a spreadsheet to make a plot of each of these wave functions for values of  $r$  ranging from 0 pm to 200 pm. Describe the differences in the plots and identify the node in the 2s wave function.
96. Before quantum mechanics was developed, Johannes Rydberg developed an equation that predicted the wavelengths ( $\lambda$ ) in the atomic spectrum of hydrogen:
- $$1/\lambda = R(1/m^2 - 1/n^2)$$
- In this equation  $R$  is a constant and  $m$  and  $n$  are integers. Use the quantum-mechanical model for the hydrogen atom to derive the Rydberg equation.
97. Find the velocity of an electron emitted by a metal whose threshold frequency is  $2.25 \times 10^{14}\text{ s}^{-1}$  when it is exposed to visible light of wavelength  $5.00 \times 10^{-7}$  m.
98. Water is exposed to infrared radiation of wavelength  $2.8 \times 10^{-4}$  cm. Assume that all the radiation is absorbed and converted to heat. How many photons are required to raise the temperature of 2.0 g of water by 2.0 K?

**99.** The 2005 Nobel Prize in physics was given, in part, to scientists who had made ultrashort pulses of light. These pulses are important in making measurements involving very short time periods. One challenge in making such pulses is the uncertainty principle, which can be stated with respect to energy and time as  $\Delta E \cdot \Delta t \geq h/4\pi$ . What is the energy uncertainty ( $\Delta E$ ) associated with a short pulse of laser light that lasts for only 5.0 femtoseconds (fs)? Suppose the low energy end of the pulse had a wavelength of 722 nm. What is the wavelength of the high energy end of the pulse that is limited only by the uncertainty principle?

**100.** A metal whose threshold frequency is  $6.71 \times 10^{14} \text{ s}^{-1}$  emits an electron with a velocity of  $6.95 \times 10^5 \text{ m/s}$  when radiation of  $1.01 \times 10^{15} \text{ s}^{-1}$  strikes the metal. Calculate the mass of the electron.

**101.** Find the longest wavelength of a wave that can travel around in a circular orbit of radius 1.8 m.

**102.** The heat of fusion of ice is 6.00 kJ/mol. Find the number of photons of wavelength =  $6.42 \times 10^{-6} \text{ m}$  that must be absorbed to melt 1.00 g of ice.

## Conceptual Problems

**103.** Explain the difference between the Bohr model for the hydrogen atom and the quantum-mechanical model. Is the Bohr model consistent with Heisenberg's uncertainty principle?

**104.** The light emitted from one of the following electronic transitions ( $n = 4 \longrightarrow n = 3$  or  $n = 3 \longrightarrow n = 2$ ) in the hydrogen atom causes the photoelectric effect in a particular metal while light from the other transition does not. Which transition causes the photoelectric effect and why?

**105.** Determine whether an interference pattern is observed on the other side of the slits in each experiment.

- a. An electron beam is aimed at two closely spaced slits. The beam is attenuated to produce only one electron per minute.
- b. An electron beam is aimed at two closely spaced slits.

A light beam is placed at each slit to determine when an electron goes through the slit.

c. A high-intensity light beam is aimed at two closely spaced slits.

d. A gun is fired at a solid wall containing two closely spaced slits. (Will the bullets that pass through the slits form an interference pattern on the other side of the solid wall?)

**106.** Which transition in the hydrogen atom will result in emitted light with the longest wavelength?

- a.  $n = 4 \longrightarrow n = 3$
- b.  $n = 2 \longrightarrow n = 1$
- c.  $n = 3 \longrightarrow n = 2$

## Answers to Conceptual Connections

### The Photoelectric Effect

**7.1** Observation A corresponds to 632 nm, observation B corresponds to 325 nm, and observation C corresponds to 455 nm. The shortest wavelength of light (highest energy per photon) must correspond to the photoelectrons with the greatest kinetic energy. The longest wavelength of light (lowest energy per photon) must correspond to the instance in which no photoelectrons were observed.

### The de Broglie Wavelength of Macroscopic Objects

**7.2** Because of the baseball's large mass, its de Broglie wavelength is minuscule. (For a 150 g baseball,  $\lambda$  is on the order of  $10^{-34} \text{ m}$ .) This minuscule wavelength is insignificant compared to the size of the baseball itself, and therefore its effects are not observable.

### The Relationship between $n$ and $l$

**7.3** (c) Since  $l$  can have a maximum value of  $n - 1$ , and since  $n = 3$ , then  $l$  can have a maximum value of 2.

### The Relationship between $l$ and $m_l$

**7.4** (d) Since  $m_l$  can have the integer values (including 0) between  $-l$  and  $+l$ , and since  $l = 2$ , the possible values of  $m_l$  are  $-2, -1, 0, +1$ , and  $+2$ .

### Emission Spectra

**7.5** (c) The energy difference between  $n = 3$  and  $n = 2$  is greatest because the energy differences get closer together with increasing  $n$ . The greater energy difference results in an emitted photon of greater energy and therefore shorter wavelength.

# 8

# Periodic Properties of the Elements

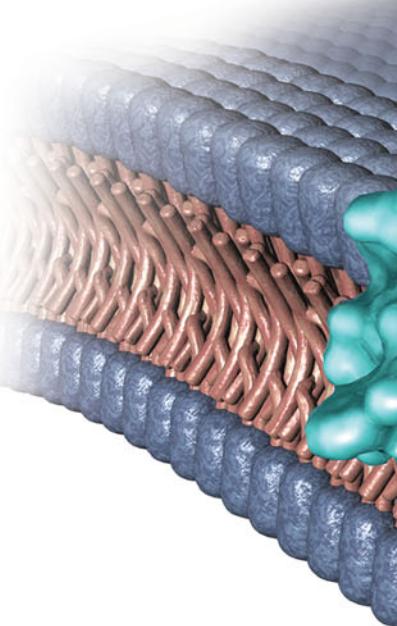
*Beginning students of chemistry often think of the science as a mere collection of disconnected data to be memorized by brute force. Not at all! Just look at it properly and everything hangs together and makes sense.*

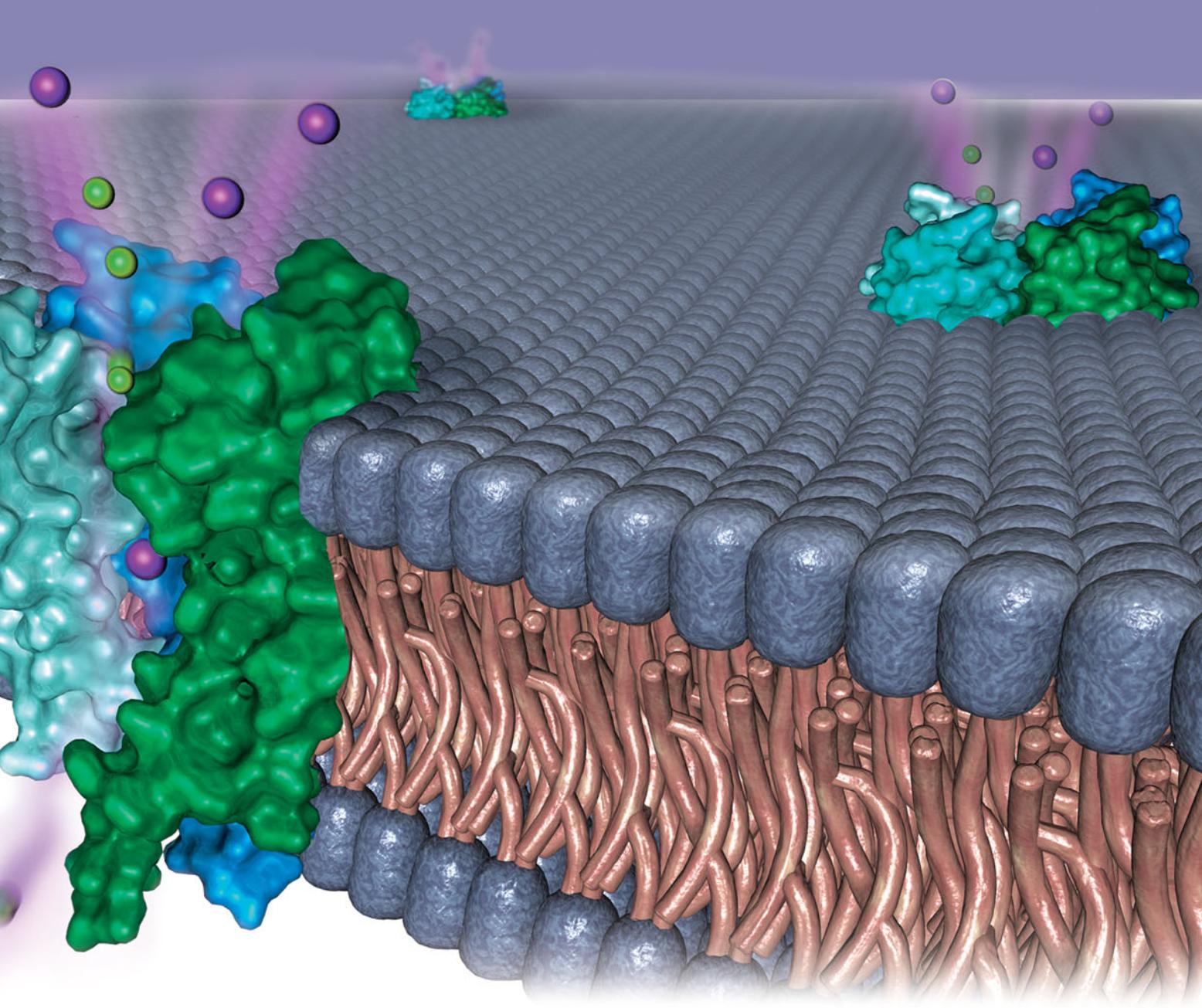
—Isaac Asimov (1920–1992)

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**G**REAT ADVANCES IN SCIENCE occur not only when a scientist sees something new, but also when a scientist sees what everyone else has seen in a new way. In other words, great scientists often see patterns where others have seen only disjointed facts. Such was the case in 1869 when Dmitri Mendeleev, a Russian chemistry professor, saw a pattern in the properties of elements. Mendeleev's insight led to the periodic table, arguably the single most important tool for chemists. Recall that scientists devise theories that explain the underlying reasons for observations. If we think of Mendeleev's periodic table as a compact way to summarize a large number of observations, then quantum mechanics (covered in Chapter 7) is the theory that explains the underlying reasons for the periodic table. Quantum mechanics explains how electrons are arranged in atoms, which in turn determines the element's properties. Since the periodic table is organized according to those properties, quantum mechanics beautifully accounts for Mendeleev's periodic table. In this chapter, we see a continuation of the theme we have been developing since page one of this book—the properties of macroscopic substances (in this case, the elements in the periodic table) are explained by the properties of the particles that compose them (in this case, atoms and their electrons).





## 8.1 Nerve Signal Transmission

As you sit reading this book, tiny pumps in the membranes of your cells are working hard to transport ions—especially sodium ( $\text{Na}^+$ ) and potassium ( $\text{K}^+$ )—through those membranes. Amazingly, the ions are pumped in opposite directions. Sodium ions are pumped *out of cells*, while potassium ions are pumped *into cells*. The result is a *chemical gradient* for each ion: the concentration of sodium is higher outside the cell than within, while just the opposite is true for potassium. These ion pumps are analogous to the water pumps in a high-rise building that pump water against the force of gravity to a tank on the roof. Other structures within the membrane, called ion channels, are like the building's faucets. When these open, sodium and potassium ions flow back down their gradients—sodium flowing in and potassium flowing out. This movement of ions is the basis for the transmission of nerve signals in the brain and throughout the body. Every move you make, every thought you have, and every sensation you experience is mediated by these ion movements.

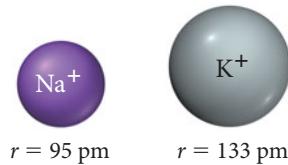
How do the pumps and channels differentiate between sodium and potassium ions to selectively move one out of the cell and the other into the cell? To answer this question, we must examine the ions more closely. Both ions are cations of group 1A metals. All group 1A

*In order for a nerve cell to transmit a signal, sodium and potassium ions must flow in opposite directions through specific ion channels in the cell membrane.*

3	Li	6.94
11	Na	22.99
19	K	39.10
37	Rb	85.47
55	Cs	132.91
87	Fr	(223.02)

▲ The group 1A metals. Potassium is directly beneath sodium in the periodic table.

metals tend to lose one electron to form cations with a  $1+$  charge, so that cannot be the decisive factor. Potassium (atomic number 19) lies directly below sodium in the periodic table (atomic number 11), indicating that it has more protons, neutrons, and electrons than sodium. How do these additional subatomic particles affect the properties of potassium? As we will see in this chapter, although a higher atomic number does not always result in a larger ion (or atom), it does in the case of potassium (relative to sodium). The potassium ion has a radius of 133 pm while the sodium ion has a radius of 95 pm. (Recall that 1 pm =  $10^{-12}$  m.) The pumps and channels within cell membranes are so sensitive that they distinguish between the sizes of these two ions and selectively allow only one or the other to pass.



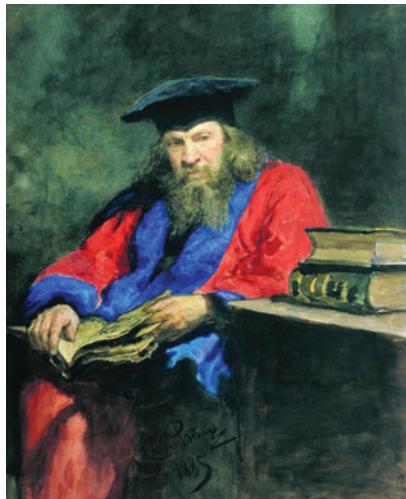
The relative size of sodium and potassium ions is an example of a **periodic property**: one that is predictable based on an element's position within the periodic table. In this chapter, we examine several periodic properties of elements, including atomic radius, ionization energy, and electron affinity. We will see that these properties, as well as the overall arrangement of the periodic table, are explained by quantum-mechanical theory, which we examined in Chapter 7. The arrangement of elements in the periodic table—originally based on similarities in the properties of the elements—reflects how electrons fill quantum-mechanical orbitals.

## 8.2 The Development of the Periodic Table

Prior to the 1700s, the number of known elements was relatively small, consisting mostly of the metals that had long been used for coinage, jewelry, and weapons. From the early 1700s to the mid-1800s, however, chemists discovered over 50 new elements. The first attempt to organize these elements according to similarities in their properties was made by the German chemist Johann Döbereiner (1780–1849), who grouped elements into *triads*: three elements with similar properties. For example, Döbereiner formed a triad out of barium, calcium, and strontium, three fairly reactive metals. About 50 years later, English chemist John Newlands (1837–1898) organized elements into *octaves*, in analogy to musical notes. When arranged this way, the properties of every eighth element were similar, much as every eighth note in the musical scale is similar. Newlands endured some ridicule for drawing an analogy between chemistry and music, including the derisive comments of one colleague who asked Newlands if he had ever tried ordering the elements according to the first letters of their names.

The modern periodic table is credited primarily to the Russian chemist Dmitri Mendeleev (1834–1907), even though a similar organization had been suggested by the German chemist Julius Lothar Meyer (1830–1895). Recall from Chapter 2 that Mendeleev's table is based on the periodic law, which states that when elements are arranged in order of increasing mass, certain properties recur periodically. Mendeleev arranged the elements in a table in which mass increases from left to right and elements with similar properties fall in the same columns.

Mendeleev's arrangement was a huge success, allowing him to predict the existence and properties of yet undiscovered elements such as eka-aluminum (later discovered and named gallium) and eka-silicon (later discovered and named germanium). The properties of these two elements are summarized in Figure 8.1 ▶. (As noted in Chapter 2, *eka* means “the one beyond” or “the next one” in a family of elements.) However, Mendeleev did encounter some difficulties. For example, according to accepted values of atomic masses, tellurium (with higher mass) should come *after* iodine. But based on their properties, Mendeleev placed tellurium *before* iodine and suggested that the mass of tellurium was erroneous. The mass was correct; later work by the English physicist Henry Moseley (1887–1915) showed that listing elements according to *atomic number*, rather than atomic mass, resolved this problem and resulted in even better correlation with elemental properties.



▲ Dmitri Mendeleev is credited with the arrangement of the periodic table.

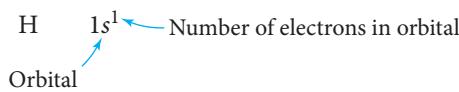
Gallium (eka-aluminum)		Germanium (eka-silicon)			
	Mendeleev's predicted properties		Mendeleev's predicted properties		
	Actual properties		Actual properties		
Atomic mass	About 68 amu	69.72 amu	Atomic mass	About 72 amu	72.64 amu
Melting point	Low	29.8 °C	Density	5.5 g/cm <sup>3</sup>	5.35 g/cm <sup>3</sup>
Density	5.9 g/cm <sup>3</sup>	5.90 g/cm <sup>3</sup>	Formula of oxide	XO <sub>2</sub>	GeO <sub>2</sub>
Formula of oxide	X <sub>2</sub> O <sub>3</sub>	Ga <sub>2</sub> O <sub>3</sub>	Formula of chloride	XCl <sub>4</sub>	GeCl <sub>4</sub>
Formula of chloride	XCl <sub>3</sub>	GaCl <sub>3</sub>			

▲ FIGURE 8.1 Eka-aluminum and Eka-silicon Mendeleev's arrangement of elements in the periodic table allowed him to predict the existence of these elements, now known as gallium and germanium, and anticipate their properties.

Notice the scientific approach in practice in the history of the periodic table. A number of related observations led to a scientific law—the periodic law. Mendeleev's table, an expression of the periodic law, had predictive power, as laws usually do. However, it did not explain *why* the properties of elements recurred, or *why* certain elements had similar properties. Recall from Chapter 1 that laws *summarize* behavior while theories *explain* behavior. The theory that explains the reasons behind the periodic law is quantum-mechanical theory. In this chapter, we turn to exploring the connection between the periodic table and quantum-mechanical theory.

## 8.3 Electron Configurations: How Electrons Occupy Orbitals

Quantum-mechanical theory describes the behavior of electrons in atoms. Since chemical bonding involves the transfer or sharing of electrons, quantum-mechanical theory helps us understand and describe chemical behavior. As we saw in Chapter 7, electrons in atoms exist within orbitals. An **electron configuration** for an atom shows the particular orbitals that electrons occupy for that atom. For example, consider the **ground state**—or lowest energy state—electron configuration for a hydrogen atom:

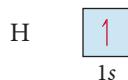


The electron configuration indicates that hydrogen's one electron is in the 1s orbital. Electrons generally occupy the lowest energy orbitals available. Since the 1s orbital is the lowest energy orbital in hydrogen (see Section 7.5), hydrogen's electron occupies that orbital. If we could write electron configurations for all the elements, we could see how the arrangements of the electrons within their atoms correlate with the element's chemical properties. However, the Schrödinger equation solutions (the atomic orbitals and their energies) that we described in Chapter 7 are for the hydrogen atom. What do the atomic orbitals of *other atoms* look like? What are their relative energies?

The Schrödinger equation for multielectron atoms has terms to account for the interactions of the electrons with one another that make it too complicated to solve exactly. However, approximate solutions indicate that the orbitals in multielectron atoms are hydrogen-like—they are similar to the s, p, d, and f orbitals that we examined in Chapter 7. In order to see how the electrons in multielectron atoms occupy these hydrogen-like orbitals, we must examine two additional concepts: *the effects of electron spin*, a fundamental property of all electrons that affects the number of electrons allowed in any one orbital; and *sublevel energy splitting*, which determines the order of orbital filling within a level.

## Electron Spin and the Pauli Exclusion Principle

We can represent the electron configuration of hydrogen ( $1s^1$ ) in a slightly different way with an **orbital diagram**, which gives similar information but symbolizes the electron as an arrow and the orbital as a box. The orbital diagram for a hydrogen atom is:



In an orbital diagram, the direction of the arrow (pointing up or pointing down) represents the orientation of the *electron's spin*. Recall from Section 7.5 that the orientation of the electron's spin is quantized, with only two possibilities—spin up ( $m_s = +\frac{1}{2}$ ) and spin down ( $m_s = -\frac{1}{2}$ ). In an orbital diagram,  $m_s = +\frac{1}{2}$  is represented with a half-arrow pointing up (↑) and  $m_s = -\frac{1}{2}$  is represented with a half-arrow pointing down (↓). In a collection of hydrogen atoms, the electrons in about half of the atoms are spin up and the electrons in the other half are spin down. Since no additional electrons are present within the hydrogen atom, we conventionally represent the hydrogen atom electron configuration with its one electron as spin up.

Helium is the first element on the periodic table that contains two electrons. Its two electrons occupy the 1s orbital.



How do the spins of the two electrons in helium align relative to each other? The answer to this question is addressed by the **Pauli exclusion principle**, formulated by Wolfgang Pauli in 1925.

**Pauli exclusion principle: no two electrons in an atom can have the same four quantum numbers.**

Since two electrons occupying the same orbital have three identical quantum numbers ( $n$ ,  $l$ , and  $m_l$ ), they must have different spin quantum numbers. Since there are only two possible spin quantum numbers ( $+\frac{1}{2}$  and  $-\frac{1}{2}$ ), the Pauli exclusion principle implies that *each orbital can have a maximum of only two electrons, with opposing spins*. By applying the exclusion principle, we can write an electron configuration and orbital diagram for helium as follows:



The following table shows the four quantum numbers for each of the two electrons in helium.

$n$	$l$	$m_l$	$m_s$
1	0	0	$+\frac{1}{2}$
1	0	0	$-\frac{1}{2}$

The two electrons have three quantum numbers in common (because they are in the same orbital) but have different spin quantum numbers (as indicated by the opposing half-arrows in the orbital diagram).

## Sublevel Energy Splitting in Multielectron Atoms

A major difference in the (approximate) solutions to the Schrödinger equation for multielectron atoms compared to the solutions for the hydrogen atom is the energy ordering of the orbitals. In the hydrogen atom, the energy of an orbital depends only on  $n$ , the principal quantum number. For example, the  $3s$ ,  $3p$ , and  $3d$  orbitals (which are empty for hydrogen in its lowest energy state) all have the same energy—they are **degenerate**. The orbitals within a principal level of a *multielectron atom*, in contrast, are

not degenerate—their energy depends on the value of  $l$ . We say that the energies of the sublevels are *split*. In general, the lower the value of  $l$  *within a principal level*, the lower the energy ( $E$ ) of the corresponding orbital. Thus, for a given value of  $n$ :

$$E(s \text{ orbital}) < E(p \text{ orbital}) < E(d \text{ orbital}) < E(f \text{ orbital})$$

In order to understand why the sublevels split in this way, we must examine three key concepts associated with the energy of an electron in the vicinity of a nucleus: (1) Coulomb's law, which describes the interactions between charged particles; (2) shielding, which describes how one electron can shield another electron from the full charge of the nucleus; and (3) penetration, which describes how one atomic orbital can overlap spatially with another, thus penetrating into a region that is close to the nucleus (and therefore less shielded from nuclear charge). We will then examine how these concepts, together with the spatial distributions of electron probability for each orbital, result in the energy ordering that we just saw.

**Coulomb's Law** The attractions and repulsions between charged particles, first introduced in Section 2.4, are described by **Coulomb's law**, which states that the potential energy ( $E$ ) of two charged particles depends on their charges ( $q_1$  and  $q_2$ ) and on their separation ( $r$ ):

$$E = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r} \quad [8.1]$$

In this equation,  $\epsilon_0$  is a constant ( $\epsilon_0 = 8.85 \times 10^{-12} \text{ C}^2/\text{J} \cdot \text{m}$ ). The potential energy is positive for charges of the same sign (plus  $\times$  plus, or minus  $\times$  minus) and negative for charges of opposite sign (plus  $\times$  minus, or minus  $\times$  plus). The *magnitude* of the potential energy depends inversely on the separation between the charged particles. We can draw three important conclusions from Coulomb's law:

- For like charges, the potential energy ( $E$ ) is positive and decreases as the particles get *farther apart* (as  $r$  increases). Since systems tend toward lower potential energy, like charges repel each other (in much the same way that like poles of two magnets repel each other).
- For opposite charges, the potential energy is negative and becomes more negative as the particles get *closer together* (as  $r$  decreases). Therefore, opposite charges (like opposite poles on a magnet) *attract each other*.
- The *magnitude* of the interaction between charged particles increases as the charges of the particles increases. Consequently, an electron with a charge of  $1^-$  is more strongly attracted to a nucleus with a charge of  $2^+$  than it would be to a nucleus with a charge of  $1^+$ .

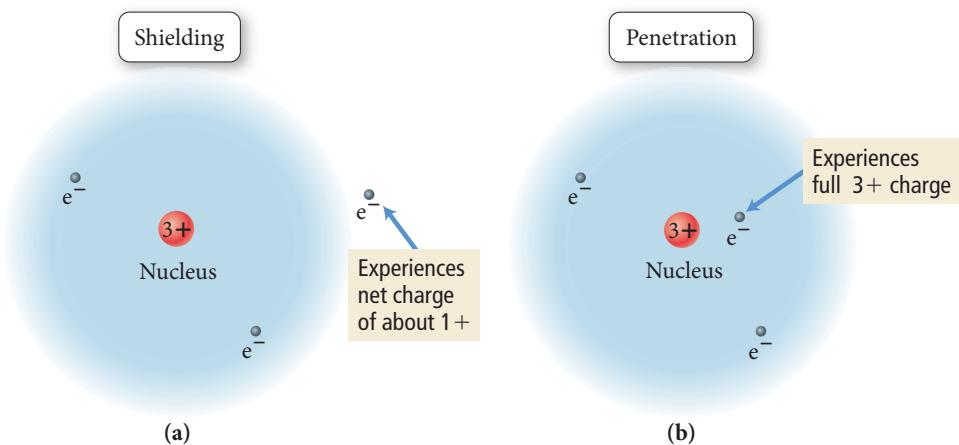
### Conceptual Connection 8.1 Coulomb's Law

According to Coulomb's law, what happens to the potential energy of two oppositely charged particles as they get closer together?

- Their potential energy decreases.
- Their potential energy increases.
- Their potential energy does not change.

**Shielding** For multielectron atoms, any one electron experiences both the positive charge of the nucleus (which is attractive) and the negative charges of the other electrons (which are repulsive). We can think of the repulsion of one electron by other electrons as *screening* or **shielding** that electron from the full effects of the nuclear charge. For example, consider a lithium ion ( $\text{Li}^+$ ). Since the lithium ion contains two electrons, its electron configuration is identical to that of helium:



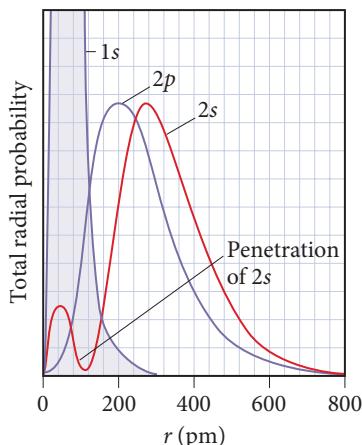


**▲ FIGURE 8.2** Shielding and Penetration (a) An electron far from the nucleus is partly shielded by the electrons in the 1s orbital, reducing the effective net nuclear charge that it experiences. (b) An electron that penetrates the electron cloud of the 1s orbital experiences more of the nuclear charge.

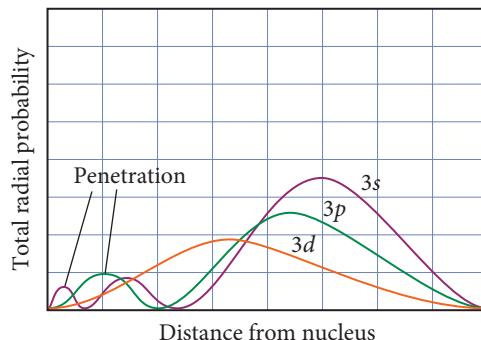
Now imagine bringing a third electron toward the lithium ion. When the third electron is far from the nucleus, it experiences the 3+ charge of the nucleus through the *screen* or *shield* of the 2– charge of the two 1s electrons, as shown in Figure 8.2a ▲. We can think of the third electron as experiencing an **effective nuclear charge ( $Z_{\text{eff}}$ )** of approximately 1+ (3+ from the nucleus and 2– from the electrons, for a net charge of 1+). The inner electrons in effect *shield* the outer electron from the full nuclear charge.

**Penetration** Now imagine allowing this third electron to come closer to the nucleus. As the electron *penetrates* the electron cloud of the 1s electrons it begins to experience the 3+ charge of the nucleus more fully because it is less shielded by the intervening electrons. If the electron could somehow get closer to the nucleus than the 1s electrons, it would experience the full 3+ charge, as shown in Figure 8.2b. In other words, as the outer electron undergoes **penetration** into the region occupied by the inner electrons, it experiences a greater nuclear charge and therefore (according to Coulomb's law) a lower energy.

**Electron Spatial Distributions and Sublevel Splitting** We now have examined the concepts we need to understand the energy splitting of the sublevels within a principal level. The splitting is a result of the spatial distributions of electrons within a sublevel. Recall from Section 7.6 that the radial distribution function for an atomic orbital shows the total probability of finding the electron within a thin spherical shell at a distance  $r$  from the nucleus. Figure 8.3 ▲ shows the radial distribution functions of the 2s and 2p orbitals superimposed on one another (the radial distribution function of the 1s orbital is also shown). Notice that, in general, an electron in a 2p orbital has a greater probability of being found closer to the nucleus than an electron in a 2s orbital. We might initially expect, therefore, that the 2p orbital would be lower in energy. However, exactly the opposite is true—the 2s orbital is actually lower in energy, *but only when the 1s orbital is occupied*. (When the 1s orbital is empty, the 2s and 2p orbitals are degenerate.) Why? The reason is the bump near  $r = 0$  (near the nucleus) for the 2s orbital. This bump represents a significant probability of the electron being found very close to the nucleus. Even more importantly, this area of the probability penetrates into the 1s orbital—it gets into the region where shielding by the 1s electrons is less effective. In contrast, most of the probability in the radial distribution function of the 2p orbital lies *outside* the radial distribution function of the 1s orbital. Consequently, almost all of the 2p orbital is shielded from nuclear charge by the 1s orbital. The end result is that the 2s orbital—since it experiences more of the nuclear charge due to its greater *penetration*—is lower in energy than the 2p orbital. The results



**▲ FIGURE 8.3** Radial Distribution Functions for the 1s, 2s, and 2p Orbitals.



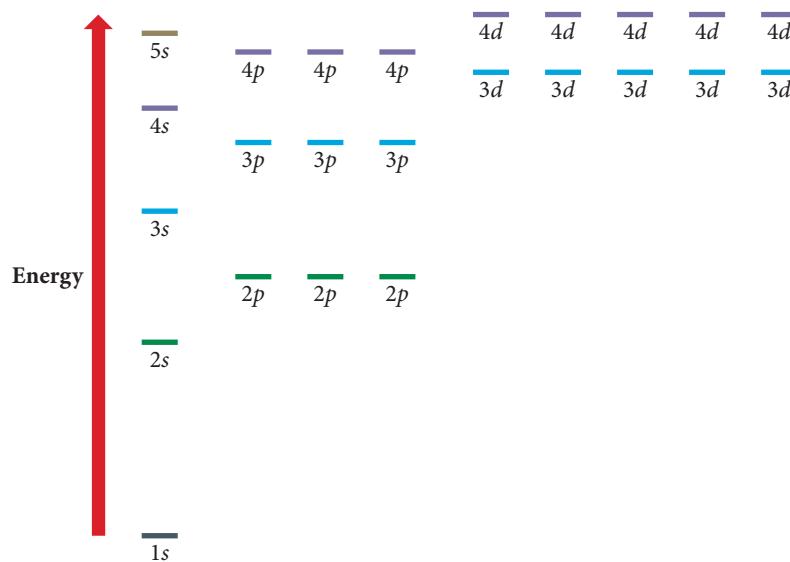
**▲ FIGURE 8.4** Radial Distribution Functions for the 3s, 3p, and 3d Orbitals The 3s electrons penetrate most deeply into the inner orbitals, are least shielded, and experience the greatest effective nuclear charge. The 3d electrons penetrate least. This accounts for the energy ordering of the sublevels:  $s < p < d$ .

are similar when we compare the 3s, 3p, and 3d orbitals. The  $s$  orbitals penetrate more fully than the  $p$  orbitals, which in turn penetrate more fully than the  $d$  orbitals, as shown in Figure 8.4 ▲.

Figure 8.5 ▼ shows the energy ordering of a number of orbitals in multielectron atoms. Notice these features of Figure 8.5:

- Because of penetration, the sublevels of each principal level are *not* degenerate for multielectron atoms.
- In the fourth and fifth principal levels, the effects of penetration become so important that the 4s orbital lies lower in energy than the 3d orbitals and the 5s orbital lies lower in energy than the 4d orbitals.
- The energy separations between one set of orbitals and the next become smaller for 4s orbitals and beyond, and the relative energy ordering of these orbitals can actually vary among elements. These variations result in irregularities in the electron configurations of the transition metals and their ions (as we shall see later).

### General Energy Ordering of Orbitals for Multielectron Atoms



**▲ FIGURE 8.5** General Energy Ordering of Orbitals for Multielectron Atoms.

## Conceptual Connection 8.2 Penetration and Shielding

Which statement is true?

- An orbital that penetrates into the region occupied by core electrons is more shielded from nuclear charge than an orbital that does not penetrate and will therefore have a higher energy.
- An orbital that penetrates into the region occupied by core electrons is less shielded from nuclear charge than an orbital that does not penetrate and will therefore have a higher energy.
- An orbital that penetrates into the region occupied by core electrons is less shielded from nuclear charge than an orbital that does not penetrate and will therefore have a lower energy.
- An orbital that penetrates into the region occupied by core electrons is more shielded from nuclear charge than an orbital that does not penetrate and will therefore have a lower energy.

## Electron Configurations for Multielectron Atoms

Unless otherwise specified, we will use the term *electron configuration* to mean the ground state (or lowest energy) configuration.

Remember that the number of electrons in a neutral atom is equal to its atomic number.

Now that we know the energy ordering of orbitals in multielectron atoms, we can determine ground state electron configurations for the rest of the elements. Since we know that electrons occupy the lowest energy orbitals available when the atom is in its ground state and that only two electrons (with opposing spins) are allowed in each orbital, we can systematically build up the electron configurations for the elements. This pattern of orbital filling is known as the **aufbau principle** (the German word *aufbau* means “build up”). For lithium, with three electrons, the electron configuration and orbital diagram are:

Electron configuration	Orbital diagram
Li $1s^2 2s^1$	 1s                  2s

For carbon, which has six electrons, the electron configuration and orbital diagram are:

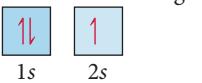
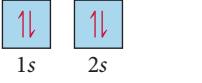
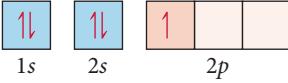
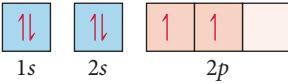
Electron configuration	Orbital diagram
C $1s^2 2s^2 2p^2$	 1s                  2s                  2p

Notice that the  $2p$  electrons occupy the  $p$  orbitals (of equal energy) singly, rather than pairing in one orbital. This way of filling orbitals is known as **Hund's rule**, which states that *when filling degenerate orbitals, electrons fill them singly first, with parallel spins*. Hund's rule is a result of an atom's tendency to find the lowest energy state possible. When two electrons occupy separate orbitals of equal energy, the repulsive interaction between them is lower than when they occupy the same orbital because the electrons are spread out over a larger region of space. By convention we denote these parallel spins with half arrows pointing up.

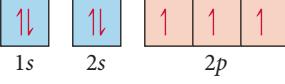
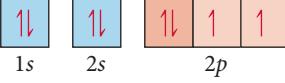
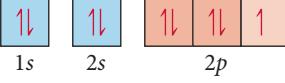
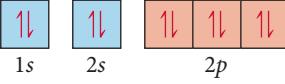
### Summarizing Orbital Filling:

- ▶ Electrons occupy orbitals so as to minimize the energy of the atom; therefore, lower energy orbitals fill before higher energy orbitals. Orbitals fill in the following order:  $1s\ 2s\ 2p\ 3s\ 3p\ 4s\ 3d\ 4p\ 5s\ 4d\ 5p\ 6s$ .
- ▶ Orbitals can hold no more than two electrons each. When two electrons occupy the same orbital, their spins are opposite. This is another way of expressing the Pauli exclusion principle (no two electrons in one atom can have the same four quantum numbers).
- ▶ When orbitals of identical energy are available, electrons first occupy these orbitals singly with parallel spins rather than in pairs. Once the orbitals of equal energy are half full, the electrons start to pair (Hund's rule).

Consider the electron configurations and orbital diagrams for elements with atomic numbers 3–10.

Symbol	Number of electrons	Electron configuration	Orbital diagram
Li	3	$1s^22s^1$	
Be	4	$1s^22s^2$	
B	5	$1s^22s^22p^1$	
C	6	$1s^22s^22p^2$	

Notice that, as a result of Hund's rule, the  $p$  orbitals fill with single electrons before the electrons pair.

N	7	$1s^22s^22p^3$	
O	8	$1s^22s^22p^4$	
F	9	$1s^22s^22p^5$	
Ne	10	$1s^22s^22p^6$	

The electron configuration of neon represents the complete filling of the  $n = 2$  principal level. When writing electron configurations for elements beyond neon, or beyond any other noble gas, we can abbreviate the electron configuration of the previous noble gas—sometimes called the *inner electron configuration*—by the symbol for the noble gas in square brackets. For example, the electron configuration of sodium is:



We can write this configuration more compactly by using [Ne] to represent the inner electrons:



[Ne] represents  $1s^2 2s^2 2p^6$ , the electron configuration for neon.

To write an electron configuration for an element, first find its atomic number from the periodic table—this number equals the number of electrons. Then use the order of filling to distribute the electrons in the appropriate orbitals. Remember that each orbital can hold a maximum of 2 electrons. Consequently,

- the  $s$  sublevel has only one orbital and can therefore hold only 2 electrons.
- the  $p$  sublevel has three orbitals and can hold 6 electrons.
- the  $d$  sublevel has five orbitals and can hold 10 electrons.
- the  $f$  sublevel has seven orbitals and can hold 14 electrons.

### EXAMPLE 8.1 Electron Configurations

Write electron configurations for each element.

- (a) Mg    (b) P    (c) Br    (d) Al

#### SOLUTION

(a) Mg

Magnesium has 12 electrons. Distribute 2 of these into the 1s orbital, 2 into the 2s orbital, 6 into the 2p orbitals, and 2 into the 3s orbital.

Mg  $1s^2 2s^2 2p^6 3s^2$  or [Ne] 3s<sup>2</sup>

(b) P

Phosphorus has 15 electrons. Distribute 2 of these into the 1s orbital, 2 into the 2s orbital, 6 into the 2p orbitals, 2 into the 3s orbital, and 3 into the 3p orbitals.

P  $1s^2 2s^2 2p^6 3s^2 3p^3$  or [Ne] 3s<sup>2</sup> 3p<sup>3</sup>

(c) Br

Bromine has 35 electrons. Distribute 2 of these into the 1s orbital, 2 into the 2s orbital, 6 into the 2p orbitals, 2 into the 3s orbital, 6 into the 3p orbitals, 2 into the 4s orbital, 10 into the 3d orbitals, and 5 into the 4p orbitals.

Br  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$   
or [Ar] 4s<sup>2</sup> 3d<sup>10</sup> 4p<sup>5</sup>

(d) Al

Aluminum has 13 electrons. Distribute 2 of these into the 1s orbital, 2 into the 2s orbital, 6 into the 2p orbitals, 2 into the 3s orbital, and 1 into the 3p orbital.

Al  $1s^2 2s^2 2p^6 3s^2 3p^1$   
or [Ne] 3s<sup>2</sup> 3p<sup>1</sup>

#### FOR PRACTICE 8.1

Write electron configurations for each element.

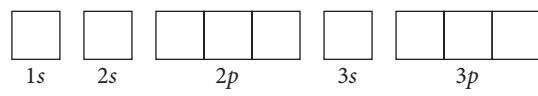
- (a) Cl    (b) Si    (c) Sr    (d) O

### EXAMPLE 8.2 Writing Orbital Diagrams

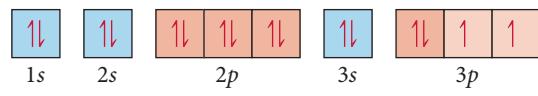
Write the orbital diagram for sulfur and determine the number of unpaired electrons.

#### SOLUTION

Since sulfur's atomic number is 16, it has 16 electrons and the electron configuration  $1s^2 2s^2 2p^6 3s^2 3p^4$ . Draw a box for each orbital, putting the lowest energy orbital (1s) on the far left and proceeding to orbitals of higher energy to the right.



Distribute the 16 electrons into the boxes representing the orbitals, allowing a maximum of 2 electrons per orbital and remembering Hund's rule. You can see from the diagram that sulfur has two unpaired electrons.



Two unpaired electrons

#### FOR PRACTICE 8.2

Write the orbital diagram for Ar and determine the number of unpaired electrons.



What are the four quantum numbers for each of the two electrons in a 4s orbital?

## 8.4 Electron Configurations, Valence Electrons, and the Periodic Table

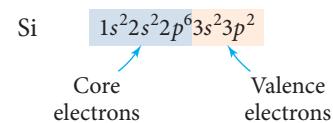
Recall that Mendeleev arranged the periodic table so that elements with similar chemical properties lie in the same column. We can begin to make the connection between an element's properties and its electron configuration by superimposing the electron configurations of the first 18 elements onto a partial periodic table, as shown in Figure 8.6 ►. As we move to the right across a row, the orbitals fill in the correct order. With each subsequent row, the highest principal quantum number increases by one. Notice that as we move down a column, *the number of electrons in the outermost principal energy level (highest n value) remains the same*. The key connection between the macroscopic world (an element's chemical properties) and the atomic world (an atom's electronic structure) lies in these outermost electrons.

An atom's **valence electrons** are those that are important in chemical bonding. *For main-group elements, the valence electrons are those in the outermost principal energy level.* For transition elements, we also count the outermost *d* electrons among the valence electrons (even though they are not in an outermost principal energy level). The chemical properties of an element depend on its valence electrons, which are instrumental in bonding because they are held most loosely (and are therefore the easiest to lose or share). We can now see why the elements in a column of the periodic table have similar chemical properties: *they have the same number of valence electrons.*

Valence electrons are distinguished from all the other electrons in an atom, which are called **core electrons**. The core electrons are those in *complete* principal energy levels and those in *complete d* and *f* sublevels. For example, silicon, with the electron configuration  $1s^2 2s^2 2p^6 3s^2 3p^2$ , has four valence electrons (those in the  $n = 3$  principal level) and ten core electrons as shown at right.

Outer Electron Configurations of Elements 1–18						
1A	8A					
1 H $1s^1$	2A	3A	4A	5A	6A	7A
3 Li $2s^1$	4 Be $2s^2$	5 B $2s^2 2p^1$	6 C $2s^2 2p^2$	7 N $2s^2 2p^3$	8 O $2s^2 2p^4$	9 F $2s^2 2p^5$
11 Na $3s^1$	12 Mg $3s^2$	13 Al $3s^2 3p^1$	14 Si $3s^2 3p^2$	15 P $3s^2 3p^3$	16 S $3s^2 3p^4$	17 Cl $3s^2 3p^5$
						18 Ar $3s^2 3p^6$

▲ FIGURE 8.6 Outer Electron Configurations of the First 18 Elements in the Periodic Table.



### EXAMPLE 8.3 Valence Electrons and Core Electrons

Write the electron configuration for Ge. Identify the valence electrons and the core electrons.

#### SOLUTION

Write the electron configuration for Ge by determining the total number of electrons from germanium's atomic number (32) and then distributing them into the appropriate orbitals.

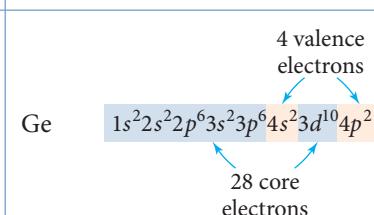
Since germanium is a main-group element, its valence electrons are those in the outermost principal energy level. For germanium, the  $n = 1, 2$ , and  $3$  principal levels are complete (or full) and the  $n = 4$  principal level is outermost. Consequently, the  $n = 4$  electrons are valence electrons and the rest are core electrons.

*Note: In this book, we write electron configurations with the orbitals in the order of filling. However, electron configurations are sometimes written in order of increasing principal quantum number. The electron configuration of germanium written in order of increasing principal quantum number is Ge  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$ .*

#### FOR PRACTICE 8.3

Write an electron configuration for phosphorus. Identify the valence electrons and core electrons.

Ge       $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$



## Orbital Blocks in the Periodic Table

A pattern similar to what we just saw for the first 18 elements exists for the entire periodic table, as shown in Figure 8.7 ▼. Note that because of the filling order of orbitals, the periodic table can be divided into blocks representing the filling of particular sublevels. The first two columns on the left side of the periodic table comprise the *s* block, with outer electron configurations of  $ns^1$  (the alkali metals) and  $ns^2$  (the alkaline earth metals). The six columns on the right side of the periodic table comprise the *p* block, with outer electron configurations of  $ns^2 np^1$ ,  $ns^2 np^2$ ,  $ns^2 np^3$ ,  $ns^2 np^4$ ,  $ns^2 np^5$  (halogens), and  $ns^2 np^6$  (noble gases). The transition elements comprise the *d* block, and the lanthanides and actinides (also called the inner transition elements) comprise the *f* block. (For compactness, the *f* block is normally printed below the *d* block instead of being imbedded within it.)

**Helium is an exception.** Even though it lies in the column with an outer electron configuration of  $ns^2 np^6$ , its electron configuration is simply  $1s^2$ .

You can see that *the number of columns in a block corresponds to the maximum number of electrons that can occupy the particular sublevel of that block*. The *s* block has 2 columns (corresponding to one *s* orbital holding a maximum of two electrons); the *p* block has 6 columns (corresponding to three *p* orbitals with two electrons each); the *d* block has 10 columns (corresponding to five *d* orbitals with two electrons each); and the *f* block has 14 columns (corresponding to seven *f* orbitals with two electrons each).

Notice also that, except for helium, *the number of valence electrons for any main-group element is equal to its lettered group number*. We can tell that chlorine has seven valence electrons because it is in group number 7A.

**Orbital Blocks of the Periodic Table**

		Groups																	
		1 1A		2A						18 8A									
Periods	1	1 H $1s^1$	2 Be $2s^2$							13 B $2s^2 2p^1$	14 C $2s^2 2p^2$	15 N $2s^2 2p^3$	16 O $2s^2 2p^4$	17 F $2s^2 2p^5$	2 He $1s^2$				
	2	3 Li $2s^1$	4 Be $2s^2$							13 Al $3s^2 3p^1$	14 Si $3s^2 3p^2$	15 P $3s^2 3p^3$	16 S $3s^2 3p^4$	17 Cl $3s^2 3p^5$	18 Ar $3s^2 3p^6$				
3	11 Na $3s^1$	12 Mg $3s^2$	3 Be $3s^2$	4 Be $3s^2$	5 Be $3s^2$	6 Be $3s^2$	7 Be $3s^2$	8 Be $3s^2$	9 Be $3s^2$	10 Be $3s^2$	11 Be $3s^2$	12 Be $3s^2$	13 Be $3s^2$	14 Be $3s^2$	15 Be $3s^2$	16 Be $3s^2$	17 Be $3s^2$	18 Be $3s^2$	
4	19 K $4s^1$	20 Ca $4s^2$	21 Sc $4s^2 3d^1$	22 Ti $4s^2 3d^2$	23 V $4s^2 3d^3$	24 Cr $4s^1 3d^5$	25 Mn $4s^2 3d^5$	26 Fe $4s^2 3d^6$	27 Co $4s^2 3d^7$	28 Ni $4s^2 3d^8$	29 Cu $4s^1 3d^{10}$	30 Zn $4s^2 3d^{10}$	31 Ga $4s^2 4p^1$	32 Ge $4s^2 4p^2$	33 As $4s^2 4p^3$	34 Se $4s^2 4p^4$	35 Br $4s^2 4p^5$	36 Kr $4s^2 4p^6$	
5	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $5s^2 4d^1$	40 Zr $5s^2 4d^2$	41 Nb $5s^1 4d^4$	42 Mo $5s^1 4d^5$	43 Tc $5s^2 4d^5$	44 Ru $5s^1 4d^7$	45 Rh $5s^1 4d^8$	46 Pd $4d^{10}$	47 Ag $5s^1 4d^{10}$	48 Cd $5s^2 4d^{10}$	49 In $5s^2 5p^1$	50 Sn $5s^2 5p^2$	51 Sb $5s^2 5p^3$	52 Te $5s^2 5p^4$	53 I $5s^2 5p^5$	54 Xe $5s^2 5p^6$	
6	55 Cs $6s^1$	56 Ba $6s^2$	57 La $6s^2 5d^1$	72 Hf $6s^2 5d^2$	73 Ta $6s^2 5d^3$	74 W $6s^2 5d^4$	75 Re $6s^2 5d^5$	76 Os $6s^2 5d^6$	77 Ir $6s^2 5d^7$	78 Pt $6s^1 5d^9$	79 Au $6s^1 5d^{10}$	80 Hg $6s^2 6p^1$	81 Tl $6s^2 6p^2$	82 Pb $6s^2 6p^3$	83 Bi $6s^2 6p^4$	84 Po $6s^2 6p^5$	85 At $6s^2 6p^6$	86 Rn $6s^2 6p^6$	
7	87 Fr $7s^1$	88 Ra $7s^2$	89 Ac $7s^2 6d^1$	104 Rf $7s^2 6d^2$	105 Db $7s^2 6d^3$	106 Sg $7s^2 6d^4$	107 Bh $7s^2 6d^5$	108 Hs $7s^2 6d^6$	109 Mt $7s^2 6d^7$	110 Ds $7s^2 6d^8$	111 Rg $7s^2 6d^9$	112 Cn $7s^2 6d^{10}$	113 **	114 Fl $7s^2 5f^11$	115 **	116 Lv $7s^2 5f^{12}$	117 **	118 **	
		Lanthanides																	
		Actinides																	
		58 Ce $6s^2 4f^1 5d^1$	59 Pr $6s^2 4f^3$	60 Nd $6s^2 4f^4$	61 Pm $6s^2 4f^5$	62 Sm $6s^2 4f^6$	63 Eu $6s^2 4f^7$	64 Gd $6s^2 4f^7 5d^1$	65 Tb $6s^2 4f^9$	66 Dy $6s^2 4f^{10}$	67 Ho $6s^2 4f^{11}$	68 Er $6s^2 4f^{12}$	69 Tm $6s^2 4f^{13}$	70 Yb $6s^2 4f^{14}$	71 Lu $6s^2 4f^{14} 6d^1$				
		90 Th $7s^2 6d^2$	91 Pa $7s^2 5f^2 6d^1$	92 U $7s^2 5f^3 6d^1$	93 Np $7s^2 5f^4 6d^1$	94 Pu $7s^2 5f^6$	95 Am $7s^2 5f^7$	96 Cm $7s^2 5f^7 6d^1$	97 Bk $7s^2 5f^9$	98 Cf $7s^2 5f^{10}$	99 Es $7s^2 5f^{11}$	100 Fm $7s^2 5f^{12}$	101 Md $7s^2 5f^{13}$	102 No $7s^2 5f^{14}$	103 Lr $7s^2 5f^{14} 6d^1$				

**▲ FIGURE 8.7** The *s*, *p*, *d*, and *f* Blocks of the Periodic Table.

Lastly, note that, for main-group elements, *the row number in the periodic table is equal to the number (or n value) of the highest principal level*. For example, because chlorine is in row 3, its highest principal level is the  $n = 3$  level.

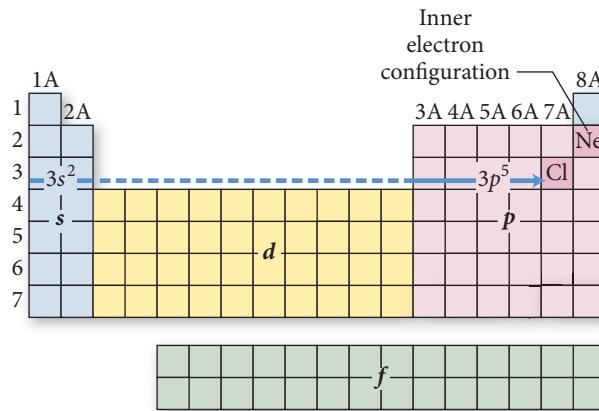
Recall from Chapter 2 that main-group elements are those in the two far left columns (groups 1A, 2A) and the six far right columns (groups 3A–8A) of the periodic table.

### **Summarizing Periodic Table Organization:**

- ▶ The periodic table is divisible into four blocks corresponding to the filling of the four quantum sublevels (*s*, *p*, *d*, and *f*).
- ▶ The group number of a main-group element is equal to the number of valence electrons for that element.
- ▶ The row number of a main-group element is equal to the highest principal quantum number of that element.

## **Writing an Electron Configuration for an Element from Its Position in the Periodic Table**

The organization of the periodic table allows us to write the electron configuration for any element based on its position in the periodic table. For example, suppose we want to write an electron configuration for Cl. The *inner electron configuration* of Cl is that of the noble gas that precedes it in the periodic table, Ne. So we can represent the inner electron configuration with [Ne]. The *outer electron configuration*—the configuration of the electrons beyond the previous noble gas—is obtained by tracing the elements between Ne and Cl and assigning electrons to the appropriate orbitals, as shown here. Remember that the highest *n* value is indicated by the row number (3 for chlorine).



So, we begin with [Ne], then add in the two 3s electrons as we trace across the *s* block, followed by five 3p electrons as we trace across the *p* block to Cl, which is in the fifth column of the *p* block. The electron configuration is:



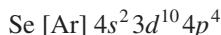
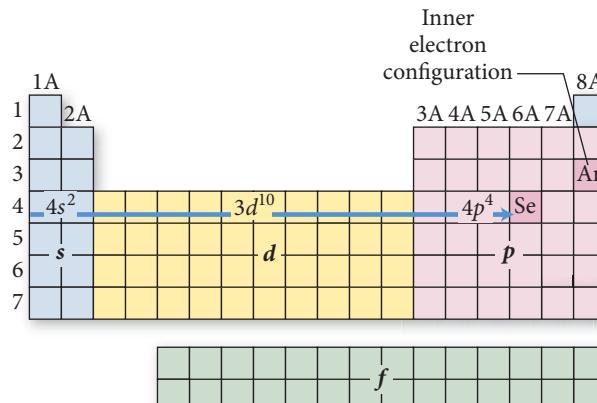
Notice that Cl is in column 7A and therefore has seven valence electrons and an outer electron configuration of  $ns^2 np^5$ .

**EXAMPLE 8.4** Writing Electron Configurations from the Periodic Table


Use the periodic table to write the electron configuration for selenium (Se).

**SOLUTION**

The atomic number of Se is 34. The noble gas that precedes Se in the periodic table is argon, so the inner electron configuration is [Ar]. Obtain the outer electron configuration by tracing the elements between Ar and Se and assigning electrons to the appropriate orbitals. Begin with [Ar]. Because Se is in row 4, add two 4s electrons as you trace across the s block ( $n = \text{row number}$ ). Next, add ten 3d electrons as you trace across the d block ( $n = \text{row number} - 1$ ). Lastly, add four 4p electrons as you trace across the p block to Se, which is in the fourth column of the p block ( $n = \text{row number}$ ).


**FOR PRACTICE 8.4**

Use the periodic table to determine the electron configuration of bismuth (Bi).

**FOR MORE PRACTICE 8.4**

Use the periodic table to write the electron configuration for iodine (I).

### The Transition and Inner Transition Elements

The electron configurations of the transition elements (d block) and inner transition elements (f block) exhibit trends that differ somewhat from those of the main-group elements. As we move to the right across a row in the d block, the d orbitals fill as shown here:

21 Sc $4s^2 3d^1$	22 Ti $4s^2 3d^2$	23 V $4s^2 3d^3$	24 Cr $4s^1 3d^5$	25 Mn $4s^2 3d^5$	26 Fe $4s^2 3d^6$	27 Co $4s^2 3d^7$	28 Ni $4s^2 3d^8$	29 Cu $4s^1 3d^{10}$	30 Zn $4s^2 3d^{10}$
39 Y $5s^2 4d^1$	40 Zr $5s^2 4d^2$	41 Nb $5s^1 4d^4$	42 Mo $5s^1 4d^5$	43 Tc $5s^2 4d^5$	44 Ru $5s^1 4d^7$	45 Rh $5s^1 4d^8$	46 Pd $4d^{10}$	47 Ag $5s^1 4d^{10}$	48 Cd $5s^2 4d^{10}$

However, *the principal quantum number of the d orbitals that fill across each row in the transition series is equal to the row number minus one*. In the fourth row, the 3d orbitals fill, and in the fifth row, the 4d orbitals fill, and so on. This happens because, as we discussed in Section 8.3, the 4s orbital is generally lower in energy than the 3d orbital (because it more efficiently penetrates into the region occupied by the core electrons). The result is that the 4s orbital fills before the 3d orbital, even though its principal quantum number ( $n = 4$ ) is higher.

Keep in mind, however, that the 4s and the 3d orbitals are extremely close to each other in energy so their relative energy ordering depends on the exact species under consideration; this causes some irregular behavior in the transition metals. For example, in the first transition series of the d block, the outer configuration is

$4s^2 3d^x$  with two exceptions: Cr is  $4s^1 3d^5$  and Cu is  $4s^1 3d^{10}$ . This behavior is related to the closely spaced  $3d$  and  $4s$  energy levels and the stability associated with a half-filled (as in Cr) or completely filled (as in Cu) sublevel. Actual electron configurations are definitively determined experimentally (through spectroscopy) and do not always conform to the general pattern. Nonetheless, the patterns we have described allow us to accurately predict electron configurations for most of the elements in the periodic table.

As we move across the  $f$  block (the inner transition series), the  $f$  orbitals fill. For these elements, the principal quantum number of the  $f$  orbitals that fill across each row is the row number *minus two*. (In the sixth row, the  $4f$  orbitals fill, and in the seventh row, the  $5f$  orbitals fill.) In addition, within the inner transition series, the close energy spacing of the  $5d$  and  $4f$  orbitals sometimes causes an electron to enter a  $5d$  orbital instead of the expected  $4f$  orbital. For example, the electron configuration of gadolinium is  $[Xe] 6s^2 4f^7 5d^1$  (instead of the expected  $[Xe] 6s^2 4f^8$ ).

## 8.5 The Explanatory Power of the Quantum-Mechanical Model

We can now see how the quantum-mechanical model accounts for the chemical properties of the elements, such as the inertness of helium or the reactivity of hydrogen, and (more generally) how it accounts for the periodic law. *The chemical properties of elements are largely determined by the number of valence electrons they contain.* Their properties are periodic because the number of valence electrons is periodic.

Since elements within a column in the periodic table have the same number of valence electrons, they also have similar chemical properties. The noble gases, for example, all have eight valence electrons, except for helium, which has two. Although we do not cover the quantitative (or numerical) aspects of the quantum-mechanical model in this book, calculations of the overall energy of the electrons within atoms with eight valence electrons (or two, in the case of helium) show that they are particularly stable. In other words, when a quantum level is completely full, the overall energy of the electrons that occupy that level is particularly low. Therefore, those electrons *cannot* lower their energy by reacting with other atoms or molecules, so the corresponding atom is relatively unreactive or inert. The noble gases are the most chemically stable and relatively unreactive family in the periodic table.

Elements with electron configurations *close* to those of the noble gases are the most reactive because they can attain noble gas electron configurations by losing or gaining a small number of electrons. For example, alkali metals (group 1A) are among the most reactive metals because their outer electron configuration ( $ns^1$ ) is one electron beyond a noble gas configuration. They readily react to lose the  $ns^1$  electron, obtaining a noble gas configuration. This explains why—as we saw in Chapter 2—the group 1A metals tend to form  $1+$  cations. Similarly, alkaline earth metals, with an outer electron configuration of  $ns^2$ , also tend to be reactive metals, losing their  $ns^2$  electrons to form  $2+$  cations. This does not mean that forming an ion with a noble gas configuration is in itself energetically favorable. In fact, forming cations always *requires energy*. But when the cation formed has a noble gas configuration, the energy cost of forming the cation is often less than the energy payback that occurs when that cation forms ionic bonds with anions, as we shall see in Chapter 9.

On the right side of the periodic table, halogens are among the most reactive non-metals because of their  $ns^2 np^5$  electron configurations. They are only one electron short of a noble gas configuration and tend to react to gain that one electron, forming  $1-$  ions. Figure 8.8 ►, first introduced in Chapter 2, shows the elements that form predictable ions. The charges of these ions reflect their electron configurations—in their reactions, these elements form ions with noble gas electron configurations.

### 8A

2	He
	$1s^2$
10	Ne
	$2s^2 2p^6$
18	Ar
	$3s^2 3p^6$
36	Kr
	$4s^2 4p^6$
54	Xe
	$5s^2 5p^6$
86	Rn
	$6s^2 6p^6$

### Noble gases

► The noble gases all have eight valence electrons except for helium, which has two. They have full outer energy levels and are particularly stable and unreactive.

### 1A

3	Li
	$2s^1$
11	Na
	$3s^1$
19	K
	$4s^1$
37	Rb
	$5s^1$
55	Cs
	$6s^1$
87	Fr
	$7s^1$

### Alkali metals

### 2A

4	Be
	$2s^2$
12	Mg
	$3s^2$
20	Ca
	$4s^2$
38	Sr
	$5s^2$
56	Ba
	$6s^2$
88	Ra
	$7s^2$

### Alkaline earth metals

► The alkaline earth metals all have two valence electrons. Each is two electrons beyond a stable electron configuration, and they tend to lose those electrons in their reactions.

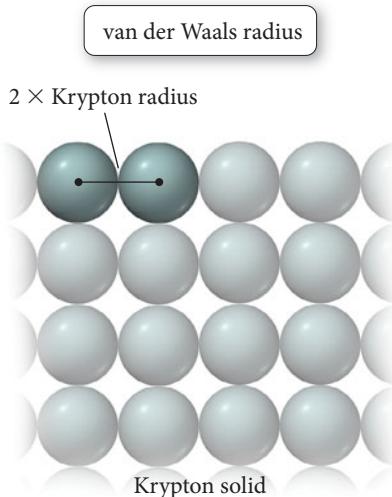
7A
9 F $2s^2 2p^5$
17 Cl $3s^2 3p^5$
35 Br $4s^2 4p^5$
53 I $5s^2 5p^5$
85 At $6s^2 6p^5$

**Halogens**

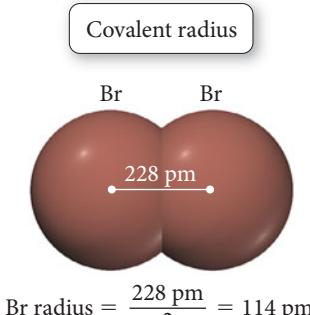
▲ The halogens all have seven valence electrons. Each is one electron short of a stable electron configuration, and they tend to gain one electron in their reactions.

		Elements That Form Ions with Predictable Charges											
		1A    2A								3A    4A    5A    6A    7A    8A			
1	Li <sup>+</sup>									N <sup>3-</sup>	O <sup>2-</sup>	F <sup>-</sup>	
2	Na <sup>+</sup>	Mg <sup>2+</sup>	3B	4B	5B	6B	7B	8B	1B	2B	Al <sup>3+</sup>	S <sup>2-</sup>	Cl <sup>-</sup>
3	K <sup>+</sup>	Ca <sup>2+</sup>										Se <sup>2-</sup>	Br <sup>-</sup>
4	Rb <sup>+</sup>	Sr <sup>2+</sup>										Te <sup>2-</sup>	I <sup>-</sup>
5	Cs <sup>+</sup>	Ba <sup>2+</sup>											

▲ FIGURE 8.8 Elements That Form Ions with Predictable Charges Notice that each ion has a noble gas electron configuration.



▲ The van der Waals radius of an atom is one-half the distance between adjacent nuclei in the atomic solid.



▲ The covalent radius of bromine is one-half the distance between two bonded bromine atoms.

## 8.6 Periodic Trends in the Size of Atoms and Effective Nuclear Charge

In previous chapters, we saw that the volume of an atom is taken up primarily by its electrons (Chapter 2) occupying quantum-mechanical orbitals (Chapter 7). We also saw that these orbitals do not have a definite boundary but represent only a statistical probability distribution for where the electron is found. So how do we define the size of an atom? One way to define atomic radii is to consider the distance between *nonbonding* atoms that are in direct contact. For example, krypton can be frozen into a solid in which the krypton atoms are touching each other but are not bonded together. The distance between the centers of adjacent krypton atoms—which can be determined from the solid’s density—is then twice the radius of a krypton atom. An atomic radius determined in this way is called the **nonbonding atomic radius** or the **van der Waals radius**. The van der Waals radius represents the radius of an atom when it is not bonded to another atom.

Another way to define the size of an atom, called the **bonding atomic radius** or **covalent radius**, is defined differently for nonmetals and metals, as follows:

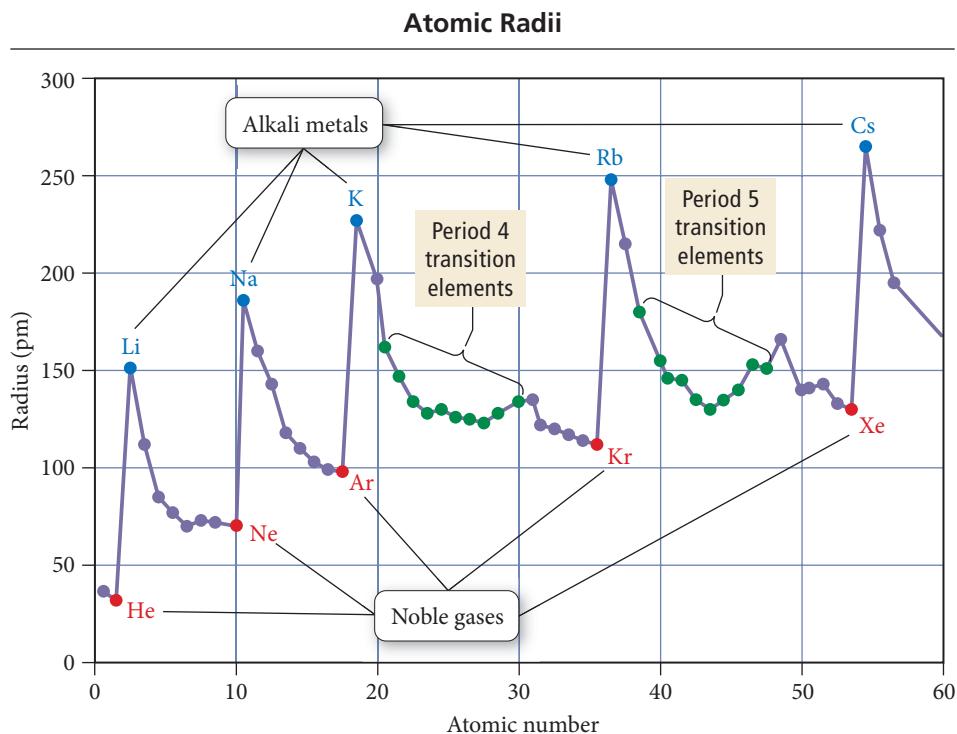
Nonmetals: one-half the distance between two of the atoms bonded together

Metals: one-half the distance between two of the atoms next to each other in a crystal of the metal

For example, the distance between Br atoms in Br<sub>2</sub> is 228 pm; therefore, the Br covalent radius is assigned to be one-half of 228 pm or 114 pm.

Using this method, we can assign radii to all elements in the periodic table that form chemical bonds or form metallic crystals. A more general term, the **atomic radius**, refers to a set of average bonding radii determined from measurements on a large number of elements and compounds. The atomic radius represents the radius of an atom when it is bonded to another atom and is always smaller than the van der Waals radius. The approximate bond length of any two covalently bonded atoms is the sum of their atomic radii. For example, the approximate bond length for ICl is iodine’s atomic radius (133 pm) plus chlorine’s atomic radius (99 pm), for a bond length of 232 pm. (The actual experimentally measured bond length in ICl is 232.07 pm.)

Figure 8.9 ► shows the atomic radius plotted as a function of atomic number for the first 57 elements in the periodic table. Notice the periodic trend in the radii. Atomic radii peak with each alkali metal. Figure 8.10 ► is a relief map of atomic radii for most of the elements in the periodic table. The general trends in the atomic radii of main-group elements, which are the same as trends observed in van der Waals radii, are:

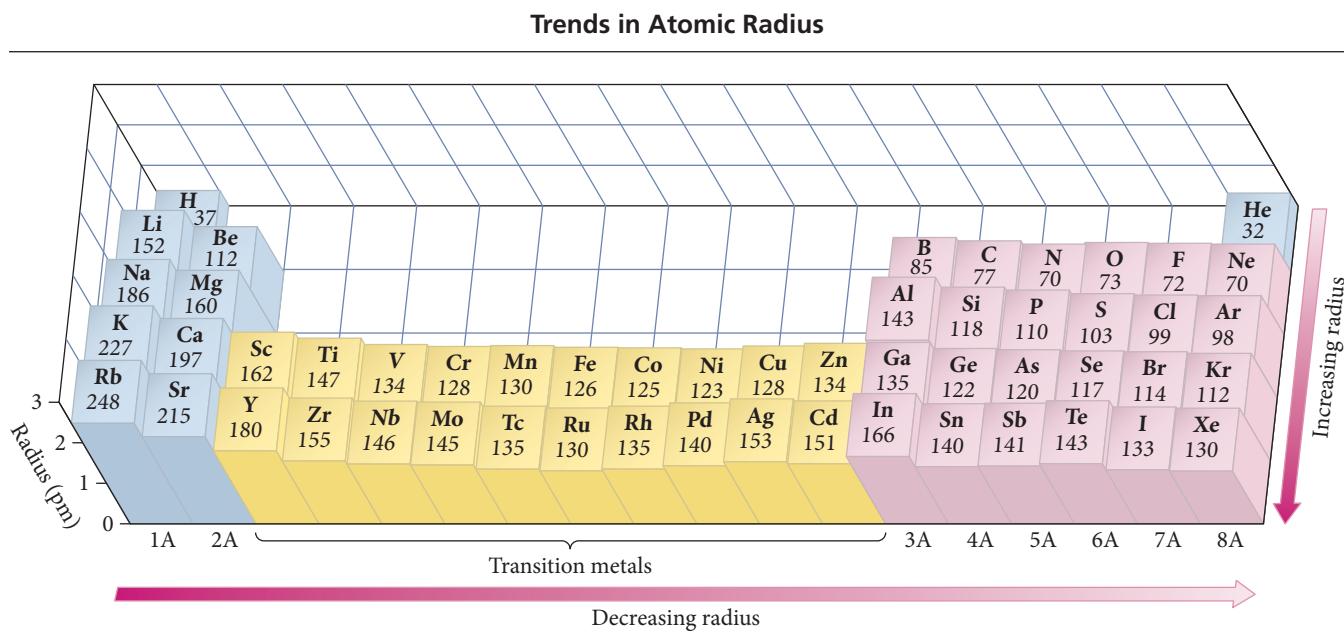


**◀ FIGURE 8.9** Atomic Radius versus Atomic Number Notice the periodic trend in atomic radius, starting at a peak with each alkali metal and falling to a minimum with each noble gas.

1. As we move down a column (or family) in the periodic table, atomic radius increases.
2. As we move to the right across a period (or row) in the periodic table, atomic radius decreases.

We can understand the observed trend in radius as we move down a column based on the trends in the sizes of atomic orbitals. The atomic radius is largely determined by the valence electrons, the electrons farthest from the nucleus. As we move down a column in the periodic table, the highest principal quantum number ( $n$ ) of the valence electrons increases. Consequently, the valence electrons occupy larger orbitals, resulting in larger atoms.

The bonding radii of some elements, such as helium and neon, must be approximated since they do not form either chemical bonds or metallic crystals.

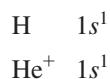


**▲ FIGURE 8.10** Trends in Atomic Radius In general, atomic radii increase as we move down a column and decrease as we move to the right across a period in the periodic table.

The observed trend in atomic radius as we move to the right across a row, however, is a bit more complex. To understand this trend, we must revisit some concepts from Section 8.3, including effective nuclear charge and shielding.

## Effective Nuclear Charge

The trend in atomic radius as we move to the right across a row in the periodic table is determined by the inward pull of the nucleus on the electrons in the outermost principal energy level (highest  $n$  value). According to Coulomb's law, the attraction between a nucleus and an electron increases with increasing magnitude of nuclear charge. For example, compare the H atom to the  $\text{He}^+$  ion:



It takes 1312 kJ/mol of energy to remove the 1s electron from hydrogen but 5251 kJ/mol of energy to remove it from  $\text{He}^+$ . Why? Although each electron is in a 1s orbital, the electron in the helium ion is attracted to the nucleus by a 2+ charge, while the electron in the hydrogen atom is attracted to the nucleus by only a 1+ charge. Therefore, the electron in the helium ion is held more tightly (it has lower potential energy according to Coulomb's law), making it more difficult to remove and making the helium ion smaller than the hydrogen atom.

As we saw in Section 8.3, any one electron in a multielectron atom experiences both the positive charge of the nucleus (which is attractive) and the negative charges of the other electrons (which are repulsive). Consider again the outermost electron in the lithium atom:



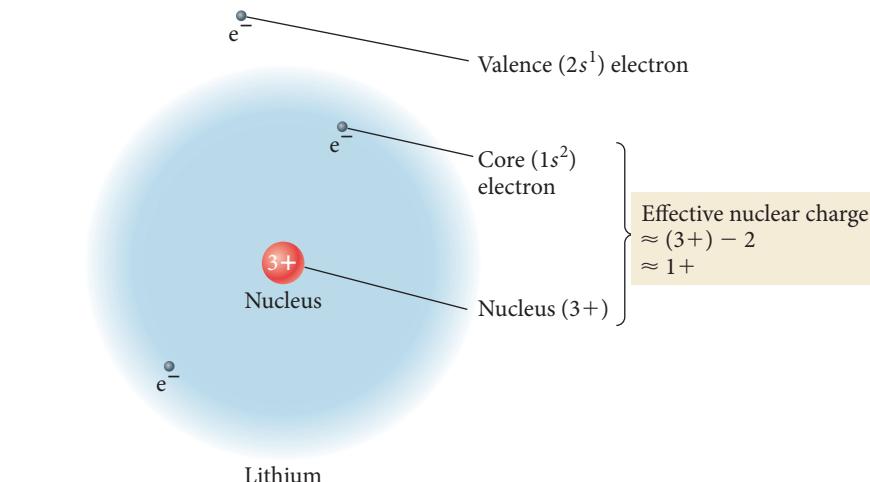
Even though the 2s orbital penetrates into the 1s orbital to some degree, the majority of the 2s orbital is outside of the 1s orbital. Therefore the electron in the 2s orbital is partially *screened* or *shielded* from the 3+ charge of the nucleus by the 2- charge of the 1s (or core) electrons, reducing the net charge experienced by the 2s electron as shown in Figure 8.11 ▶.

As we have seen, we can define the average or net charge experienced by an electron as the *effective nuclear charge*. The effective nuclear charge experienced by a particular electron in an atom is the *actual nuclear charge* ( $Z$ ) minus the *charge shielded by other electrons* ( $S$ ):

$$Z_{\text{eff}} = Z - S$$

Effective nuclear charge      Actual nuclear charge      Charge screened by other electrons

### Screening and Effective Nuclear Charge



**► FIGURE 8.11** Screening and Effective Nuclear Charge The valence electron in lithium experiences the 3+ charge of the nucleus through the screen of the 2- charge of the core electrons. The effective nuclear charge acting on the valence electron is approximately 1+.

For lithium, we estimate that the two core electrons shield the valence electron from the nuclear charge with high efficiency ( $S$  is nearly 2). The effective nuclear charge experienced by lithium's valence electron is therefore slightly greater than  $1+$ .

Now consider the valence electrons in beryllium (Be), with atomic number 4. Its electron configuration is:



To estimate the effective nuclear charge experienced by the  $2s$  electrons in beryllium, we must distinguish between two different types of shielding: (1) the shielding of the outermost electrons by the core electrons and (2) the shielding of the outermost electrons by *each other*. The key to understanding the trend in atomic radius is the difference between these two types of shielding.

**Core electrons efficiently shield electrons in the outermost principal energy level from nuclear charge, but outermost electrons do not efficiently shield one another from nuclear charge.**

For example, the two outermost electrons in beryllium experience the  $4+$  charge of the nucleus through the shield of the two  $1s$  core electrons without shielding each other from that charge very much. We estimate that the shielding ( $S$ ) experienced by any one of the outermost electrons due to the core electrons is nearly 2, but that the shielding due to the other outermost electron is nearly zero. The effective nuclear charge experienced by beryllium's outermost electrons is therefore slightly greater than  $2+$ .

The effective nuclear charge experienced by *beryllium's* outermost electrons is greater than that experienced by *lithium's* outermost electron. Consequently, beryllium's outermost electrons are held more tightly than lithium's, resulting in a smaller atomic radius for beryllium. The effective nuclear charge experienced by an atom's outermost electrons continues to become more positive as we move to the right across the rest of the second row in the periodic table, resulting in successively smaller atomic radii. The same trend is generally observed in all main-group elements.

#### **Summarizing Atomic Radii for Main-Group Elements:**

- ▶ As we move down a column in the periodic table, the principal quantum number ( $n$ ) of the electrons in the outermost principal energy level increases, resulting in larger orbitals and therefore larger atomic radii.
- ▶ As we move to the right across a row in the periodic table, the effective nuclear charge ( $Z_{\text{eff}}$ ) experienced by the electrons in the outermost principal energy level increases, resulting in a stronger attraction between the outermost electrons and the nucleus, and smaller atomic radii.

#### **Conceptual Connection 8.4 Effective Nuclear Charge**

Which electrons experience the greatest effective nuclear charge?

- The valence electrons in Mg
- The valence electrons in Al
- The valence electrons in S

#### **Atomic Radii and the Transition Elements**

In Figure 8.10, we can see that as we move down the first two rows of a column within the transition metals, the elements follow the same general trend in atomic radii as the main-group elements (the radii get larger). However, with the exception of the first couple of elements in each transition series, the atomic radii of the transition elements *do not* follow the same trend as the main-group elements as we move to the right across a row. Instead of decreasing in size, *the radii of transition elements stay roughly constant across*

each row. Why? 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 (recall from Section 8.3, for example, that the  $4s$  orbital fills before the  $3d$ ). As another proton is added to the nucleus of each successive element, another electron is added as well, but the electron goes into an  $n_{\text{highest}} - 1$  orbital. The number of outermost electrons stays constant, and they experience a roughly constant effective nuclear charge, keeping the radius approximately constant.

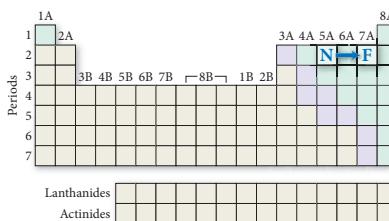
### EXAMPLE 8.5 Atomic Size

On the basis of periodic trends, choose the larger atom in each pair (if possible). Explain your choices.

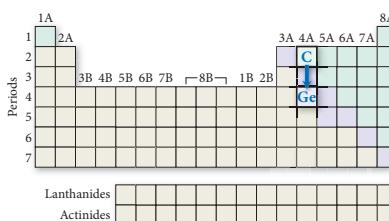
- (a) N or F      (b) C or Ge      (c) N or Al      (d) Al or Ge

#### SOLUTION

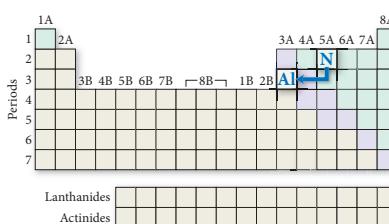
- (a) N atoms are larger than F atoms because as you trace the path between N and F on the periodic table, you move to the right within the same period. As you move to the right across a period, the effective nuclear charge experienced by the outermost electrons increases, resulting in a smaller radius.



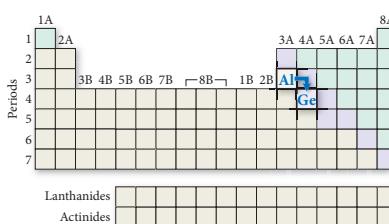
- (b) Ge atoms are larger than C atoms because as you trace the path between C and Ge on the periodic table, you move down a column. Atomic size increases as you move down a column because the outermost electrons occupy orbitals with a higher principal quantum number that are therefore larger, resulting in a larger atom.



- (c) Al atoms are larger than N atoms because as you trace the path between N and Al on the periodic table, you move down a column (atomic size increases) and then to the left across a period (atomic size increases). These effects add together for an overall increase.



- (d) Based on periodic trends alone, you cannot tell which atom is larger, because as you trace the path between Al and Ge you go to the right across a period (atomic size decreases) and then down a column (atomic size increases). These effects tend to counter each other, and it is not easy to tell which will predominate.



#### FOR PRACTICE 8.5

On the basis of periodic trends, choose the larger atom in each pair (if possible):

- (a) Sn or I      (b) Ge or Po      (c) Cr or W      (d) F or Se

#### FOR MORE PRACTICE 8.5

Arrange the elements in order of decreasing radius: S, Ca, F, Rb, Si.

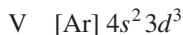
## 8.7 Ions: Electron Configurations, Magnetic Properties, Ionic Radii, and Ionization Energy

Recall that ions are simply atoms (or groups of atoms) that have lost or gained electrons. In this section, we examine periodic trends in ionic electron configurations, magnetic properties, ionic radii, and ionization energies.

### Electron Configurations and Magnetic Properties of Ions

We can deduce the electron configuration of a main-group monoatomic ion from the electron configuration of the neutral atom and the charge of the ion. For anions, we *add* the number of electrons indicated by the magnitude of the charge of the anion. For example, the electron configuration of fluorine (F) is  $1s^2 2s^2 2p^5$  and that of the fluoride ion ( $F^-$ ) is  $1s^2 2s^2 2p^6$ .

We determine the electron configuration of cations by *subtracting* the number of electrons indicated by the magnitude of the charge. For example, the electron configuration of lithium (Li) is  $1s^2 2s^1$  and that of the lithium ion ( $Li^+$ ) is  $1s^2 2s^0$  (or simply  $1s^2$ ). For main-group cations, we remove the required number of electrons in the reverse order of filling. However for transition metal cations, the trend is different. When writing the electron configuration of a transition metal cation, we *remove the electrons in the highest  $n$ -value orbitals first, even if this does not correspond to the reverse order of filling*. For example, the electron configuration of vanadium is:



The  $V^{2+}$  ion, however, has the following electron configuration:

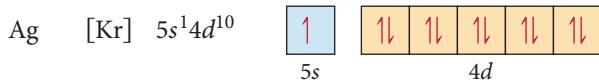


In other words, for transition metal cations, the order in which electrons are removed upon ionization is *not* the reverse of the filling order. During filling, the  $4s$  orbital normally fills before the  $3d$  orbital. When a fourth period transition metal ionizes, however, it normally loses its  $4s$  electrons before its  $3d$  electrons. Why this unexpected behavior? The full answer to this question is beyond our scope, but the following two factors contribute to this phenomenon.

- As discussed previously, the  $ns$  and  $(n - 1)d$  orbitals are extremely close in energy and, depending on the exact configuration, can vary in relative energy ordering.
- As the  $(n - 1)d$  orbitals begin to fill in the first transition series, the increasing nuclear charge stabilizes the  $(n - 1)d$  orbitals relative to the  $ns$  orbitals. This happens because the  $(n - 1)d$  orbitals are not the outermost (or highest  $n$ ) orbitals and are therefore not effectively shielded from the increasing nuclear charge by the  $ns$  orbitals.

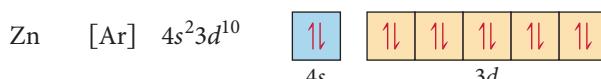
The bottom-line experimental observation is that an  $ns^0(n - 1)d^x$  configuration is lower in energy than an  $ns^2(n - 1)d^{x-2}$  configuration for transition metal ions. Therefore, we remove the  $ns$  electrons before the  $(n - 1)d$  electrons when writing electron configurations for transition metal ions.

The magnetic properties of transition metal ions support these assignments. Recall from Section 8.3 that an unpaired electron generates a magnetic field due to its spin. Consequently, an atom or ion that contains unpaired electrons is attracted to an external magnetic field, and we say that the atom or ion is **paramagnetic**. For example, consider the electron configuration of silver:



Silver's unpaired  $5s$  electron causes silver to be paramagnetic. In fact, an early demonstration of electron spin—called the Stern–Gerlach experiment—involved the interaction of a beam of silver atoms with a magnetic field. An atom or ion in which all electrons are paired is not

attracted to an external magnetic field—it is instead slightly repelled—and we say that the atom or ion is **diamagnetic**. The zinc atom is diamagnetic.



The magnetic properties of the zinc ion provide confirmation that the  $4s$  electrons are indeed lost before  $3d$  electrons in the ionization of zinc. If zinc lost two  $3d$  electrons upon ionization, then the  $Zn^{2+}$  would become paramagnetic (because the two electrons would come out of two different filled  $d$  orbitals, leaving each of them with one unpaired electron). But the zinc ion, like the zinc atom, is diamagnetic because the  $4s$  electrons are lost instead.



Observations in other transition metals confirm that the  $ns$  electrons are lost before the  $(n - 1)d$  electrons upon ionization.

### EXAMPLE 8.6 Electron Configurations and Magnetic Properties for Ions

Write the electron configuration and orbital diagram for each ion and determine whether each is diamagnetic or paramagnetic.

- (a)  $Al^{3+}$       (b)  $S^{2-}$       (c)  $Fe^{3+}$

#### SOLUTION

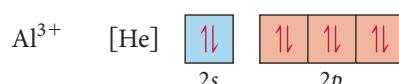
**(a)  $Al^{3+}$**

Begin by writing the electron configuration of the neutral atom.

Since this ion has a  $3+$  charge, remove three electrons to write the electron configuration of the ion. Write the orbital diagram by drawing half-arrows to represent each electron in boxes representing the orbitals. Because there are no unpaired electrons,  $Al^{3+}$  is diamagnetic.

$Al$       [Ne]  $3s^2 3p^1$

$Al^{3+}$       [Ne] or [He]  $2s^2 2p^6$



Diamagnetic

**(b)  $S^{2-}$**

Begin by writing the electron configuration of the neutral atom.

Since this ion has a  $2-$  charge, add two electrons to write the electron configuration of the ion. Write the orbital diagram by drawing half-arrows to represent each electron in boxes representing the orbitals. Because there are no unpaired electrons,  $S^{2-}$  is diamagnetic.

$S$       [Ne]  $3s^2 3p^4$

$S^{2-}$       [Ne]  $3s^2 3p^6$



Diamagnetic

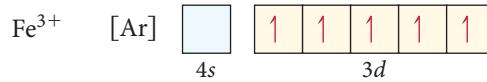
**(c)  $Fe^{3+}$**

Begin by writing the electron configuration of the neutral atom.

Since this ion has a  $3+$  charge, remove three electrons to write the electron configuration of the ion. Since it is a transition metal, remove the electrons from the  $4s$  orbital before removing electrons from the  $3d$  orbitals. Write the orbital diagram by drawing half-arrows to represent each electron in boxes representing the orbitals. There are unpaired electrons, so  $Fe^{3+}$  is paramagnetic.

$Fe$       [Ar]  $4s^2 3d^6$

$Fe^{3+}$       [Ar]  $4s^0 3d^5$



Paramagnetic

#### FOR PRACTICE 8.6

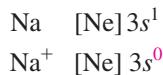
Write the electron configuration and orbital diagram for each ion and predict whether each will be paramagnetic or diamagnetic.

- (a)  $Co^{2+}$       (b)  $N^{3-}$       (c)  $Ca^{2+}$



## Ionic Radii

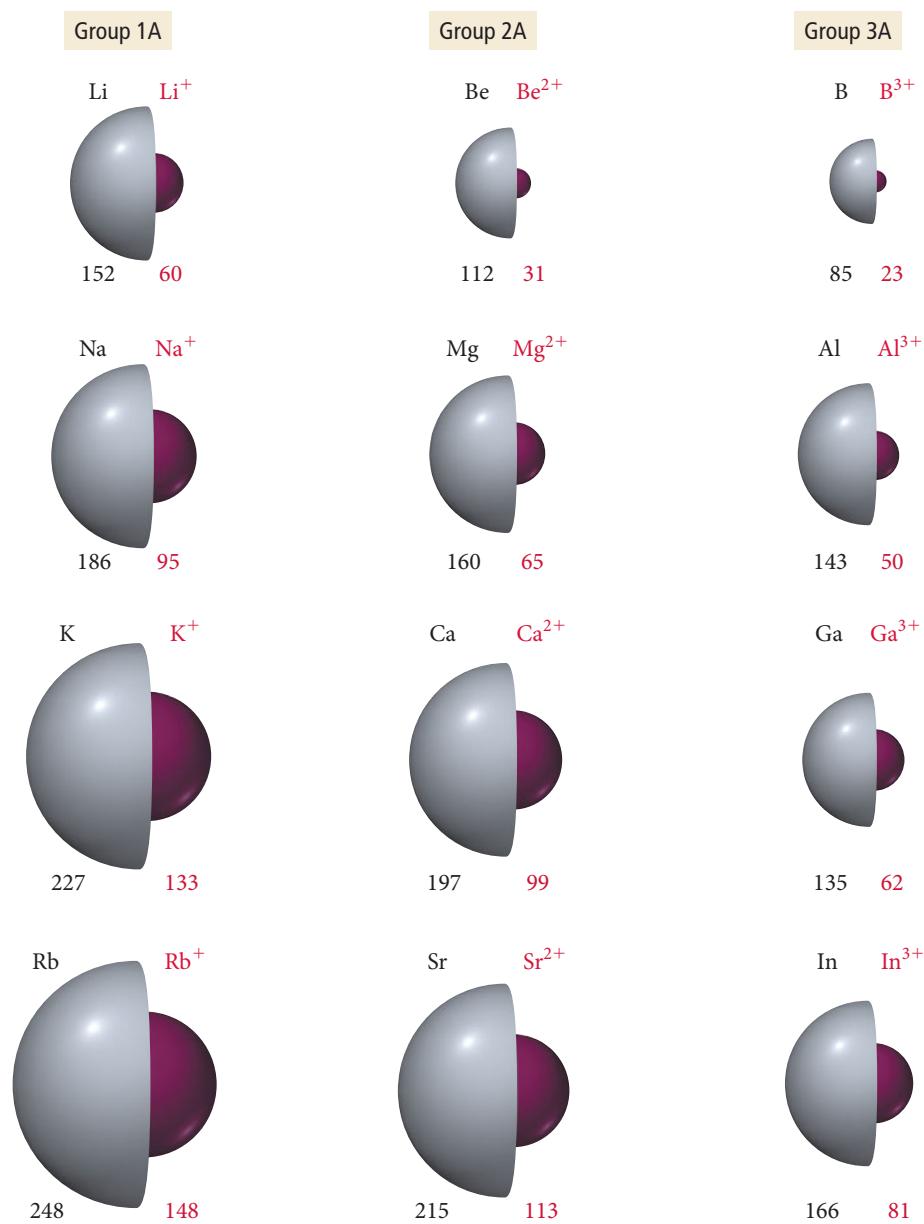
What happens to the radius of an atom when it becomes a cation? An anion? Consider, for example, the difference between the Na atom and the  $\text{Na}^+$  ion. Their electron configurations are:



The sodium atom has an outer  $3s$  electron and a neon core. Since the  $3s$  electron is the outermost electron, and since it is shielded from the nuclear charge by the core electrons, it contributes greatly to the size of the sodium atom. The sodium cation, having lost the outermost  $3s$  electron, has only the neon core and carries a charge of  $1+$ . Without the  $3s$  electron, the sodium cation (ionic radius = 95 pm) becomes much smaller than the sodium atom (covalent radius = 186 pm). The trend is the same with all cations and their atoms, as shown in Figure 8.12 ▶.

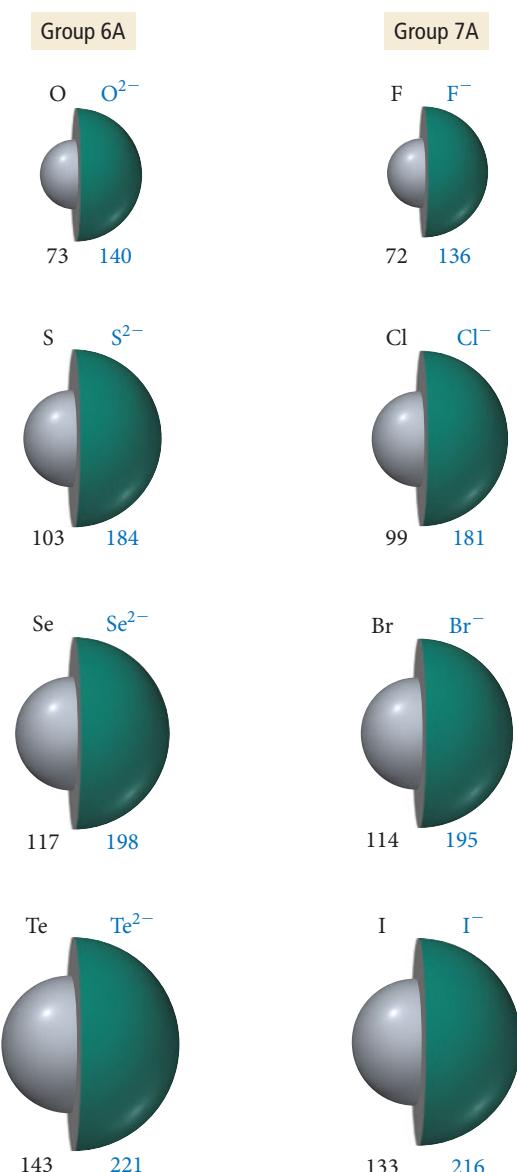
**Cations are much smaller than their corresponding atoms.**

**Radii of Atoms and Their Cations (pm)**



◀ **FIGURE 8.12** Sizes of Atoms and Their Cations Atomic and ionic radii (pm) for the first three columns of main-group elements.

### Radii of Atoms and Their Anions (pm)



What about anions? Consider, for example, the difference between Cl and Cl<sup>-</sup>. Their electron configurations are:



The chlorine anion has one additional outermost electron but no additional proton to increase the nuclear charge. The extra electron increases the repulsions among the outermost electrons, resulting in a chloride anion that is larger than the chlorine atom. The trend is the same with all anions and their atoms, as shown in Figure 8.13 ◀.

#### Anions are much larger than their corresponding atoms.

We can observe an interesting trend in ionic size by examining the radii of an *isoelectronic* series of ions—ions with the same number of electrons. Consider the following ions and their radii:

S <sup>2-</sup> (184 pm)	Cl <sup>-</sup> (181 pm)	K <sup>+</sup> (133 pm)	Ca <sup>2+</sup> (99 pm)
18 electrons	18 electrons	18 electrons	18 electrons
16 protons	17 protons	19 protons	20 protons

All of these ions have 18 electrons in exactly the same orbitals, but the radius of each ion gets successively smaller. Why? The reason is the progressively greater number of protons. The S<sup>2-</sup> ion has 16 protons and therefore a charge of 16+ pulling on 18 electrons. The Ca<sup>2+</sup> ion, however, has 20 protons, and therefore a charge of 20+ pulling on the same 18 electrons. The result is a much smaller radius. For a given number of electrons, a greater nuclear charge results in a smaller atom or ion.

◀ FIGURE 8.13 Sizes of Atoms and Their Anions Atomic and ionic radii for groups 6A and 7A in the periodic table.

### EXAMPLE 8.7 Ion Size

Choose the larger atom or ion from each pair.

- (a) S or S<sup>2-</sup>    (b) Ca or Ca<sup>2+</sup>    (c) Br<sup>-</sup> or Kr

#### SOLUTION

- (a) The S<sup>2-</sup> ion is larger than an S atom because anions are larger than the atoms from which they are formed.  
 (b) A Ca atom is larger than Ca<sup>2+</sup> because cations are smaller than the atoms from which they are formed.  
 (c) A Br<sup>-</sup> ion is larger than a Kr atom because, although they are isoelectronic, Br<sup>-</sup> has one fewer proton than Kr, resulting in a lesser pull on the electrons and therefore a larger radius.

#### FOR PRACTICE 8.7

Choose the larger atom or ion from each pair.

- (a) K or K<sup>+</sup>    (b) F or F<sup>-</sup>    (c) Ca<sup>2+</sup> or Cl<sup>-</sup>

#### FOR MORE PRACTICE 8.7

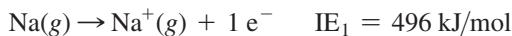
Arrange the following in order of decreasing radius: Ca<sup>2+</sup>, Ar, Cl<sup>-</sup>.

## Conceptual Connection 8.5 Ions, Isotopes, and Atomic Size

In the previous sections, we have seen how the number of electrons and the number of protons affects the size of an atom or ion. However, we have not considered how the number of neutrons affects the size of an atom. Why not? Would you expect isotopes—for example, C-12 and C-13—to have different atomic radii?

### Ionization Energy

The **ionization energy (IE)** of an atom or ion is the energy required to remove an electron from the atom or ion in the gaseous state. Ionization energy is always positive because removing an electron always takes energy. (The process is similar to an endothermic reaction, which absorbs heat and therefore has a positive  $\Delta H$ .) The energy required to remove the first electron is called the *first ionization energy (IE<sub>1</sub>)*. For example, we represent the first ionization of sodium with the equation:



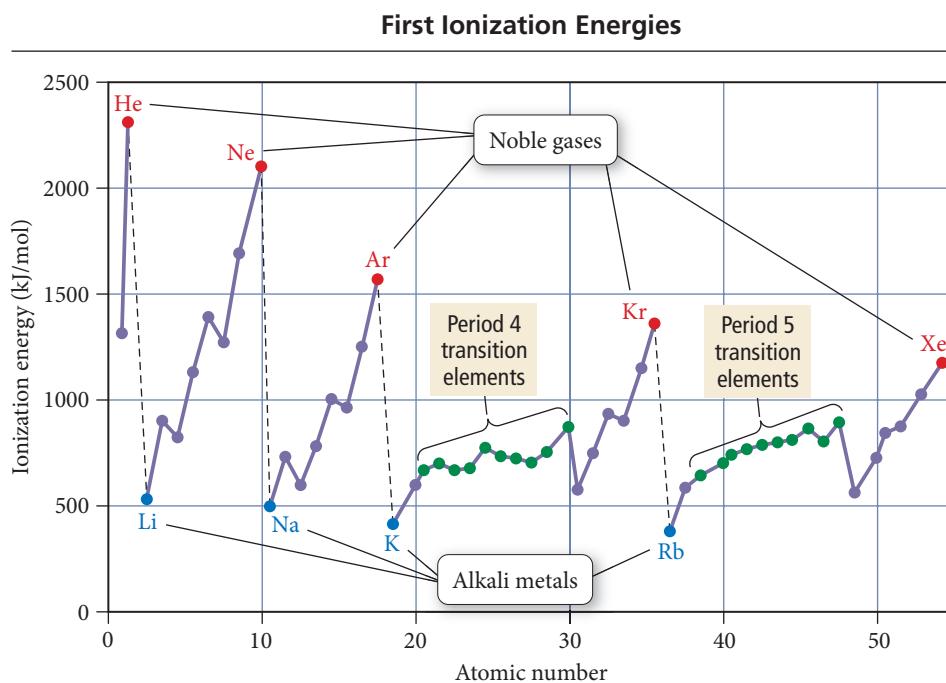
The energy required to remove the second electron is the *second ionization energy (IE<sub>2</sub>)*, the energy required to remove the third electron is the *third ionization energy (IE<sub>3</sub>)*, and so on. We represent the second ionization energy of sodium as:



Notice that the second ionization energy is not the energy required to remove *two* electrons from sodium (that quantity is the sum of IE<sub>1</sub> and IE<sub>2</sub>), but rather the energy required to remove one electron from Na<sup>+</sup>. We look at trends in IE<sub>1</sub> and IE<sub>2</sub> separately.

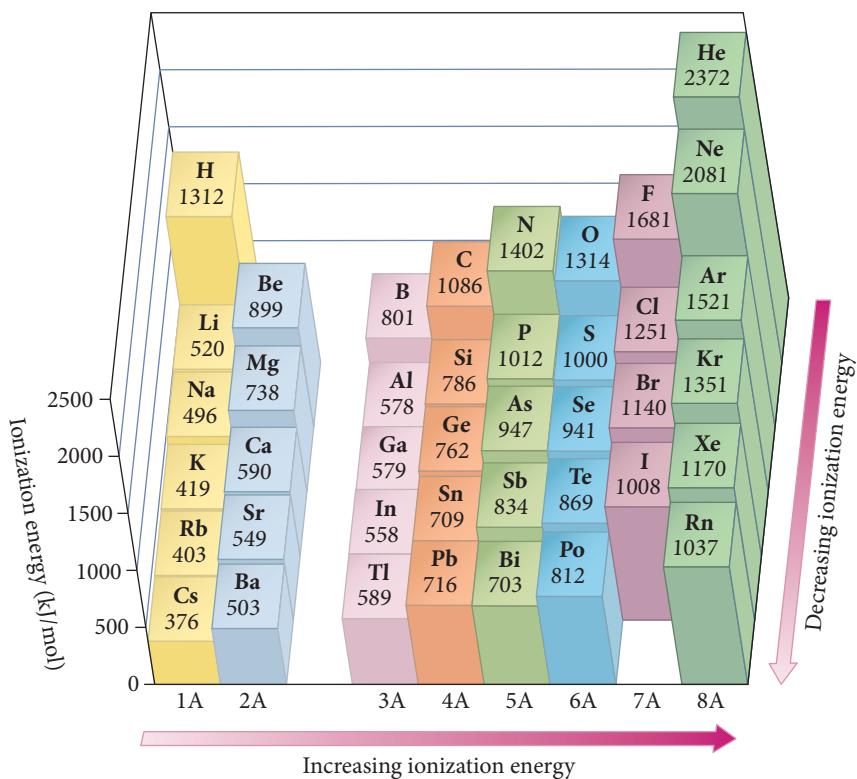
### Trends in First Ionization Energy

The first ionization energies of the elements through Xe are shown in Figure 8.14 ▶. Notice the periodic trend in ionization energy, peaking at each noble gas and bottoming at each alkali metal. Based on what we have learned about electron configurations and effective nuclear charge, how can we account for the observed trend? As we have seen,



◀ FIGURE 8.14 First Ionization Energy versus Atomic Number for the Elements through Xenon Ionization starts at a minimum with each alkali metal and rises to a peak with each noble gas.

### Trends in First Ionization Energy



▲ FIGURE 8.15 Trends in Ionization Energy Ionization energy increases as we move to the right across a period and decreases as we move down a column in the periodic table.

the principal quantum number,  $n$ , increases as we move down a column. Within a given sublevel, orbitals with higher principal quantum numbers are larger than orbitals with smaller principal quantum numbers. Consequently, electrons in the outermost principal level are farther away from the positively charged nucleus—and are therefore held less tightly—as we move down a column. This results in a lower ionization energy as we move down a column, as shown in Figure 8.15 ▲.

What about the trend as we move to the right across a row? For example, would it take more energy to remove an electron from Na or from Cl, two elements on either end of the third row in the periodic table? We know that Na has an outer electron configuration of  $3s^1$  and Cl has an outer electron configuration of  $3s^2 3p^5$ . As discussed previously, the outermost electrons in chlorine experience a higher effective nuclear charge than the outermost electrons in sodium (which is why chlorine has a smaller atomic radius than sodium). Consequently, we would expect chlorine to have a higher ionization energy than sodium, which is indeed the case. We can make a similar argument for the other main-group elements: ionization energy generally increases as we move to the right across a row in the periodic table, as shown in Figure 8.15.

#### Summarizing Ionization Energy for Main-Group Elements:

- ▶ Ionization energy generally *decreases* as we move down a column (or family) in the periodic table because electrons in the outermost principal level are increasingly farther away from the positively charged nucleus and are therefore held less tightly.
- ▶ Ionization energy generally *increases* as we move to the right across a row (or period) in the periodic table because electrons in the outermost principal energy level generally experience a greater effective nuclear charge ( $Z_{\text{eff}}$ ).

### EXAMPLE 8.8 Ionization Energy

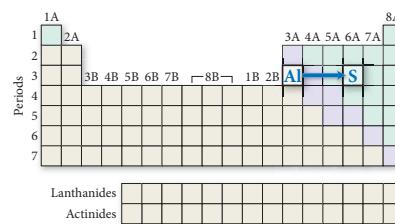
On the basis of periodic trends, determine which element in each pair has the higher first ionization energy (if possible).

- (a) Al or S
- (b) As or Sb
- (c) N or Si
- (d) O or Cl

#### SOLUTION

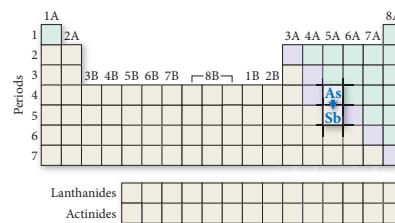
- (a) Al or S

S has a higher ionization energy than Al because as you trace the path between Al and S on the periodic table, you move to the right within the same row. Ionization energy increases as you go to the right due to increasing effective nuclear charge.



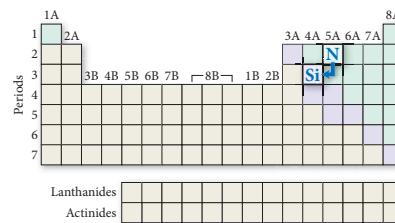
- (b) As or Sb

As has a higher ionization energy than Sb because as you trace the path between As and Sb on the periodic table, you move down a column. Ionization energy decreases as you go down a column as a result of the increasing size of orbitals with increasing  $n$ .



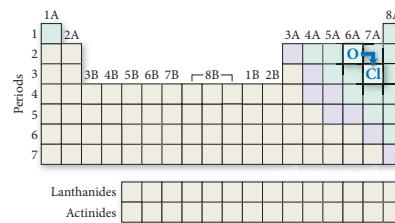
- (c) N or Si

N has a higher ionization energy than Si because as you trace the path between N and Si on the periodic table, you move down a column (ionization energy decreases) and then to the left across a row (ionization energy decreases). These effects sum together for an overall decrease.



- (d) O or Cl

Based on periodic trends alone, it is impossible to tell which has a higher ionization energy because, as you trace the path between O and Cl, you go to the right across a row (ionization energy increases) and then down a column (ionization energy decreases). These effects tend to counter each other, and it is not obvious which will dominate.



#### FOR PRACTICE 8.8

On the basis of periodic trends, determine the element in each pair with the higher first ionization energy (if possible).

- (a) Sn or I
- (b) Ca or Sr
- (c) C or P
- (d) F or S

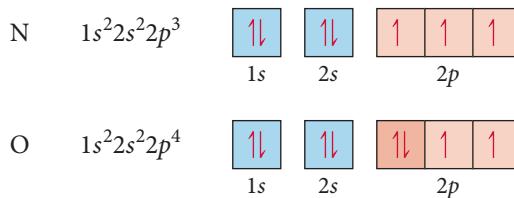
#### FOR MORE PRACTICE 8.8

Arrange the following elements in order of decreasing first ionization energy: S, Ca, F, Rb, Si.

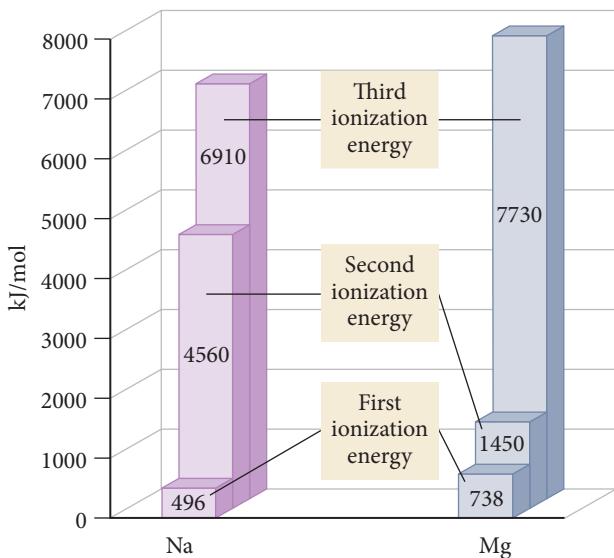
## Exceptions to Trends in First Ionization Energy

If we carefully examine Figure 8.15, we can see some exceptions to the trends in first ionization energies. For example, boron has a smaller ionization energy than beryllium, even though it lies to the right of beryllium in the same row. This exception is caused by the change in going from the *s* block to the *p* block. Recall from Section 8.3 that the  $2p$  orbital penetrates into the nuclear region *less than* the  $2s$  orbital. Consequently, the  $1s$  electrons shield the electron in the  $2p$  orbital from nuclear charge more than they shield the electrons in the  $2s$  orbital. The result, as we saw in Section 8.3, is that the  $2p$  orbitals are higher in energy, and therefore the electron is easier to remove (it has a lower ionization energy). Similar exceptions occur for aluminum and gallium, both directly below boron in group 3A.

Another exception occurs between nitrogen and oxygen. Although oxygen is to the right of nitrogen in the same row, it has a lower ionization energy. This exception is caused by the repulsion between electrons when they occupy the same orbital. Examine the electron configurations and orbital diagrams of nitrogen and oxygen shown here.



Nitrogen has three electrons in three  $p$  orbitals, while oxygen has four. In nitrogen, the  $2p$  orbitals are half-filled (which makes the configuration particularly stable). Oxygen's fourth electron must pair with another electron, making it easier to remove (and less stable). Exceptions for similar reasons occur for S and Se, directly below oxygen in group 6A.

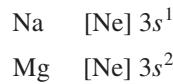


## Trends in Second and Successive Ionization Energies

Notice the trends in the first, second, and third ionization energies of sodium (group 1A) and magnesium (group 2A), as shown at left.

For sodium, there is a huge jump between the first and second ionization energies. For magnesium, the ionization energy roughly doubles from the first to the second, but then a huge jump occurs between the second and third ionization energies. What is the reason for these jumps?

We can understand these trends by examining the electron configurations of sodium and magnesium:



The first ionization of sodium involves removing the valence electron in the  $3s$  orbital. Recall that these valence electrons are held more loosely than the core electrons, and that the resulting ion has a noble gas configuration, which is particularly stable. Consequently, the first ionization energy is fairly low. The second ionization of sodium, however, involves removing a core electron from an ion with a noble gas configuration. This requires a tremendous amount of energy, making the value of  $\text{IE}_2$  very high.

As with sodium, the first ionization of magnesium involves removing a valence electron in the  $3s$  orbital. This requires a bit more energy than the corresponding ionization of sodium because of the trends in  $Z_{\text{eff}}$  that we discussed earlier ( $Z_{\text{eff}}$  increases as we move to the right across a row). The second ionization of magnesium also involves removing an outer electron in the  $3s$  orbital, but this time from an ion with a  $1+$  charge (instead of from a neutral atom). This requires roughly twice the energy as removing the electron from the neutral atom. The third ionization of magnesium is analogous to the

**TABLE 8.1 Successive Values of Ionization Energies for the Elements Sodium through Argon (kJ/mol)**

Element	IE <sub>1</sub>	IE <sub>2</sub>	IE <sub>3</sub>	IE <sub>4</sub>	IE <sub>5</sub>	IE <sub>6</sub>	IE <sub>7</sub>
Na	496	4560					
Mg	738	1450	7730				
Al	578	1820	2750	11,600			
Si	786	1580	3230	4360	16,100		
P	1012	1900	2910	4960	6270	22,200	
S	1000	2250	3360	4560	7010	8500	27,100
Cl	1251	2300	3820	5160	6540	9460	11,000
Ar	1521	2670	3930	5770	7240	8780	12,000

second ionization of sodium—it requires removing a core electron from an ion with a noble gas configuration. This requires a tremendous amount of energy, making the value of IE<sub>3</sub> very high.

As shown in Table 8.1, similar trends exist for the successive ionization energies of many elements. The ionization energy increases fairly uniformly with each successive removal of an outermost electron, but then takes a large jump with the removal of the first core electron.

### Conceptual Connection 8.6 Ionization Energies and Chemical Bonding

Based on what you just learned about ionization energies, explain why valence electrons are more important than core electrons in determining the reactivity and bonding in atoms.

## 8.8 Electron Affinities and Metallic Character

Electron affinity and metallic character also exhibit periodic trends. Electron affinity is a measure of how easily an atom will accept an additional electron and is crucial to chemical bonding because bonding involves the transfer or sharing of electrons. Metallic character is important because of the high proportion of metals in the periodic table and the large role they play in our lives. Of the roughly 110 elements, 87 are metals. We examine each of these periodic properties individually in this section.

### Electron Affinity

The **electron affinity (EA)** of an atom or ion is the energy change associated with the gaining of an electron by the atom in the gaseous state. Electron affinity is usually—though not always—negative because an atom or ion usually releases energy when it gains an electron. (The process is analogous to an exothermic reaction, which releases heat and therefore has a negative  $\Delta H$ .) In other words, the coulombic attraction between the nucleus of an atom and the incoming electron usually results in the release of energy as the electron is gained. For example, we can represent the electron affinity of chlorine with the equation:

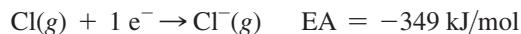


Figure 8.16 ▶ displays the electron affinities for a number of main-group elements. As you can see from this figure, the trends in electron affinity are not as regular as trends in other properties we have examined. For instance, we might expect electron affinities to

Electron Affinities (kJ/mol)							
1A		8A					
H -73	2A	3A	4A	5A	6A	7A	He >0
Li -60	Be >0	B -27	C -122	N >0	O -141	F -328	Ne >0
Na -53	Mg >0	Al -43	Si -134	P -72	S -200	Cl -349	Ar >0
K -48	Ca -2	Ga -30	Ge -119	As -78	Se -195	Br -325	Kr >0
Rb -47	Sr -5	In -30	Sn -107	Sb -103	Te -190	I -295	Xe >0

▲ FIGURE 8.16 Electron Affinities of Selected Main-Group Elements.

become relatively more positive (so that the addition of an electron is less exothermic) as we move down a column because the electron is entering orbitals with successively higher principal quantum numbers and will therefore be farther from the nucleus. This trend applies to the group 1A metals but does not hold for the other columns in the periodic table.

A more regular trend in electron affinity occurs as we move to the right across a row, however. Based on the periodic properties we have learned so far, would you expect more energy to be released by Na or Cl when an electron is gained? We know that Na has an outer electron configuration of  $3s^1$  and Cl has an outer electron configuration of  $3s^2 3p^5$ . Since adding an electron to chlorine gives it a noble gas configuration and adding an electron to sodium does not, and since the outermost electrons in chlorine experience a higher  $Z_{\text{eff}}$  than the outermost electrons in sodium, we would expect chlorine to

have a more negative electron affinity—the process should be more exothermic for chlorine. This is in fact the case. For main-group elements, electron affinity generally becomes more negative (more exothermic) as we move to the right across a row in the periodic table. The halogens (group 7A) therefore have the most negative electron affinities. But exceptions do occur. For example, notice that nitrogen and the other group 5A elements do not follow the general trend. These elements have  $ns^2 np^3$  outer electron configurations. When an electron is added to this configuration, it must pair with another electron in an already occupied  $p$  orbital. The repulsion between two electrons occupying the same orbital causes the electron affinity to be more positive than for elements in the previous column.

#### Summarizing Electron Affinity for Main-Group Elements:

- ▶ Most groups (columns) of the periodic table do not exhibit any definite trend in electron affinity. Among the group 1A metals, however, electron affinity becomes more positive as we move down the column (adding an electron becomes less exothermic).
- ▶ Electron affinity generally becomes more negative (adding an electron becomes more exothermic) as we move to the right across a period (row) in the periodic table.

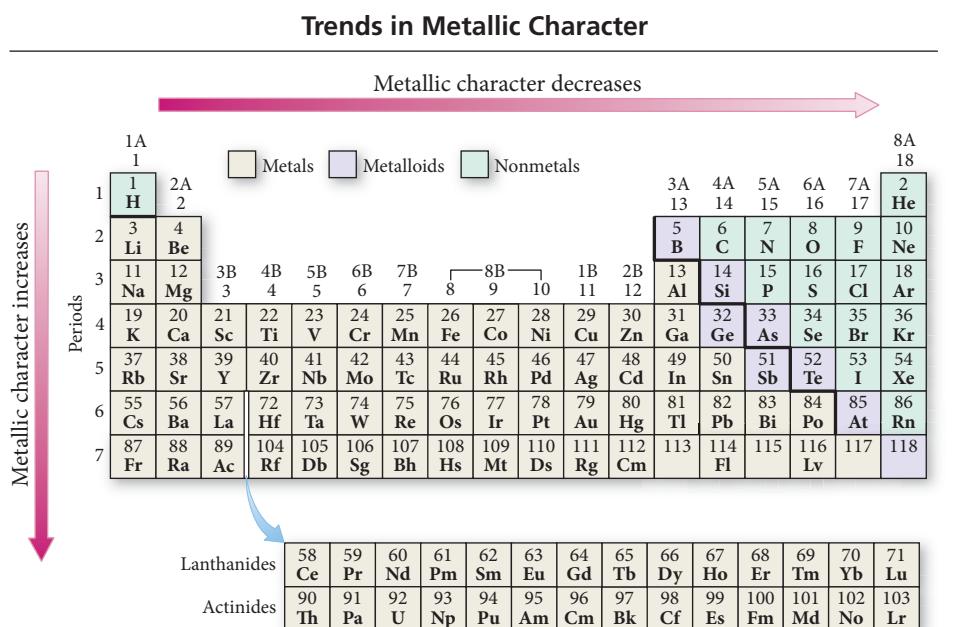
## Metallic Character

As we discussed in Chapter 2, metals are good conductors of heat and electricity: they can be pounded into flat sheets (malleability), they can be drawn into wires (ductility), they are often shiny, and they tend to lose electrons in chemical reactions. Nonmetals, in contrast, have more varied physical properties; some are solids at room temperature, others are gases, but in general nonmetals are typically poor conductors of heat and electricity, and they all tend to gain electrons in chemical reactions. As we move to the right across a row in the periodic table, ionization energy increases and electron affinity becomes more negative; therefore, elements on the left side of the periodic table are more likely to lose electrons than elements on the right side of the periodic table (which are more likely to gain them). The other properties associated with metals follow the same general trend (even though we do not quantify them here). Consequently, as shown in Figure 8.17 ▶:

**As we move to the right across a row (or period) in the periodic table, metallic character decreases.**

As we move down a column in the periodic table, ionization energy decreases, making electrons more likely to be lost in chemical reactions. Therefore,

**As we move down a column (or family) in the periodic table, metallic character increases.**

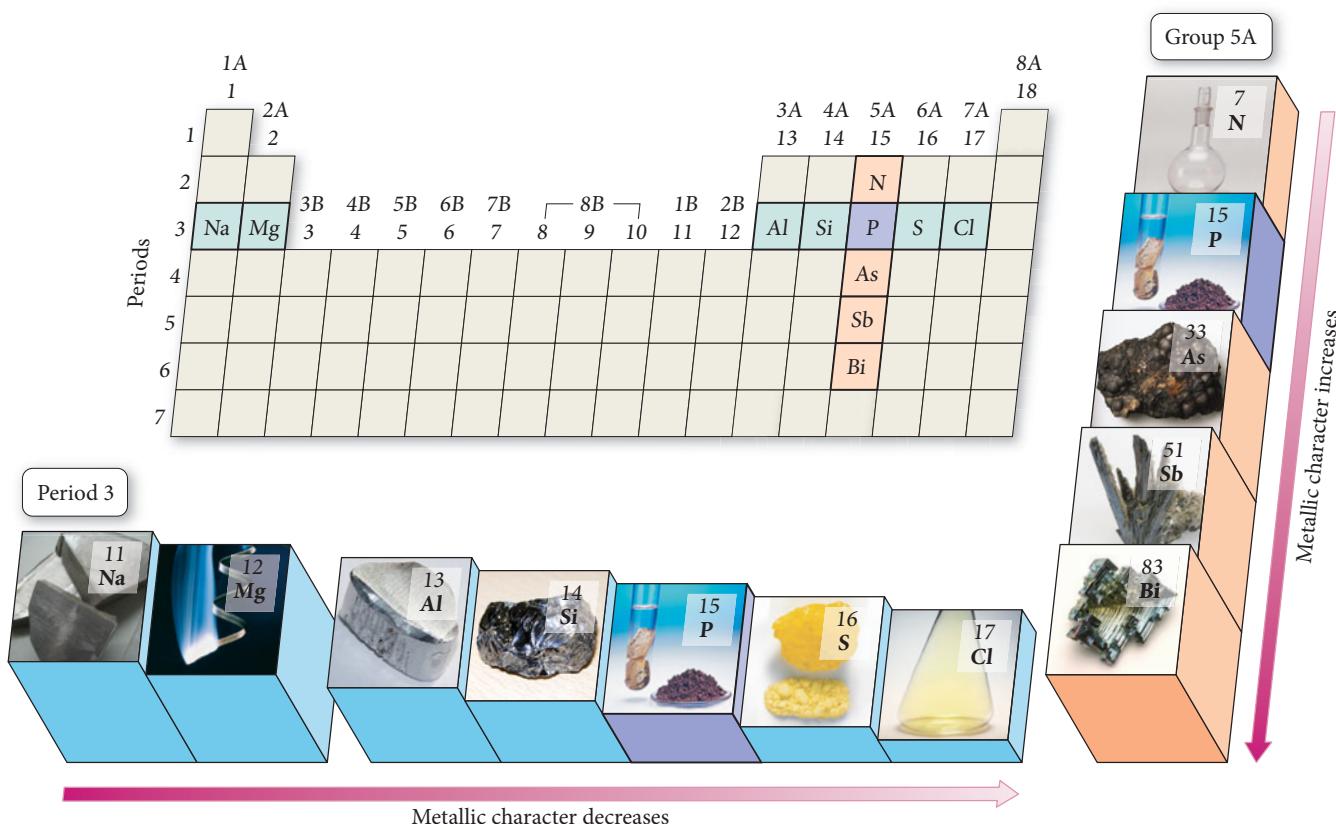
**► FIGURE 8.17 Trends in Metallic Character I**

Metallic character decreases as we move to the right across a period and increases as we move down a column in the periodic table.

These trends, based on the quantum-mechanical model, explain the distribution of metals and nonmetals in the periodic table discussed in Chapter 2. Metals are found on the left side and toward the center and nonmetals on the upper right side. The change in chemical behavior from metallic to nonmetallic can be seen most clearly as we proceed to the right across period 3, or down along group 5A as can be seen in Figure 8.18 ▼.

**▼ FIGURE 8.18 Trends in Metallic Character II**

As we move down group 5A in the periodic table, metallic character increases. As we move across period 3, metallic character decreases.

**Trends in Metallic Character**

### EXAMPLE 8.9 Metallic Character

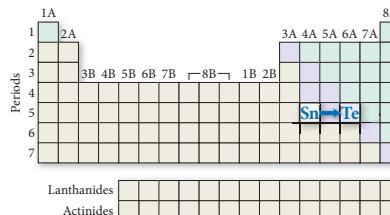
On the basis of periodic trends, choose the more metallic element from each pair (if possible).

- (a) Sn or Te      (b) P or Sb      (c) Ge or In      (d) S or Br

#### SOLUTION

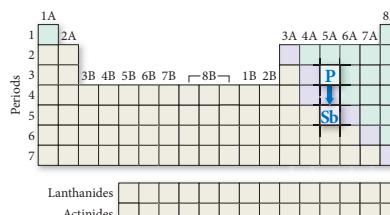
- (a) Sn or Te

Sn is more metallic than Te because as you trace the path between Sn and Te on the periodic table, you move to the right within the same period. Metallic character decreases as we go to the right.



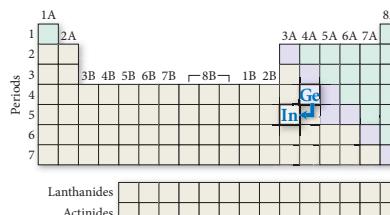
- (b) P or Sb

Sb is more metallic than P because as you trace the path between P and Sb on the periodic table, you move down a column. Metallic character increases as we go down a column.



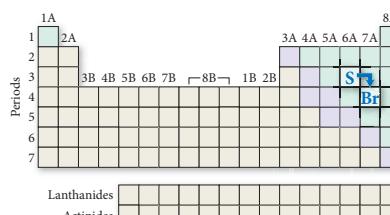
- (c) Ge or In

In is more metallic than Ge because as you trace the path between Ge and In on the periodic table, you move down a column (metallic character increases) and then to the left across a period (metallic character increases). These effects add together for an overall increase.



- (d) S or Br

Based on periodic trends alone, we cannot tell which is more metallic because as you trace the path between S and Br, you go to the right across a period (metallic character decreases) and then down a column (metallic character increases). These effects tend to counter each other, and it is not easy to tell which will predominate.



#### FOR PRACTICE 8.9

On the basis of periodic trends, choose the more metallic element from each pair (if possible).

- (a) Ge or Sn      (b) Ga or Sn      (c) P or Bi      (d) B or N

#### FOR MORE PRACTICE 8.9

Arrange the following elements in order of increasing metallic character: Si, Cl, Na, Rb.

### Conceptual Connection 8.7 Periodic Trends

Use the trends in ionization energy and electron affinity to explain why sodium chloride has the formula NaCl and not Na<sub>2</sub>Cl or NaCl<sub>2</sub>.

## 8.9 Some Examples of Periodic Chemical Behavior: The Alkali Metals, the Halogens, and the Noble Gases

In this section, we explore some of the properties and chemical reactions of three families in the periodic table: the alkali metals, the halogens, and the noble gases. These families exemplify the connection between chemical behavior and electron configuration. The

alkali metals (group 1A) have  $ns^1$  outer electron configurations. The single valence electron that keeps these metals from having noble gas configurations is easily removed (the metals have low ionization energies), making these elements the most active metals in the periodic table. The halogens (group 7A) have  $ns^2 np^5$  outer electron configurations. The one electron needed to attain noble gas configurations is easily acquired (the halogens have highly negative electron affinities), making these elements among the most active nonmetals in the periodic table. The noble gases (group 8A) have electron configurations with full outer principal quantum levels ( $ns^2 np^6$ ) and so are the most chemically inert family in the periodic table. We will examine the properties of each of these groups separately. (Even though hydrogen is often listed in group 1A, it behaves like a nonmetal because of its high ionization energy: 1312 kJ/mol. We therefore do not include hydrogen in our discussion of the group 1A metals.)

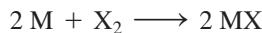
## The Alkali Metals (Group 1A)

Table 8.2 lists some selected properties of the alkali metals. Notice that, in general, the properties of the alkali metals vary fairly regularly as we proceed down the column. As expected from periodic trends, the atomic radius increases steadily while the first ionization energy decreases steadily.

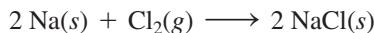
With the exception of potassium, density increases as we move down the column. This is a general trend that occurs in other columns within the periodic table. As we move down a column, the increase in mass (due to the additional protons and neutrons) outpaces the increase in volume caused by greater atomic radius. The result is successively greater densities. The melting points of the alkali metals as a group are anomalously low for metals, and they steadily decrease as we move down the column. (This is not a general trend for the rest of the periodic table, which shows more irregular patterns in melting points.)

Because of their generally low ionization energies, the alkali metals are excellent reducing agents—they are readily oxidized, losing electrons to other substances. Consequently, the alkali metals exist naturally in their oxidized state, either in compounds or as dissolved ions in seawater. Since ionization energy *decreases* as we go down the column, the relative reactivities of the alkali metals tend to *increase* as we move down the column. In other words, the lower the ionization energy of an alkali metal, the greater tendency it will have to lose its electron and the more reactive it is.

The reactions of the alkali metals with nonmetals are vigorous. For example, the alkali metals (M) react with halogens (X) according to the reaction:



The reaction of sodium and chlorine to form sodium chloride is typical:



This reaction emits heat and sparks as it occurs (Figure 8.19 ▶). Each successive alkali metal reacts even more vigorously with chlorine. The alkali metals also react with water to form the dissolved alkali metal ion, the hydroxide ion, and hydrogen gas:



▲ FIGURE 8.19 Reaction of Sodium and Chlorine to Form Sodium Chloride.

**TABLE 8.2 Properties of the Alkali Metals\***

Element	Electron Configuration	Atomic Radius (pm)	IE <sub>1</sub> (kJ/mol)	Density at 25 °C (g/cm <sup>3</sup> )	Melting Point (°C)
Li	[He] 2s <sup>1</sup>	152	520	0.535	181
Na	[Ne] 3s <sup>1</sup>	186	496	0.968	102
K	[Ar] 4s <sup>1</sup>	227	419	0.856	98
Rb	[Kr] 5s <sup>1</sup>	248	403	1.532	39
Cs	[Xe] 6s <sup>1</sup>	265	376	1.879	29

\*Francium is omitted because it has no stable isotopes.

### Reactions of the Alkali Metals with Water



Lithium

Sodium

Potassium

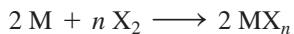
**▲ FIGURE 8.20** Reactions of the Alkali Metals with Water The reactions become progressively more vigorous as we move down the group.

The reaction is highly exothermic and can be explosive because the heat from the reaction can ignite the hydrogen gas. The reaction becomes more explosive as we move down the column from one metal to the next, as shown in Figure 8.20 ▲.\*

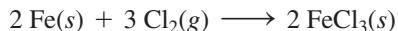
### The Halogens (Group 7A)

Table 8.3 lists selected properties of the first four halogens. Notice that the properties of the halogens, like those of the alkali metals, vary fairly regularly as we proceed down the column. As expected from periodic trends, the atomic radius and the density increase for each successive halogen. We can see from the melting and boiling points that fluorine and chlorine are both gases at room temperature, bromine is a liquid, and iodine is a solid.

All of the halogens are powerful oxidizing agents—they are readily reduced, gaining electrons from other substances in their reactions. Fluorine is the most powerful oxidizing agent of the group—reacting with almost everything, including the heavier noble gases—and iodine is the least. The halogens all react with metals to form *metal halides* according to the equation:



where M is the metal, X is the halogen, and  $\text{MX}_n$  is the metal halide. For example, chlorine reacts with iron according to the equation:



**TABLE 8.3** Properties of the Halogens\*

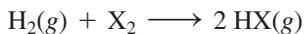
Element	Electron Configuration	Atomic Radius (pm)	EA (kJ/mol)	Melting Point (°C)	Boiling Point (°C)	Density of Liquid (g/cm <sup>3</sup> )
F	[He] 2s <sup>2</sup> 2p <sup>5</sup>	72	-328	-219	-188	1.51
Cl	[Ne] 3s <sup>2</sup> 3p <sup>5</sup>	99	-349	-101	-34	2.03
Br	[Ar] 4s <sup>2</sup> 4p <sup>5</sup>	114	-325	-7	59	3.19
I	[Kr] 5s <sup>2</sup> 5p <sup>5</sup>	133	-295	114	184	3.96

\*At is omitted because it is rare and radioactive.

\*The rate of the alkali metal reaction with water, and therefore its vigor, is enhanced by the successively lower melting points of the alkali metals as we move down the column. The low melting points of the heavier metals allow the emitted heat to actually melt the metal, increasing the reaction rate.

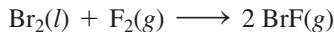
Since metals tend to lose electrons and the halogens tend to gain them, the metal halides—like all compounds that form between metals and nonmetals—contain ionic bonds.

The halogens also react with hydrogen to form *hydrogen halides* according to the equation:

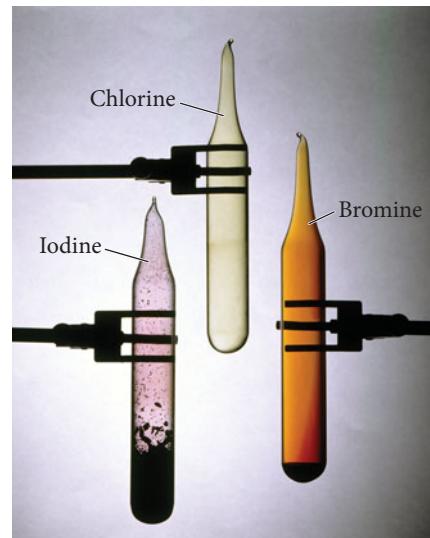


The hydrogen halides—like all compounds that form between two nonmetals—contain covalent bonds. All of the hydrogen halides form acidic solutions when combined with water.

The halogens also react with each other to form *interhalogen compounds*. For example, bromine reacts with fluorine according to the equation:



Again, like all compounds that form between two nonmetals, the interhalogen compounds contain covalent bonds.



### EXAMPLE 8.10 Alkali Metal and Halogen Reactions

Write a balanced chemical equation for each reaction.

- (a) the reaction between potassium metal and bromine gas
- (b) the reaction between rubidium metal and liquid water
- (c) the reaction between gaseous chlorine and solid iodine

#### SOLUTION

<p>(a) Alkali metals react with halogens to form metal halides. Write the formulas for the reactants and the metal halide product (making sure to write the correct ionic chemical formula for the metal halide, as outlined in Section 3.5), and then balance the equation.</p>	$2 \text{K}(s) + \text{Br}_2(g) \longrightarrow 2 \text{KBr}(s)$
<p>(b) Alkali metals react with water to form the dissolved metal ion, the hydroxide ion, and hydrogen gas. Write the skeletal equation including each of these and then balance it.</p>	$2 \text{Rb}(s) + 2 \text{H}_2\text{O}(l) \longrightarrow 2 \text{Rb}^+(aq) + 2 \text{OH}^-(aq) + \text{H}_2(g)$
<p>(c) Halogens react with each other to form interhalogen compounds. Write the skeletal equation with each of the halogens as the reactants and the interhalogen compound as the product and balance the equation.</p>	$\text{Cl}_2(g) + \text{I}_2(s) \longrightarrow 2 \text{ICl}(g)$

#### FOR PRACTICE 8.10

Write a balanced chemical equation for each reaction.

- (a) the reaction between aluminum metal and chlorine gas
- (b) the reaction between lithium metal and liquid water
- (c) the reaction between gaseous hydrogen and liquid bromine



## Chemistry and Medicine

### Potassium Iodide in Radiation Emergencies

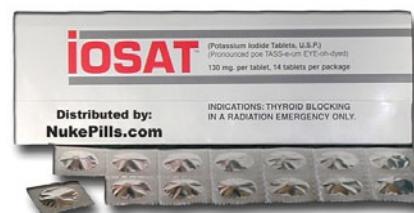
Since the attack on the World Trade Center on September 11, 2001, the United States has been concerned about the threat of additional terrorist strikes, including the possibility of nuclear attack. One danger of such an attack is radiation from the decay of radioisotopes released by a nuclear device—especially a so-called dirty bomb. This radiation can produce elevated rates of many cancers for years following exposure. The risk of developing thyroid cancer after ingesting radioactive isotopes of iodine, for example, is particularly high, especially in children. The number of thyroid cancers among children and adolescents in Belarus and Ukraine (areas affected by the radioactive plume from the 1986 nuclear accident at Chernobyl in the former Soviet Union) is 30–100 times higher than in the normal population.

The U.S. Food and Drug Administration (FDA), in cooperation with other federal agencies, recommends the administration of potassium iodide (KI) to citizens in the event of a nuclear radiation emergency. The 2011 nuclear accident at the Fukushima Daiichi Nuclear Power Plant in Japan caused panicked buying of KI, even in the United States. Although KI does not prevent exposure to radiation, it does decrease the risk of thyroid cancer that follows the intake of radioactive isotopes, particularly I-131. The chief function of the thyroid gland is to synthesize and release the hormone thyroxine, which regulates many aspects of human metabolism. In order to produce thyroxine, which contains iodine, the thyroid normally accumulates iodine in concentrations far greater than those found elsewhere in the body.

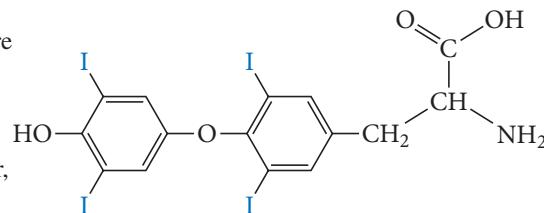
When potassium iodide is taken in the recommended doses, it floods the thyroid with nonradioactive iodine, preventing the thyroid from absorbing the cancer-causing radioactive iodine, which is then excreted in the urine.

In the United States, the FDA prioritizes KI treatment in the event of a nuclear emergency based on age. Infants, children, and pregnant females are at highest risk and are therefore treated at the lowest threshold exposure levels. Adults aged 18 to 40 are treated at slightly higher exposure levels, and those over 40 are only treated if the exposure level is actually high enough to destroy the thyroid.

The federal government has purchased stockpiles of potassium iodide for all states with nuclear reactors. Potassium iodide, also available over the counter, works best if taken 3–4 hours after exposure. Because of the increased threat of terrorist attacks after 9/11, potassium iodide pills have been distributed to residents, schools, and businesses within a 10-mile radius of a nuclear reactor. In the event of a terrorist attack on a nuclear reactor, residents are advised to take the potassium iodide pill and evacuate the area as soon as possible.



▲ The U.S. Food and Drug Administration recommends taking potassium iodide pills in the event of a nuclear emergency.



▲ Each molecule of thyroxine, a thyroid hormone that plays a key role in metabolism, contains four iodine atoms.

### The Noble Gases (Group 8A)

Table 8.4 lists selected properties of the noble gases. Notice that the properties of the noble gases, like those of the alkali metals and halogens, vary fairly regularly as we proceed down the column. As expected from periodic trends, the atomic radius and the density increase for each successive noble gas, and the ionization energy decreases. As their boiling points indicate, all of the noble gases are gases at room temperature and must be cooled to extremely low temperatures before they liquefy. For this reason some noble gases can be cryogenic liquids—liquids used to cool other substances to low temperatures. For example, researchers often submerge samples of interest in boiling liquid helium to cool them down to 4.2 K (or lower) and study their properties at this extremely low temperature.

The high ionization energies of the noble gases and their completely full outer quantum levels make them exceptionally unreactive. In fact, before the 1960s, no noble gas compounds were known. Since then, two of the noble gases have been shown to react



▲ Liquid helium, a cryogenic liquid, cools substances to temperatures as low as 1.2 K.

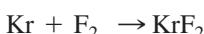
**TABLE 8.4 Properties of the Noble Gases\***

Element	Electron Configuration	Atomic Radius (pm)**	$\text{IE}_1 (\text{kJ/mol})$	Boiling Point (K)	Density of Gas (g/L at STP)
He	$1s^2$	32	2372	4.2	0.18
Ne	$[\text{He}]2s^2 2p^6$	70	2081	27.1	0.90
Ar	$[\text{Ne}]3s^2 3p^6$	98	1521	87.3	1.78
Kr	$[\text{Ar}]4s^2 4p^6$	112	1351	119.9	3.74
Xe	$[\text{Kr}]5s^2 5p^6$	130	1170	165.1	5.86

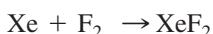
\*Radon is omitted because it is radioactive.

\*\*Since only the heavier noble gases form compounds, covalent radii for the smaller noble gases are estimated.

with fluorine (the most reactive nonmetal on the periodic table) under fairly extreme conditions. Krypton reacts with fluorine to form  $\text{KrF}_2$ :



Similarly, Xe reacts with fluorine to form three different xenon fluorides:



The inertness of the noble gases has led to their use in situations where reactions are undesirable. For example, argon is used in lightbulbs to prevent the hot tungsten filament from oxidizing, and helium is part of the mixture breathed by deep-sea divers to prevent the toxicity caused by too much oxygen and nitrogen under high pressures. (The helium replaces some of the oxygen and nitrogen in the tank, lowering the concentrations of oxygen and nitrogen in the blood.)

Xenon can also be forced to react with oxygen to form  $\text{XeO}_3$  and  $\text{XeO}_4$ .

## CHAPTER IN REVIEW

### Self Assessment Quiz

- Q1.** According to Coulomb's law, if the separation between two particles of the same charge is doubled, the potential energy of the two particles:

- a) becomes twice as high as it was before the distance separation.
- b) becomes one-half as high as it was before the separation.
- c) does not change.
- d) becomes one-fourth as high as it was before the separation.

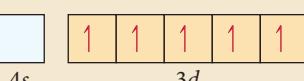
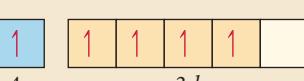
- Q2.** Which electron in sulfur is most shielded from nuclear charge?

- a) An electron in the  $1s$  orbital
- b) An electron in a  $2p$  orbital
- c) An electron in a  $3p$  orbital
- d) none of the above (All of these electrons are equally shielded from nuclear charge.)

- Q3.** Choose the correct electron configuration for Se.

- a)  $1s^2 2s^2 2p^6 3s^2 3p^4$
- b)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^4$
- c)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^4$
- d)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$

- Q4.** Choose the correct orbital diagram for vanadium.

- a) [Ar]  4s 3d
- b) [Ar]  4s 3d
- c) [Ar]  4s 3d
- d) [Ar]  4s 3d

- Q5.** Which set of four quantum numbers corresponds to an electron in a  $4p$  orbital?

- a)  $n = 4, l = 1, m_l = 0, m_s = \frac{1}{2}$
- b)  $n = 4, l = 3, m_l = 3, m_s = -\frac{1}{2}$
- c)  $n = 4, l = 2, m_l = 0, m_s = \frac{1}{2}$
- d)  $n = 4, l = 4, m_l = 3, m_s = -\frac{1}{2}$

- Q6.** Which element has the smallest atomic radius?  
 a) C      b) Si      c) Be      d) F
- Q7.** Which statement is true about electron shielding of nuclear charge?  
 a) Outermost electrons efficiently shield one another from nuclear charge.  
 b) Core electrons efficiently shield one another from nuclear charge.  
 c) Outermost electrons efficiently shield core electrons from nuclear charge.  
 d) Core electrons efficiently shield outermost electrons from nuclear charge.
- Q8.** Which statement is true about effective nuclear charge?  
 a) Effective nuclear charge *increases* as you move to the right across a row in the periodic table and *increases* as you move down a column.  
 b) Effective nuclear charge *increases* as you move to the right across a row in the periodic table and *decreases* as you move down a column.  
 c) Effective nuclear charge *decreases* as you move to the right across a row in the periodic table and *decreases* as you move down a column.  
 d) Effective nuclear charge *decreases* as you move to the right across a row in the periodic table and *increases* as you move down a column.
- Q9.** What is the electron configuration for  $\text{Fe}^{2+}$ ?  
 a)  $[\text{Ar}]4s^23d^6$       b)  $[\text{Ar}]4s^23d^4$   
 c)  $[\text{Ar}]4s^03d^6$       d)  $[\text{Ar}]4s^23d^8$
- Q10.** Which species is diamagnetic?  
 a)  $\text{Cr}^{2+}$       b) Zn      c) Mn      d) C
- Q11.** Arrange these atoms and ions in order of increasing radius:  
 $\text{Cs}^+$ ,  $\text{Xe}$ ,  $\text{I}^-$ .  
 a)  $\text{I}^- < \text{Xe} < \text{Cs}^+$       b)  $\text{Cs}^+ < \text{Xe} < \text{I}^-$   
 c)  $\text{Xe} < \text{Cs}^+ < \text{I}^-$       d)  $\text{I}^- < \text{Cs}^+ < \text{Xe}$
- Q12.** Arrange these elements in order of increasing first ionization energy: Cl, Sn, Si.  
 a)  $\text{Cl} < \text{Si} < \text{Sn}$       b)  $\text{Sn} < \text{Si} < \text{Cl}$   
 c)  $\text{Si} < \text{Cl} < \text{Sn}$       d)  $\text{Sn} < \text{Cl} < \text{Si}$
- Q13.** The ionization energies of an unknown third period element are shown below. Identify the element.  
 $\text{IE}_1 = 786 \text{ kJ/mol}$ ;  $\text{IE}_2 = 1580 \text{ kJ/mol}$ ;  $\text{IE}_3 = 3230 \text{ kJ/mol}$ ;  $\text{IE}_4 = 4360 \text{ kJ/mol}$ ;  $\text{IE}_5 = 16,100 \text{ kJ/mol}$   
 a) Mg      b) Al      c) Si      d) P
- Q14.** Which statement is true about trends in metallic character?  
 a) Metallic character *increases* as you go to the right across a row in the periodic table and *increases* as you go down a column.  
 b) Metallic character *decreases* as you go to the right across a row in the periodic table and *increases* as you go down a column.  
 c) Metallic character *decreases* as you go to the right across a row in the periodic table and *decreases* as you go down a column.  
 d) Metallic character *decreases* as you go to the right across a row in the periodic table and *increases* as you go down a column.
- Q15.** For which element is the gaining of an electron most exothermic?  
 a) Li      b) N      c) F      d) B

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

## Key Terms

### Section 8.1

periodic property (336)

### Section 8.3

electron configuration (337)  
 ground state (337)  
 orbital diagram (338)  
 Pauli exclusion principle (338)  
 degenerate (338)

Coulomb's law (339)

shielding (339)

effective nuclear charge ( $Z_{\text{eff}}$ ) (340)

penetration (340)

aufbau principle (342)

Hund's rule (342)

### Section 8.4

valence electrons (345)

core electrons (345)

### Section 8.6

van der Waals radius

(nonbonding  
atomic radius) (350)

covalent radius (bonding  
atomic radius) (350)

atomic radius (350)

### Section 8.7

paramagnetic (355)

diamagnetic (356)

ionization energy (IE) (359)

### Section 8.8

electron affinity (EA) (363)

## Key Concepts

### Periodic Properties and the Development of the Periodic Table (8.1, 8.2)

- The periodic table was primarily developed by Dmitri Mendeleev in the nineteenth century. Mendeleev arranged the elements in a table so that atomic mass increased from left to right in a row and elements with similar properties fell in the same columns.
- Periodic properties are predictable based on an element's position within the periodic table. Periodic properties include atomic radius, ionization energy, electron affinity, density, and metallic character.

- Quantum mechanics explains the periodic table by explaining how electrons fill the quantum-mechanical orbitals within the atoms that compose the elements.

### Electron Configurations (8.3)

- An electron configuration for an atom shows which quantum-mechanical orbitals are occupied by the atom's electrons. For example, the electron configuration of helium ( $1s^2$ ) indicates that helium's two electrons exist within the  $1s$  orbital.

- The order of filling quantum-mechanical orbitals in multielectron atoms is  $1s\ 2s\ 2p\ 3s\ 3p\ 4s\ 3d\ 4p\ 5s\ 4d\ 5p\ 6s$ .
- According to the Pauli exclusion principle, each orbital can hold a maximum of two electrons with opposing spins.
- According to Hund's rule, orbitals of the same energy first fill singly with electrons with parallel spins before pairing.

### Electron Configurations and the Periodic Table (8.4, 8.5)

- Because quantum-mechanical orbitals fill sequentially with increasing atomic number, we can infer the electron configuration of an element from its position in the periodic table.
- The most stable configurations are those with completely full principal energy levels. Therefore, the most stable and unreactive elements—those with the lowest energy electron configurations—are the noble gases.
- Elements with one or two valence electrons are among the most active metals, readily losing their valence electrons to attain noble gas configurations.
- Elements with six or seven valence electrons are among the most active nonmetals, readily gaining enough electrons to attain a noble gas configuration.

### Effective Nuclear Charge and Periodic Trends in Atomic Size (8.6)

- The size of an atom is largely determined by its outermost electrons. As we move down a column in the periodic table, the principal quantum number ( $n$ ) of the outermost electrons increases, resulting in successively larger orbitals and therefore larger atomic radii.
- As we move across a row in the periodic table, atomic radii decrease because the effective nuclear charge—the net or average charge experienced by the atom's outermost electrons—increases.
- The atomic radii of the transition elements stay roughly constant as we move across each row because electrons are added to the  $n_{\text{highest}} - 1$  orbitals while the number of highest  $n$  electrons stays roughly constant.

### Ion Properties (8.7)

- We can determine the electron configuration of an ion by adding or subtracting the corresponding number of electrons to the electron configuration of the neutral atom.

- For main-group ions, the order of removing electrons is the same as the order in which they are added in building up the electron configuration.
- For transition metal atoms, the  $ns$  electrons are removed before the  $(n - 1)d$  electrons.
- The radius of a cation is much *smaller* than that of the corresponding atom, and the radius of an anion is much *larger* than that of the corresponding atom.
- The ionization energy—the energy required to remove an electron from an atom in the gaseous state—generally decreases as we move down a column in the periodic table and increases when we move to the right across a row.
- Successive ionization energies increase smoothly from one valence electron to the next, but the ionization energy increases dramatically for the first core electron.

### Electron Affinities and Metallic Character (8.8)

- Electron affinity—the energy associated with an element in its gaseous state gaining an electron—does not show a general trend as we move down a column in the periodic table, but it generally becomes more negative (more exothermic) to the right across a row.
- Metallic character—the tendency to lose electrons in a chemical reaction—generally increases down a column in the periodic table and decreases to the right across a row.

### The Alkali Metals, Halogens, and Noble Gases (8.9)

- The most active metals are the alkali metals (group 1A), and the most active nonmetals are the halogens (group 7A).
- The alkali metals are powerful reducing agents, reacting with many nonmetals—including the halogens and water—to form ionic compounds.
- The halogens are powerful oxidizing agents, reacting with many metals to form ionic compounds. The halogens also react with many nonmetals to form covalent compounds.
- The noble gases are relatively unreactive; only krypton and xenon form compounds, typically only with fluorine, the most reactive element in the periodic table.

## Key Equations and Relationships

### Order of Filling Quantum-Mechanical Orbitals (8.3)

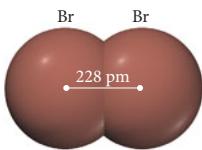
$1s\ 2s\ 2p\ 3s\ 3p\ 4s\ 3d\ 4p\ 5s\ 4d\ 5p\ 6s$

## Key Learning Outcomes

Chapter Objectives	Assessment
Writing Electron Configurations (8.3)	Example 8.1 For Practice 8.1 Exercises 41, 42
Writing Orbital Diagrams (8.3) 	Example 8.2 For Practice 8.2 Exercises 43, 44
Valence Electrons and Core Electrons (8.4)	Example 8.3 For Practice 8.3 Exercises 51, 52
Electron Configurations from the Periodic Table (8.4)	Example 8.4 For Practice 8.4 For More Practice 8.4 Exercises 45, 46

## Key Learning Outcomes, continued

Using Periodic Trends to Predict Atomic Size (**8.6**)



Example 8.5 For Practice 8.5 For More Practice 8.5 Exercises 61–64

Writing Electron Configurations for Ions (**8.7**)

Example 8.6 For Practice 8.6 Exercises 65, 66

Using Periodic Trends to Predict Ion Size (**8.7**)

Example 8.7 For Practice 8.7 For More Practice 8.7 Exercises 69–72

Using Periodic Trends to Predict Relative Ionization Energies (**8.7**)

Example 8.8 For Practice 8.8 For More Practice 8.8 Exercises 73–76

Predicting Metallic Character Based on Periodic Trends (**8.8**)



Example 8.9 For Practice 8.9 For More Practice 8.9 Exercises 81–84

Writing Reactions for Alkali Metal and Halogen Reactions (**8.9**)

Example 8.10 For Practice 8.10 Exercises 85–90

## EXERCISES

### Review Questions

- What are periodic properties?
- Which periodic property is particularly important to nerve signal transmission? Why?
- Explain the contributions of Johann Döbereiner and John Newlands to the organization of elements according to their properties.
- Who is credited with arranging the periodic table? How were elements arranged in this table?
- Explain the contributions of Meyer and Moseley to the periodic table.
- The periodic table is a result of the periodic law. What observations led to the periodic law? What theory explains the underlying reasons for the periodic law?
- What is an electron configuration? Give an example.
- What is Coulomb's law? Explain how the potential energy of two charged particles depends on the distance between the charged particles and on the magnitude and sign of their charges.
- What is shielding? In an atom, which electrons tend to do the most shielding (core electrons or valence electrons)?
- What is penetration? How does the penetration of an orbital into the region occupied by core electrons affect the energy of an electron in that orbital?
- Why are the sublevels within a principal level split into different energies for multielectron atoms but not for the hydrogen atom?
- What is an orbital diagram? Provide an example.
- Why is electron spin important when writing electron configurations? Explain in terms of the Pauli exclusion principle.
- What are degenerate orbitals? According to Hund's rule, how are degenerate orbitals occupied?
- List all orbitals from  $1s$  through  $5s$  according to increasing energy for multielectron atoms.

- What are valence electrons? Why are they important?

- Copy this blank periodic table onto a sheet of paper and label each of the blocks within the table: *s* block, *p* block, *d* block, and *f* block.

	1A															8A	
Periods	1	2A	3B		4B	5B	6B	7B	8B		1B	2B	13–18				
1			3	4	5	6	7	8	9	10	11	12			Lanthanides		
2																Actinides	
3																	
4																	
5																	
6																	
7																	

- Explain why the *s* block in the periodic table has only two columns while the *p* block has six.
- Why do the rows in the periodic table get progressively longer as you move down the table? For example, the first row contains 2 elements, the second and third rows each contain 8 elements, and the fourth and fifth rows each contain 18 elements. Explain.
- Explain the relationship between a main-group element's lettered group number (the number of the element's column) and its valence electrons.
- Explain the relationship between an element's row number in the periodic table and the highest principal quantum number in the element's electron configuration. How does this relationship differ for main-group elements, transition elements, and inner transition elements?

22. Which of the transition elements in the first transition series have anomalous electron configurations?
23. Explain how to write the electron configuration for an element based on its position in the periodic table.
24. Explain the relationship between the properties of an element and the number of valence electrons that it contains.
25. List the number of valence electrons for each family in the periodic table, and explain the relationship between the number of valence electrons and the resulting chemistry of the elements in the family.
- a. alkali metals
  - b. alkaline earth metals
  - c. halogens
  - d. oxygen family
26. Define atomic radius. For main-group elements, give the observed trends in atomic radius as you
- a. move across a period in the periodic table.
  - b. move down a column in the periodic table.
27. What is effective nuclear charge? What is shielding?
28. Use the concepts of effective nuclear charge, shielding, and  $n$  value of the valence orbital to explain the trend in atomic radius as you move across a period in the periodic table.
29. For transition elements, give the trends in atomic radius as you
- a. move across a period in the periodic table.
  - b. move down a column in the periodic table.
- Explain the reasons for the trends described in parts a and b.
30. How is the electron configuration of an anion different from that of the corresponding neutral atom? How is the electron configuration of a cation different?
31. Explain how to write an electron configuration for a transition metal cation. Is the order of electron removal upon ionization simply the reverse of electron addition upon filling? Why or why not?
32. Describe the relationship between
- a. the radius of a cation and that of the atom from which it is formed.
  - b. the radius of an anion and that of the atom from which it is formed.
33. What is ionization energy? What is the difference between first ionization energy and second ionization energy?
34. What is the general trend in ionization energy as you move down a column in the periodic table? As you move across a row?
35. What are the exceptions to the periodic trends in ionization energy? Why do they occur?
36. Examination of the first few successive ionization energies for a given element usually reveals a large jump between two ionization energies. For example, the successive ionization energies of magnesium show a large jump between  $\text{IE}_2$  and  $\text{IE}_3$ . The successive ionization energies of aluminum show a large jump between  $\text{IE}_3$  and  $\text{IE}_4$ . Explain why these jumps occur and how you might predict them.
37. What is electron affinity? What are the observed periodic trends in electron affinity?
38. What is metallic character? What are the observed periodic trends in metallic character?
39. Write a general equation for the reaction of an alkali metal with
- a. a halogen.
  - b. water.
40. Write a general equation for the reaction of a halogen with
- a. a metal.
  - b. hydrogen.
  - c. another halogen.

## Problems by Topic

### Electron Configurations

41. Write the full electron configuration for each element.
- a. Si
  - b. O
  - c. K
  - d. Ne
42. Write the full electron configuration for each element.
- a. C
  - b. P
  - c. Ar
  - d. Na
43. Write the full orbital diagram for each element.
- a. N
  - b. F
  - c. Mg
  - d. Al
44. Write the full orbital diagram for each element.
- a. S
  - b. Ca
  - c. Ne
  - d. He
45. Use the periodic table to write an electron configuration for each element. Represent core electrons with the symbol of the previous noble gas in brackets.
- a. P
  - b. Ge
  - c. Zr
  - d. I
46. Use the periodic table to determine the element corresponding to each electron configuration.
- a.  $[\text{Ar}] 4s^2 3d^{10} 4p^6$
  - b.  $[\text{Ar}] 4s^2 3d^2$
  - c.  $[\text{Kr}] 5s^2 4d^{10} 5p^2$
  - d.  $[\text{Kr}] 5s^2$
47. Use the periodic table to determine each quantity.
- a. The number of  $2s$  electrons in Li
  - b. The number of  $3d$  electrons in Cu
  - c. The number of  $4p$  electrons in Br
  - d. The number of  $4d$  electrons in Zr

48. Use the periodic table to determine each quantity.
- a. The number of  $3s$  electrons in Mg
  - b. The number of  $3d$  electrons in Cr
  - c. The number of  $4d$  electrons in Y
  - d. The number of  $6p$  electrons in Pb
49. Name an element in the fourth period (row) of the periodic table with
- a. five valence electrons.
  - b. four  $4p$  electrons.
  - c. three  $3d$  electrons.
  - d. a complete outer shell.
50. Name an element in the third period (row) of the periodic table with
- a. three valence electrons.
  - b. four  $3p$  electrons.
  - c. six  $3p$  electrons.
  - d. two  $3s$  electrons and no  $3p$  electrons.

### Valence Electrons and Simple Chemical Behavior from the Periodic Table

51. Determine the number of valence electrons in each element.
- a. Ba
  - b. Cs
  - c. Ni
  - d. S
52. Determine the number of valence electrons in each element. Which elements do you expect to lose electrons in their chemical reactions? Which do you expect to gain electrons?
- a. Al
  - b. Sn
  - c. Br
  - d. Se

53. Which outer electron configuration would you expect to belong to a reactive metal? To a reactive nonmetal?  
 a.  $ns^2$       b.  $ns^2 np^6$   
 c.  $ns^2 np^5$       d.  $ns^2 np^2$
54. Which outer electron configurations would you expect to belong to a noble gas? To a metalloid?  
 a.  $ns^2$       b.  $ns^2 np^6$   
 c.  $ns^2 np^5$       d.  $ns^2 np^2$

### Coulomb's Law and Effective Nuclear Charge

55. According to Coulomb's Law, which pair of charged particles has the lowest potential energy?  
 a. a particle with a 1 $-$  charge separated by 150 pm from a particle with a 2 $+$  charge  
 b. a particle with a 1 $-$  charge separated by 150 pm from a particle with a 1 $+$  charge  
 c. a particle with a 1 $-$  charge separated by 100 pm from a particle with a 3 $+$  charge
56. According to Coulomb's law, rank the interactions between charged particles from lowest potential energy to highest potential energy.  
 a. a 1 $+$  charge and a 1 $-$  charge separated by 100 pm  
 b. a 2 $+$  charge and a 1 $-$  charge separated by 100 pm  
 c. a 1 $+$  charge and a 1 $+$  charge separated by 100 pm  
 d. a 1 $+$  charge and a 1 $-$  charge separated by 200 pm
57. Which electrons experience a greater effective nuclear charge: the valence electrons in beryllium or the valence electrons in nitrogen? Why?
58. Arrange the atoms according to decreasing effective nuclear charge experienced by their valence electrons: S, Mg, Al, Si.
59. If core electrons completely shielded valence electrons from nuclear charge (i.e., if each core electron reduced nuclear charge by 1 unit) and if valence electrons did not shield one another from nuclear charge at all, what would be the effective nuclear charge experienced by the valence electrons of each atom?  
 a. K      b. Ca      c. O      d. C
60. In Section 8.6, we estimated the effective nuclear charge on beryllium's valence electrons to be slightly greater than 2 $+$ . What would a similar treatment predict for the effective nuclear charge on boron's valence electrons? Would you expect the effective nuclear charge to be different for boron's 2s electrons compared to its 2p electron? In what way? (Hint: Consider the shape of the 2p orbital compared to that of the 2s orbital.)

### Atomic Radius

61. Choose the larger atom from each pair.  
 a. Al or In      b. Si or N      c. P or Pb      d. C or F
62. Choose the larger atom from each pair.  
 a. Sn or Si      b. Br or Ga  
 c. Sn or Bi      d. Se or Sn
63. Arrange these elements in order of increasing atomic radius: Ca, Rb, S, Si, Ge, F.
64. Arrange these elements in order of decreasing atomic radius: Cs, Sb, S, Pb, Se.

### Ionic Electron Configurations, Ionic Radii, Magnetic Properties, and Ionization Energy

65. Write the electron configuration for each ion.  
 a.  $O^{2-}$       b.  $Br^-$       c.  $Sr^{2+}$   
 d.  $Co^{3+}$       e.  $Cu^{2+}$

66. Write the electron configuration for each ion.  
 a.  $Cl^-$       b.  $P^{3-}$       c.  $K^+$   
 d.  $Mo^{3+}$       e.  $V^{3+}$
67. Write orbital diagrams for each ion and determine if the ion is diamagnetic or paramagnetic.  
 a.  $V^{5+}$       b.  $Cr^{3+}$       c.  $Ni^{2+}$       d.  $Fe^{3+}$
68. Write orbital diagrams for each ion and determine if the ion is diamagnetic or paramagnetic.  
 a.  $Cd^{2+}$       b.  $Au^+$       c.  $Mo^{3+}$       d.  $Zr^{2+}$
69. Which is the larger species in each pair?  
 a. Li or  $Li^+$       b.  $I^-$  or  $Cs^+$   
 c. Cr or  $Cr^{3+}$       d. O or  $O^{2-}$
70. Which is the larger species in each pair?  
 a. Sr or  $Sr^{2+}$       b. N or  $N^{3-}$   
 c. Ni or  $Ni^{2+}$       d.  $S^{2-}$  or  $Ca^{2+}$
71. Arrange this isoelectronic series in order of decreasing radius:  $F^-$ , Ne,  $O^{2-}$ ,  $Mg^{2+}$ ,  $Na^+$ .
72. Arrange this isoelectronic series in order of increasing atomic radius:  $Se^{2-}$ , Kr,  $Sr^{2+}$ ,  $Rb^+$ ,  $Br^-$ .
73. Choose the element with the higher first ionization energy from each pair.  
 a. Br or Bi      b. Na or Rb  
 c. As or At      d. P or Sn
74. Choose the element with the higher first ionization energy from each pair.  
 a. P or I      b. Si or Cl  
 c. P or Sb      d. Ga or Ge
75. Arrange these elements in order of increasing first ionization energy: Si, F, In, N.
76. Arrange these elements in order of decreasing first ionization energy: Cl, S, Sn, Pb.
77. For each element, predict where the "jump" occurs for successive ionization energies. (For example, does the jump occur between the first and second ionization energies, the second and third, or the third and fourth?)  
 a. Be      b. N      c. O      d. Li
78. Consider this set of successive ionization energies:
- $$\begin{aligned} IE_1 &= 578 \text{ kJ/mol} \\ IE_2 &= 1820 \text{ kJ/mol} \\ IE_3 &= 2750 \text{ kJ/mol} \\ IE_4 &= 11,600 \text{ kJ/mol} \end{aligned}$$
- To which third-period element do these ionization values belong?
- Electron Affinities and Metallic Character**

79. Choose the element with the more negative (more exothermic) electron affinity from each pair.  
 a. Na or Rb      b. B or S  
 c. C or N      d. Li or F

80. Choose the element with the more negative (more exothermic) electron affinity from each pair.  
 a. Mg or S      b. K or Cs  
 c. Si or P      d. Ga or Br

81. Choose the more metallic element from each pair.  
 a. Sr or Sb      b. As or Bi  
 c. Cl or O      d. S or As

82. Choose the more metallic element from each pair.  
 a. Sb or Pb      b. K or Ge  
 c. Ge or Sb      d. As or Sn

83. Arrange these elements in order of increasing metallic character: Fr, Sb, In, S, Ba, Se.
84. Arrange these elements in order of decreasing metallic character: Sr, N, Si, P, Ga, Al.

### Chemical Behavior of the Alkali Metals and the Halogens

85. Write a balanced chemical equation for the reaction of solid strontium with iodine gas.
86. Based on the ionization energies of the alkali metals, which alkali metal would you expect to undergo the most exothermic

reaction with chlorine gas? Write a balanced chemical equation for the reaction.

87. Write a balanced chemical equation for the reaction of solid lithium with liquid water.
88. Write a balanced chemical equation for the reaction of solid potassium with liquid water.
89. Write a balanced equation for the reaction of hydrogen gas with bromine gas.
90. Write a balanced equation for the reaction of chlorine gas with fluorine gas.

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## Cumulative Problems

91. Bromine is a highly reactive liquid while krypton is an inert gas. Explain the difference based on their electron configurations.
92. Potassium is a highly reactive metal while argon is an inert gas. Explain the difference based on their electron configurations.
93. Both vanadium and its  $3+$  ion are paramagnetic. Use electron configurations to explain this statement.
94. Use electron configurations to explain why copper is paramagnetic while its  $1+$  ion is not.
95. Suppose you were trying to find a substitute for  $K^+$  in nerve signal transmission. Where would you begin your search? What ions would be most like  $K^+$ ? For each ion you propose, explain the ways in which it would be similar to  $K^+$  and the ways it would be different. Refer to periodic trends in your discussion.
96. Suppose you were trying to find a substitute for  $Na^+$  in nerve signal transmission. Where would you begin your search? What ions would be most like  $Na^+$ ? For each ion you propose, explain the ways in which it would be similar to  $Na^+$  and the ways it would be different. Use periodic trends in your discussion.
97. Life on Earth evolved based on the element carbon. Based on periodic properties, what two or three elements would you expect to be most like carbon?
98. Which pair of elements would you expect to have the most similar atomic radii, and why?  
a. Si and Ga      b. Si and Ge      c. Si and As
99. Consider these elements: N, Mg, O, F, Al.  
a. Write the electron configuration for each element.  
b. Arrange the elements in order of decreasing atomic radius.  
c. Arrange the elements in order of increasing ionization energy.  
d. Use the electron configurations in part a to explain the differences between your answers to parts b and c.
100. Consider these elements: P, Ca, Si, S, Ga.  
a. Write the electron configuration for each element.  
b. Arrange the elements in order of decreasing atomic radius.  
c. Arrange the elements in order of increasing ionization energy.  
d. Use the electron configurations in part a to explain the differences between your answers to parts b and c.
101. Explain why atomic radius decreases as we move to the right across a period for main-group elements but not for transition elements.

102. Explain why vanadium (radius = 134 pm) and copper (radius = 128 pm) have nearly identical atomic radii, even though the atomic number of copper is about 25% higher than that of vanadium. What would you predict about the relative densities of these two metals? Look up the densities in a reference book, periodic table, or on the Web. Are your predictions correct?
103. The lightest noble gases, such as helium and neon, are completely inert—they do not form any chemical compounds whatsoever. The heavier noble gases, in contrast, do form a limited number of compounds. Explain this difference in terms of trends in fundamental periodic properties.
104. The lightest halogen is also the most chemically reactive, and reactivity generally decreases as we move down the column of halogens in the periodic table. Explain this trend in terms of periodic properties.
105. Write general outer electron configurations ( $ns^x np^y$ ) for groups 6A and 7A in the periodic table. The electron affinity of each group 7A element is more negative than that of each corresponding group 6A element. Use the electron configurations to explain why this is so.
106. The electron affinity of each group 5A element is more positive than that of each corresponding group 4A element. Use the outer electron configurations for these columns to suggest a reason for this behavior.
107. The elements with atomic numbers 35 and 53 have similar chemical properties. Based on their electronic configurations, predict the atomic number of a heavier element that also should have these chemical properties.
108. Write the electronic configurations of the six cations that form from sulfur by the loss of one to six electrons. For those cations that have unpaired electrons, write orbital diagrams.
109. You have cracked a secret code that uses elemental symbols to spell words. The code uses numbers to designate the elemental symbols. Each number is the sum of the atomic number and the highest principal quantum number of the highest occupied orbital of the element whose symbol is to be used. The message may be written forward or backward. Decode the following messages:  
a. 10, 12, 58, 11, 7, 44, 63, 66  
b. 9, 99, 30, 95, 19, 47, 79
110. The electron affinity of sodium is lower than that of lithium, while the electron affinity of chlorine is higher than that of fluorine. Suggest an explanation for this observation.

- 111.** Use Coulomb's law to calculate the ionization energy in kJ/mol of an atom composed of a proton and an electron separated by 100.00 pm. What wavelength of light would have sufficient energy to ionize the atom?

- 112.** The first ionization energy of sodium is 496 kJ/mol. Use Coulomb's law to estimate the average distance between the sodium nucleus and the 3s electron. How does this distance compare to the atomic radius of sodium? Explain the difference.

## Challenge Problems

- 113.** Consider the densities and atomic radii of the noble gases at 25 °C:

Element	Atomic Radius (pm)	Density (g/L)
He	32	0.18
Ne	70	0.90
Ar	98	—
Kr	112	3.75
Xe	130	—
Rn	—	9.73

- a. Estimate the densities of argon and xenon by interpolation from the data.
- b. Provide an estimate of the density of the yet undiscovered element with atomic number 118 by extrapolation from the data.
- c. Use the molar mass of neon to estimate the mass of a neon atom. Then use the atomic radius of neon to calculate the average density of a neon atom. How does this density compare to the density of neon gas? What does this comparison suggest about the nature of neon gas?
- d. Use the densities and molar masses of krypton and neon to calculate the number of atoms of each element found in a volume of 1.0 L. Use these values to estimate the number of atoms that occur in 1.0 L of Ar. Now use the molar mass of argon to estimate the density of Ar. How does this estimate compare to that in part a?
- 114.** As you have seen, the periodic table is a result of empirical observation (i.e., the periodic law), but quantum-mechanical theory explains *why* the table is so arranged. Suppose that, in another universe, quantum theory was such that there were one *s* orbital but only two *p* orbitals (instead of three) and only three *d* orbitals (instead of five). Draw out the first four periods of the periodic table in this alternative universe. Which elements would be the equivalent of the noble gases? Halogens? Alkali metals?
- 115.** Consider the metals in the first transition series. Use periodic trends to predict a trend in density as you move to the right across the series.
- 116.** Imagine a universe in which the value of  $m_s$  can be  $+\frac{1}{2}$ , 0, and  $-\frac{1}{2}$ . Assuming that all the other quantum numbers can take only the values possible in our world and that the Pauli exclusion principle applies, determine
- a. the new electronic configuration of neon.
  - b. the atomic number of the element with a completed  $n = 2$  shell.
  - c. the number of unpaired electrons in fluorine.
- 117.** A carbon atom can absorb radiation of various wavelengths with resulting changes in its electronic configuration. Write orbital diagrams for the electronic configuration of carbon that would result from absorption of the three longest wavelengths of radiation it can absorb.
- 118.** Only trace amounts of the synthetic element darmstadtium, atomic number 110, have been obtained. The element is so highly unstable that no observations of its properties have been possible. Based on its position in the periodic table, propose three different reasonable valence electron configurations for this element.
- 119.** What is the atomic number of the as yet undiscovered element in which the *8s* and *8p* electron energy levels fill? Predict the chemical behavior of this element.
- 120.** The trend in second ionization energy for the elements from lithium to fluorine is not a regular one. Predict which of these elements has the highest second ionization energy and which has the lowest and explain. Of the elements N, O, and F, O has the highest and N the lowest second ionization energy. Explain.
- 121.** Unlike the elements in groups 1A and 2A, those in group 3A do not show a regular decrease in first ionization energy in going down the column. Explain the irregularities.
- 122.** Using the data in Figures 8.15 and 8.16, calculate  $\Delta E$  for the reaction  $\text{Na}(g) + \text{Cl}(g) \rightarrow \text{Na}^+(g) + \text{Cl}^-(g)$ .
- 123.** Even though adding two electrons to O or S forms an ion with a noble gas electron configuration, the second electron affinity of both of these elements is positive. Explain.
- 124.** In Section 2.7 we discussed the metalloids, which form a diagonal band separating the metals from the nonmetals. There are other instances in which elements such as lithium and magnesium that are diagonal to each other have comparable metallic character. Suggest an explanation for this observation.
- 125.** The heaviest known alkaline earth metal is radium, atomic number 88. Find the atomic numbers of the as yet undiscovered next two members of the series.
- 126.** Predict the electronic configurations of the first two excited states (next higher energy states beyond the ground state) of Pd.
- 127.** Table 8.2 does not include francium because none of its isotopes are stable. Predict the values of the entries for Fr in Table 8.2. Predict the nature of the products of the reaction of Fr with (a) water, (b) oxygen, and (c) chlorine.
- 128.** From its electronic configuration, predict which of the first ten elements would be most similar in chemical behavior to the as yet undiscovered element 165.

## Conceptual Problems

- 129.** Imagine that in another universe atoms and elements are identical to ours, except that atoms with six valence electrons have particular stability (in contrast to our universe where atoms with eight valence electrons have particular stability). Give an example of an element in the alternative universe that corresponds to
- a noble gas.
  - a reactive nonmetal.
  - a reactive metal.
- 130.** The outermost valence electron in atom A experiences an effective nuclear charge of  $2+$  and is on average 225 pm from the nucleus. The outermost valence electron in atom B experiences an effective nuclear charge of  $1+$  and is on average 175 pm from the nucleus. Which atom (A or B) has the highest first ionization energy? Explain.
- 131.** Determine whether each statement regarding penetration and shielding is true or false. (Assume that all lower energy orbitals are fully occupied.)
- An electron in a  $3s$  orbital is more shielded than an electron in a  $2s$  orbital.

- An electron in a  $3s$  orbital penetrates into the region occupied by core electrons more than electrons in a  $3p$  orbital.
- An electron in an orbital that penetrates closer to the nucleus will always experience more shielding than an electron in an orbital that does not penetrate as far.
- An electron in an orbital that penetrates close to the nucleus will tend to experience a higher effective nuclear charge than one that does not.

- 132.** Give a combination of four quantum numbers that could be assigned to an electron occupying a  $5p$  orbital. Do the same for an electron occupying a  $6d$  orbital.

- 133.** Use the trends in ionization energy and electron affinity to explain why calcium fluoride has the formula  $\text{CaF}_2$  and not  $\text{Ca}_2\text{F}$  or  $\text{CaF}$ .

## Answers to Conceptual Connections

### Coulomb's Law

- 8.1** (a) Since the charges are opposite, the potential energy of the interaction is negative. As the charges get closer together,  $r$  becomes smaller and the potential energy decreases (becomes more negative).

### Penetration and Shielding

- 8.2** (c) Penetration results in less shielding from nuclear charge and therefore lower energy.

### Electron Configurations and Quantum Numbers

- 8.3**  $n = 4, l = 0, m_l = 0, m_s = +\frac{1}{2}; n = 4, l = 0, m_l = 0, m_s = -\frac{1}{2}$

### Effective Nuclear Charge

- 8.4** (c) Since  $Z_{\text{eff}}$  increases from left to right across a row in the periodic table, the valence electrons in S experience a greater effective nuclear charge than the valence electrons in Al or in Mg.

### Ions, Isotopes, and Atomic Size

- 8.5** The isotopes of an element all have the same radii for two reasons: (1) neutrons are negligibly small compared to the size of an atom and therefore extra neutrons do not increase atomic size, and (2) neutrons have no charge and therefore do not attract electrons in the way that protons do.

### Ionization Energies and Chemical Bonding

- 8.6** As you can see from the successive ionization energies of any element, valence electrons are held most loosely and can therefore be transferred or shared most easily. Core electrons, on the other hand, are held tightly and are not easily transferred or shared. Consequently, valence electrons are most important to chemical bonding.

### Periodic Trends

- 8.7** The  $3s$  electron in sodium has a relatively low ionization energy (496 kJ/mol) because it is a valence electron. The energetic cost for sodium to lose a second electron is extraordinarily high (4560 kJ/mol) because the next electron to be lost is a core electron ( $2p$ ). Similarly, the electron affinity of chlorine to gain one electron ( $-349$  kJ/mol) is highly exothermic since the added electron completes chlorine's valence shell. The gain of a second electron by the negatively charged chlorine anion would not be so favorable. Therefore, we would expect sodium and chlorine to combine in a 1:1 ratio.

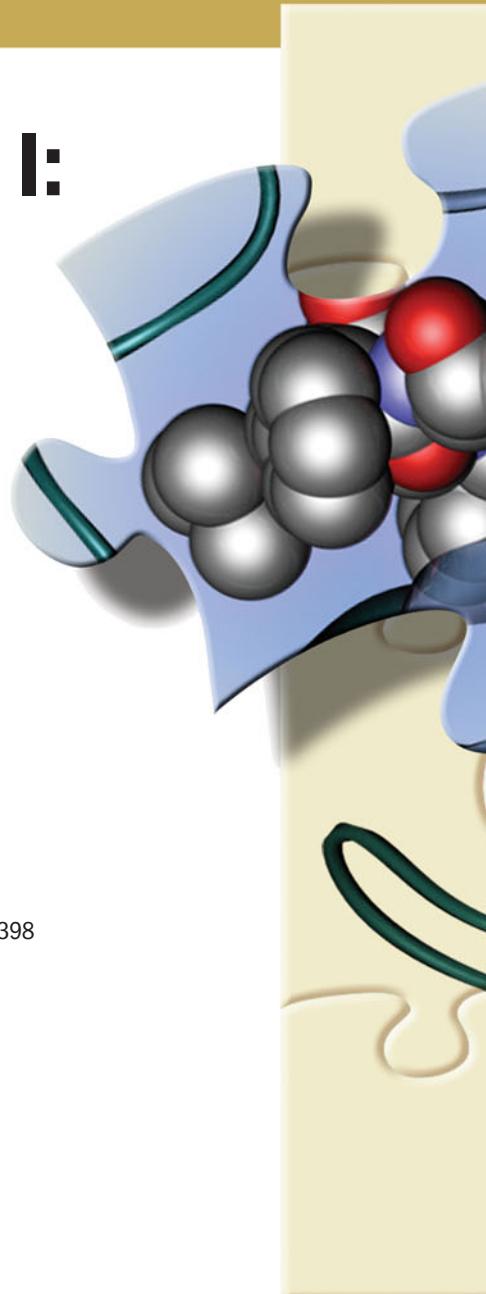
# 9

# Chemical Bonding I: The Lewis Model

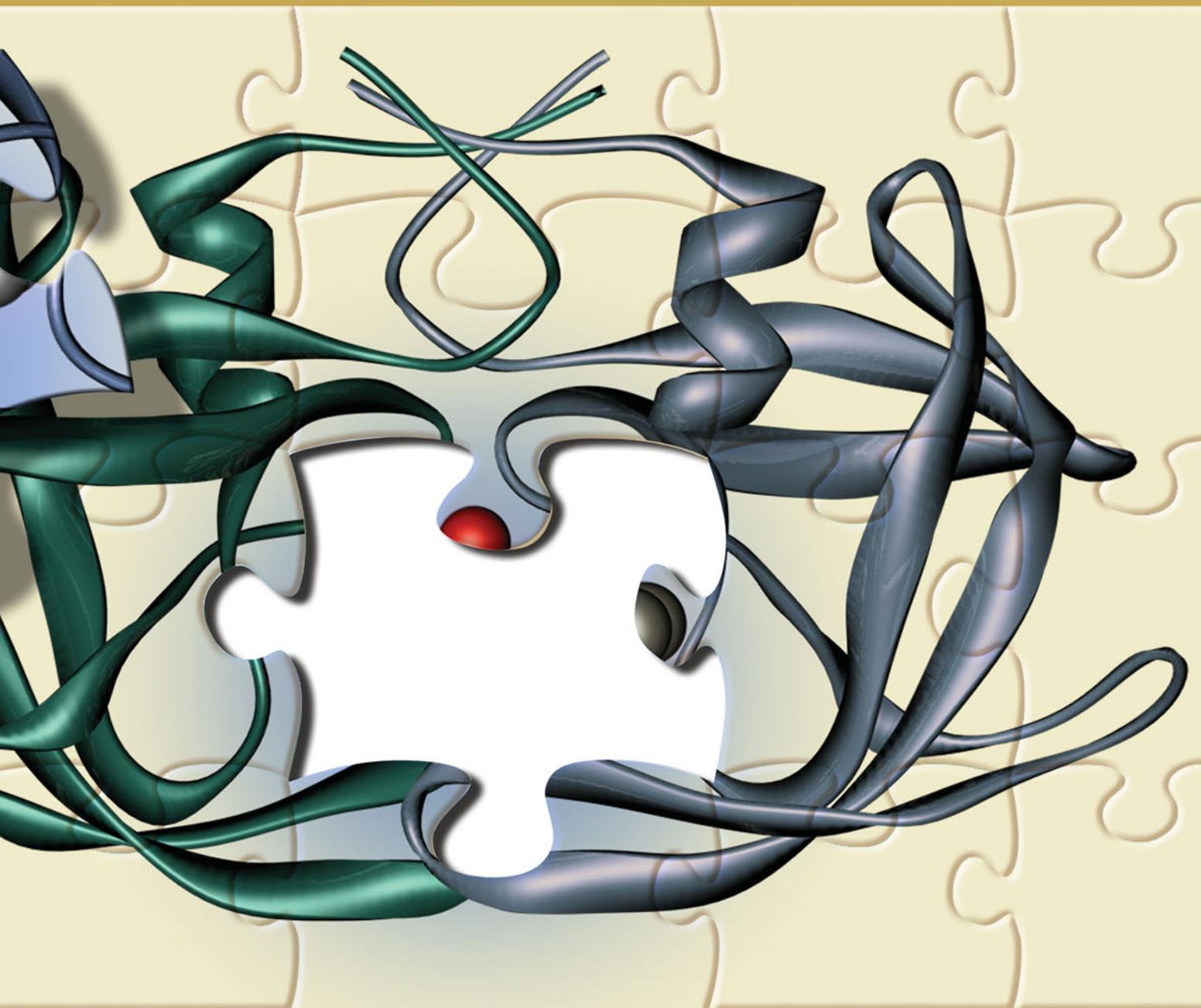
*Theories are nets cast to catch what we call ‘the world’: to rationalize, to explain, and to master it. We endeavor to make the mesh ever finer and finer.*  
—Karl Popper (1902–1994)

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- 9.11** Bonding in Metals: The Electron Sea Model 413

**Key Learning Outcomes** 418



**C**HEMICAL BONDING IS AT THE HEART of chemistry. The bonding theories that we are about to examine are—as Karl Popper, a philosopher of science, eloquently states in the chapter-opening quote—nets cast to understand the world. In the next two chapters, we will examine three theories with successively finer “meshes.” The first is the Lewis model, a simple model of chemical bonding, which can be carried out on the back of an envelope. With just a few dots, dashes, and chemical symbols, the Lewis model can help us to understand and predict a myriad of chemical observations. The second is valence bond theory, which treats electrons in a more quantum-mechanical manner but stops short of viewing them as belonging to the entire molecule. The third is molecular orbital theory, essentially a full quantum-mechanical treatment of the molecule and its electrons as a whole. Molecular orbital theory has great predictive power, but at the expense of great complexity and intensive computational requirements. Which theory is “correct”? Remember that theories are models that help us understand and predict behavior. All three of these theories are extremely useful, depending on exactly what aspect of chemical bonding we want to predict or understand.



The AIDS drug Indinavir—shown here as the missing piece in a puzzle depicting the protein HIV-protease—was developed with the help of chemical bonding theories.

## 9.1 Bonding Models and AIDS Drugs

In 1989, researchers using X-ray crystallography—a technique in which X-rays are scattered from crystals of the molecule of interest—determined the structure of a molecule called HIV-protease. HIV-protease is a protein (a class of large biological molecules) synthesized by the human immunodeficiency virus (HIV). This particular protein is crucial to the virus’s ability to multiply and cause acquired immune deficiency syndrome, or AIDS. Without HIV-protease, HIV cannot spread in the human body because the virus cannot replicate. In other words, without HIV-protease, AIDS can’t develop.

With knowledge of the HIV-protease structure, pharmaceutical companies set out to create a molecule that would disable HIV-protease by attaching to the working part of the molecule, called the active site. To design such a molecule, researchers used *bonding theories*—models that predict how atoms bond together to form molecules—to simulate the shape of potential drug molecules and determine how they would interact with the protease molecule. By the early 1990s, pharmaceutical companies had developed several

We will discuss X-ray crystallography in more detail in Section 11.10.

We will discuss proteins in more detail in Chapter 21.



▲ G. N. Lewis

drug molecules that seemed to work. Since these molecules inhibit the action of HIV-protease, they were named *protease inhibitors*. Protease inhibitors, when given in combination with other drugs, decrease the viral count in HIV-infected individuals to undetectable levels. Although protease inhibitors do not cure AIDS, many AIDS patients are still alive today because of these drugs.

Bonding theories are central to chemistry because they explain how atoms bond together to form molecules. They explain why some combinations of atoms are stable and others are not. For example, bonding theories explain why table salt is NaCl and not NaCl<sub>2</sub> and why water is H<sub>2</sub>O and not H<sub>3</sub>O. Bonding theories also predict the shapes of molecules—a topic in the next chapter—which in turn determine many of the physical and chemical properties of compounds. The bonding model we examine in this chapter is called the **Lewis model**, named after the American chemist G. N. Lewis (1875–1946). In the Lewis model, valence electrons are represented as dots, and we draw **Lewis electron-dot structures** (or simply **Lewis structures**) to depict molecules. These structures, which are fairly simple to draw, have tremendous predictive power. With minimal computation, the Lewis model can be used to predict whether a particular set of atoms will form a stable molecule and what that molecule might look like. Although we will also examine more advanced theories in the following chapter, the Lewis model remains the simplest model for making quick, everyday predictions about most molecules.

## 9.2 Types of Chemical Bonds

We begin our discussion of chemical bonding by asking why bonds form in the first place. This seemingly simple question is vitally important. Imagine our universe without chemical bonding. Such a universe would contain only 91 different kinds of substances (the 91 naturally occurring elements). With such a poor diversity of substances, life would be impossible, and we would not be around to wonder why. The *answer* to the question of why bonds form, however, is not simple and involves not only quantum mechanics but also some thermodynamics that we will not introduce until Chapter 17. Nonetheless, we can address an important *aspect* of the answer now: *chemical bonds form because they lower the potential energy between the charged particles that compose atoms*.

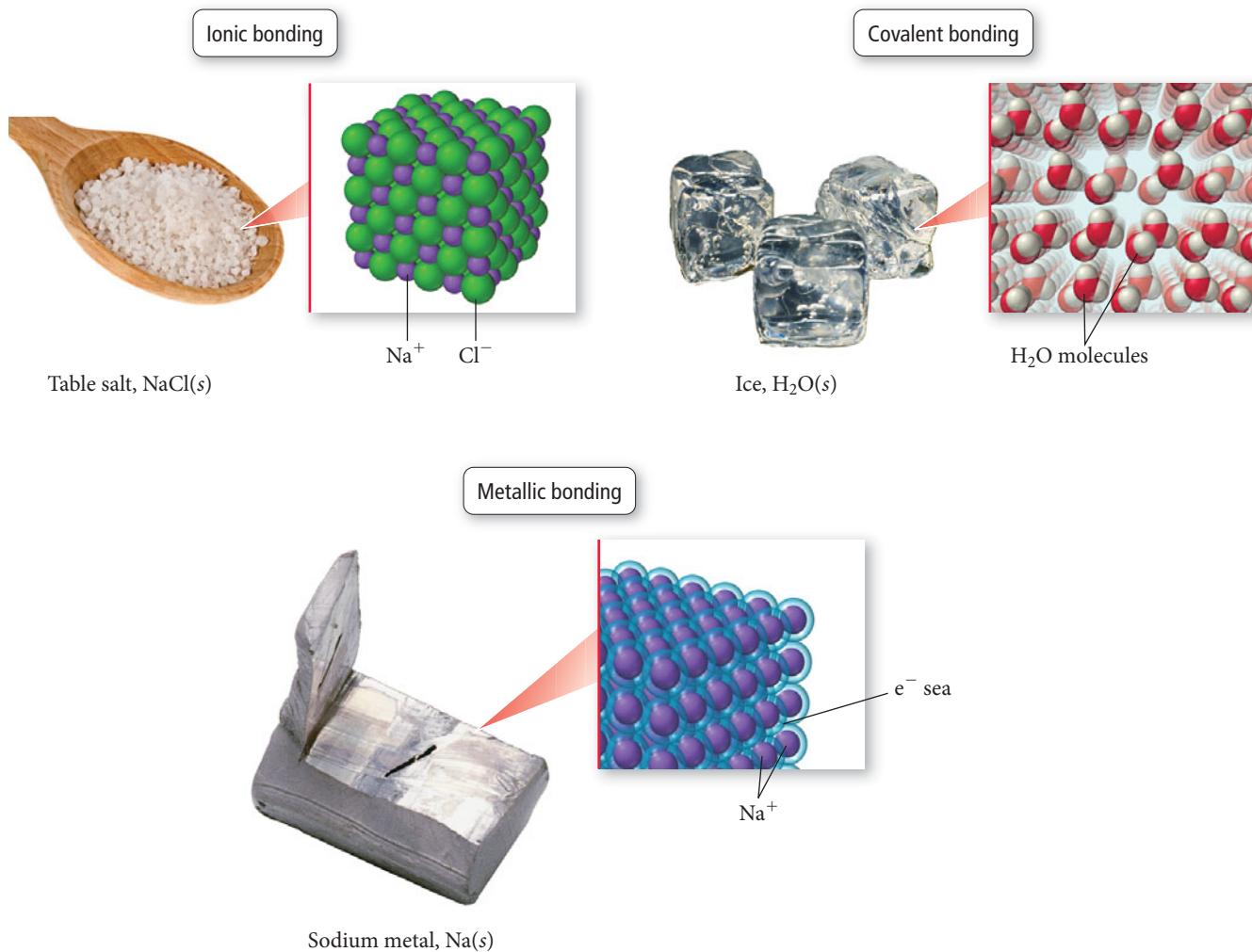
As you already know, atoms are composed of particles with positive charges (the protons in the nucleus) and negative charges (the electrons). When two atoms approach each other, the electrons of one atom are attracted to the nucleus of the other according to Coulomb's law (see Section 8.3) and vice versa. However, at the same time, the electrons of each atom repel the electrons of the other, and the nucleus of each atom repels the nucleus of the other. The result is a complex set of interactions among a potentially large number of charged particles. If these interactions lead to an overall net reduction of energy between the charged particles, a chemical bond forms. Bonding theories help us to predict the circumstances under which bonds form and also the properties of the resultant molecules.

We can broadly classify chemical bonds into three types depending on the kind of atoms involved in the bonding (Figure 9.1 ▶).

Types of Atoms	Type of Bond	Characteristic of Bond
Metal and nonmetal	Ionic	Electrons transferred
Nonmetal and nonmetal	Covalent	Electrons shared
Metal and metal	Metallic	Electrons pooled

In Chapter 8 we discussed that metals tend to have low ionization energies (their electrons are relatively easy to remove) and that nonmetals tend to have negative electron affinities (they readily gain electrons). When a metal bonds with a nonmetal, it transfers one or more electrons to the nonmetal. The metal atom becomes a cation and the nonmetal atom an anion. These oppositely charged ions then attract one another, lowering their overall potential energy as described by Coulomb's law. The resulting bond is an **ionic bond**.

We also discussed in Chapter 8 that nonmetals tend to have high ionization energies (their electrons are relatively difficult to remove). Therefore when a nonmetal bonds with another nonmetal, neither atom transfers electrons to the other. Instead, the two atoms

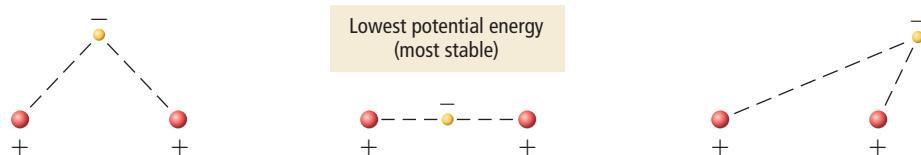


▲ FIGURE 9.1 Ionic, Covalent, and Metallic Bonding

share some electrons. The shared electrons interact with the nuclei of both of the bonding atoms, lowering their potential energy in accordance with Coulomb's law. The resulting bond is a **covalent bond**.

Recall from Section 3.2 that we can understand the stability of a covalent bond by considering the most stable arrangement (the one with the lowest potential energy) of two positively charged particles separated by a small distance and a negatively charged particle. As you can see in Figure 9.2 ▼, the arrangement in which the negatively charged particle lies *between* the two positively charged ones has the lowest potential energy because in this arrangement, the negatively charged particle interacts most strongly with *both of the positively charged ones*. In a sense, the negatively charged particle holds the two positively charged ones together. Similarly, shared electrons in a covalent chemical bond *hold* the bonding atoms together by attracting the positive charges of their nuclei.

A third type of bonding, **metallic bonding**, occurs in metals. Since metals have low ionization energies, they tend to lose electrons easily. In the simplest model for metallic bonding—called the *electron sea* model—all of the atoms in a metal lattice pool their valence electrons. These pooled electrons are no longer localized on a single atom, but delocalized over the entire metal. The positively charged metal atoms are then attracted to the sea of electrons, holding the metal together. We discuss metallic bonding in more detail in Section 9.11.



◀ FIGURE 9.2 Possible Configurations of One Negatively Charged Particle and Two Positively Charged Ones

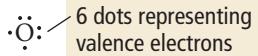
Remember, the number of valence electrons for any main group is equal to the group number of the element (except for helium, which is in group 8A but has only two valence electrons).

## 9.3 Representing Valence Electrons with Dots

In Chapter 8, we saw that, for main-group elements, valence electrons are those electrons in the outermost principal energy level. Since valence electrons are held most loosely, and since chemical bonding involves the transfer or sharing of electrons between two or more atoms, valence electrons are most important in bonding, so the Lewis model focuses on these. In a **Lewis symbol**, we represent the valence electrons of main-group elements as dots surrounding the abbreviation for the element. For example, the electron configuration of O is:



And the Lewis symbol is:



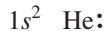
While the exact location of dots is not critical, in this book we will first place dots singly before pairing (except for helium, which always has two paired dots signifying its duet).

Each dot represents a valence electron. The dots are placed around the element's symbol with a maximum of two dots per side. The Lewis symbols for all of the period 2 elements are drawn in a similar way:



Lewis symbols provide a simple way to visualize the number of valence electrons in a main-group atom. Notice that atoms with eight valence electrons—which are particularly stable because they have a full outer level—are easily identified because they have eight dots, an **octet**.

Helium is somewhat of an exception. Its electron configuration and Lewis symbol are:



The Lewis symbol of helium contains only two dots (a **duet**). For helium, a duet represents a stable electron configuration because the  $n = 1$  quantum level fills with only two electrons.

In the Lewis model, a **chemical bond** is the sharing or transfer of electrons to attain stable electron configurations for the bonding atoms. If electrons are transferred, as occurs between a metal and a nonmetal, the bond is an *ionic bond*. If the electrons are shared, as occurs between two nonmetals, the bond is a *covalent bond*. In either case, the bonding atoms obtain stable electron configurations; since the stable configuration is usually eight electrons in the outermost shell, this is known as the **octet rule**. When applying the Lewis model we do not try to calculate the energies associated with the attractions and repulsions between electrons and nuclei on neighboring atoms. The energy changes that occur because of these interactions are central to chemical bonding (as we saw in Section 9.2), yet the Lewis model ignores them because calculating these energy changes is extremely complicated. Instead the Lewis model uses the simple octet rule, a practical approach that accurately predicts what we see in nature for a large number of compounds—hence the success and longevity of the Lewis model.

## 9.4 Ionic Bonding: Lewis Symbols and Lattice Energies

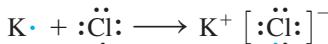
Although the Lewis model's strength is in modeling covalent bonding, it can also be applied to ionic bonding. To represent ionic bonding, we move electron dots from the Lewis symbol of the metal to the Lewis symbol of the nonmetal and then allow the resultant ions to form a crystalline lattice composed of alternating cations and anions.

### Ionic Bonding and Electron Transfer

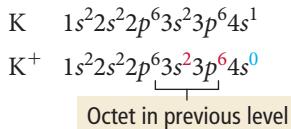
Consider potassium and chlorine, which have the following Lewis symbols:



When these atoms bond, potassium transfers its valence electron to chlorine:



The transfer of the electron gives chlorine an octet (shown as eight dots around chlorine) and leaves potassium without any valence electrons but with an octet in the *previous* principal energy level (which is now the outermost level).

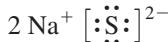


The potassium, because it has lost an electron, becomes positively charged (a cation), while the chlorine, which has gained an electron, becomes negatively charged (an anion). The Lewis symbol of an anion is usually written within brackets with the charge in the upper right-hand corner, outside the brackets. The positive and negative charges attract one another, resulting in the compound KCl.

So we can use the Lewis model to predict the correct chemical formulas for ionic compounds. For the compound that forms between K and Cl, for example, the Lewis model predicts a ratio of one potassium cation to every one chloride anion, KCl. In nature, when we examine the compound formed between potassium and chlorine, we indeed find one potassium ion to every chloride ion. As another example, consider the ionic compound formed between sodium and sulfur. The Lewis symbols for sodium and sulfur are:



Sodium must lose its one valence electron in order to have an octet (in the previous principal shell), while sulfur must gain two electrons to get an octet. Consequently, the compound that forms between sodium and sulfur requires a ratio of two sodium atoms to every one sulfur atom.



The two sodium atoms each lose their one valence electron while the sulfur atom gains two electrons and gets an octet. The Lewis model predicts that the correct chemical formula is Na<sub>2</sub>S, exactly what we see in nature.

Recall that solid ionic compounds do not contain distinct molecules; they are composed of alternating positive and negative ions in a three-dimensional crystalline array.

### EXAMPLE 9.1 Using Lewis Symbols to Predict the Chemical Formula of an Ionic Compound

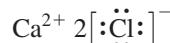
Use Lewis symbols to predict the formula for the compound that forms between calcium and chlorine.

#### SOLUTION

Draw Lewis symbols for calcium and chlorine based on their number of valence electrons, obtained from their group number in the periodic table.



Calcium must lose its two valence electrons (to be left with an octet in its previous principal shell), while chlorine only needs to gain one electron to get an octet. Draw two chlorine anions, each with an octet and a 1<sup>-</sup> charge, and one calcium cation with a 2<sup>+</sup> charge. Place brackets around the chlorine anions and indicate the charges on each ion.



Finally, write the formula with subscripts to indicate the number of atoms.

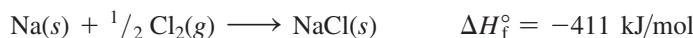


#### FOR PRACTICE 9.1

Use Lewis symbols to predict the formula for the compound that forms between magnesium and nitrogen.

## Lattice Energy: The Rest of the Story

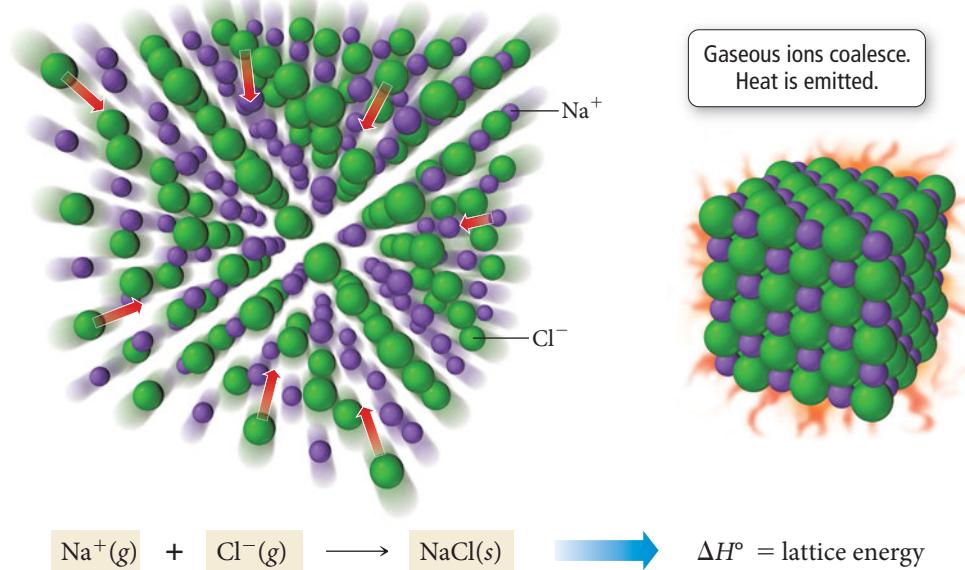
The formation of an ionic compound from its constituent elements is usually quite exothermic. For example, when sodium chloride (table salt) forms from elemental sodium and chlorine, 411 kJ of heat is evolved in the following violent reaction:



Where does this energy come from? You might think that it comes solely from the tendency of metals to lose electrons and nonmetals to gain electrons—but it does not. In fact, the transfer of an electron from sodium to chlorine—by itself—actually *absorbs* energy. The first ionization energy of sodium is +496 kJ/mol, and the electron affinity of Cl is only −349 kJ/mol. Based only on these energies, the reaction should be *endothermic* by +147 kJ/mol. So why is the reaction so *exothermic*?

The answer lies in the **lattice energy**—the energy associated with the formation of a crystalline lattice of alternating cations and anions from the gaseous ions. Since the sodium ions are positively charged and the chlorine ions are negatively charged, the potential energy decreases—as prescribed by Coulomb’s law—when these ions come together to form a lattice. That energy is emitted as heat when the lattice forms, as shown in Figure 9.3 ▶. The exact value of the lattice energy, however, is not simple to determine because it involves a large number of interactions among many charged particles in a lattice. The easiest way to calculate lattice energy is with the *Born–Haber cycle*.

### Lattice Energy of an Ionic Compound



► FIGURE 9.3 Lattice Energy

The lattice energy of an ionic compound is the energy associated with the formation of a crystalline lattice of the compound from the gaseous ions.

Recall that Hess's law states that the change in the overall enthalpy of a stepwise process is the sum of the enthalpy changes of the steps.

## The Born–Haber Cycle

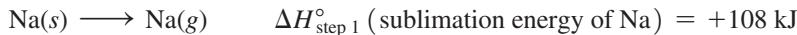
The **Born–Haber cycle** is a hypothetical series of steps that represents the formation of an ionic compound from its constituent elements. The steps are chosen so that the change in enthalpy of each step is known except for the last one, which is the lattice energy. The change in enthalpy for the overall process is also known. Using Hess's law (see Section 6.8), we can therefore determine the enthalpy change for the unknown last step, the lattice energy.

Consider the formation of NaCl from its constituent elements in their standard states. The enthalpy change for the overall reaction is simply the standard enthalpy of formation of NaCl(s):

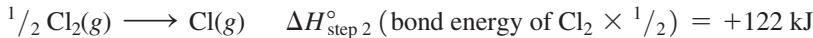


Now consider the following set of steps—the Born–Haber cycle—from which  $\text{NaCl}(s)$  can also be made from  $\text{Na}(s)$  and  $\text{Cl}_2(g)$ :

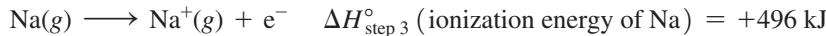
- The first step is the formation of gaseous sodium from solid sodium.



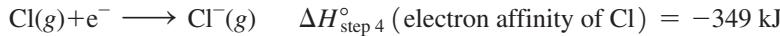
- The second step is the formation of a chlorine atom from a chlorine molecule.



- The third step is the ionization of gaseous sodium. The enthalpy change for this step is the ionization energy of sodium.



- The fourth step is the addition of an electron to gaseous chlorine. The enthalpy change for this step is the electron affinity of chlorine.



- The fifth and final step is the formation of the crystalline solid from the gaseous ions. The enthalpy change for this step is the lattice energy, the unknown quantity.

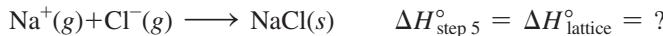
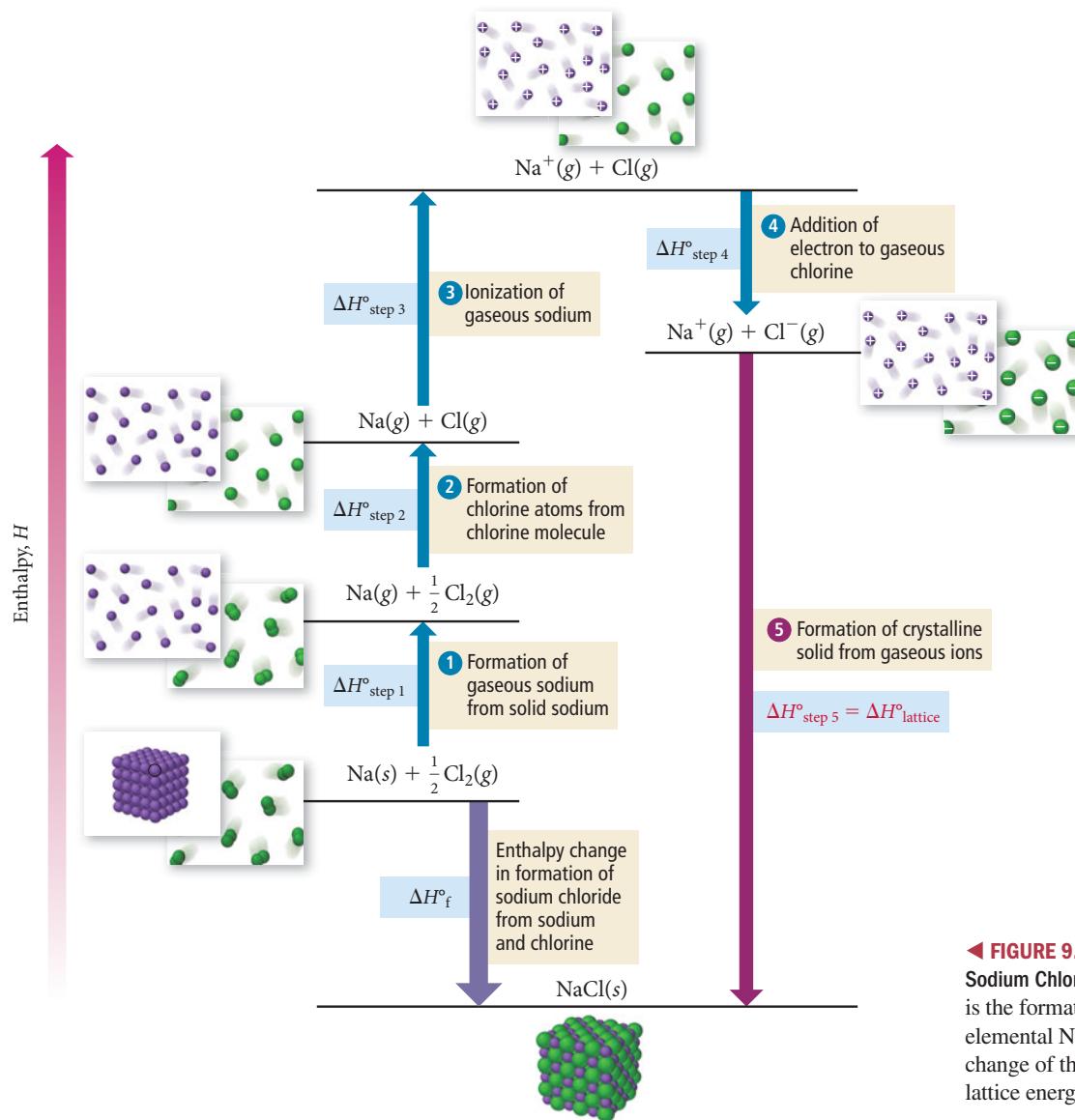


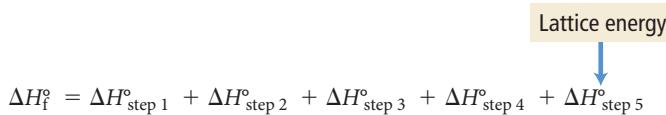
Figure 9.4 ▼ illustrates the entire Born–Haber cycle for  $\text{NaCl}$ .

**Born–Haber Cycle for Production of  $\text{NaCl}$  from  $\text{Na}(s)$  and  $\text{Cl}_2(g)$**



◀ **FIGURE 9.4** Born–Haber Cycle for Sodium Chloride The sum of the steps is the formation of  $\text{NaCl}$  from elemental  $\text{Na}$  and  $\text{Cl}_2$ . The enthalpy change of the last step is the lattice energy.

Since the overall reaction obtained by summing the steps in the Born–Haber cycle is equivalent to the formation of NaCl from its constituent elements, we use Hess's law to set the overall enthalpy of formation for NaCl(s) equal to the sum of the steps in the Born–Haber cycle:



We then solve this equation for  $\Delta H_{\text{step 5}}^\circ$ , which is  $\Delta H_{\text{lattice}}^\circ$ , and substitute the appropriate values to calculate the lattice energy.

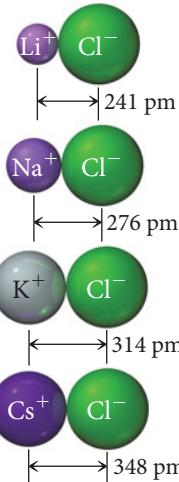
$$\begin{aligned}\Delta H_{\text{lattice}}^\circ &= \Delta H_{\text{step 5}}^\circ = \Delta H_f^\circ - (\Delta H_{\text{step 1}}^\circ + \Delta H_{\text{step 2}}^\circ + \Delta H_{\text{step 3}}^\circ + \Delta H_{\text{step 4}}^\circ) \\ &= -411 \text{ kJ} - (+108 \text{ kJ} + 122 \text{ kJ} + 496 \text{ kJ} - 349 \text{ kJ}) \\ &= -788 \text{ kJ}\end{aligned}$$

Some books define the lattice energy as the energy associated with separating one mole of an ionic lattice into its gaseous constituents, which makes the sign of the lattice energy positive instead of negative.

The value of the lattice energy is a large negative number. The formation of the crystalline NaCl lattice from sodium cations and chloride anions is highly exothermic and more than compensates for the endothermicity of the electron transfer process. In other words, the formation of ionic compounds is not exothermic because sodium “wants” to lose electrons and chlorine “wants” to gain them; rather, it is exothermic because of the large amount of heat released when sodium and chlorine ions coalesce to form a crystalline lattice.

## Trends in Lattice Energies: Ion Size

Consider the lattice energies of the following alkali metal chlorides:



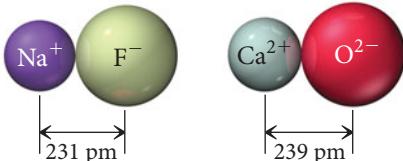
▲ Bond lengths of the group 1A metal chlorides.

Metal Chloride	Lattice Energy kJ/mol
LiCl	-834
NaCl	-788
KCl	-701
CsCl	-657

Why does the magnitude of the lattice energy decrease as we move down the column? We know from the periodic trends discussed in Chapter 8 that ionic radius increases as we move down a column in the periodic table (see Section 8.7). We also know, from our discussion of Coulomb's law in Section 8.3, that the potential energy of oppositely charged ions becomes less negative (or more positive) as the distance between the ions increases. As the size of the alkali metal ions increases down the column, so does the distance between the metal cations and the chloride anions. The magnitude of the lattice energy of the chlorides decreases accordingly, making the formation of the chlorides less exothermic. In other words, *as the ionic radii increase as we move down the column, the ions cannot get as close to each other and therefore do not release as much energy when the lattice forms.*

## Trends in Lattice Energies: Ion Charge

Consider the lattice energies of the following two compounds:



Compound	Lattice Energy (kJ/mol)
NaF	-910
CaO	-3414

Why is the magnitude of the lattice energy of CaO so much greater than the lattice energy of NaF? Na<sup>+</sup> has a radius of 95 pm and F<sup>-</sup> has a radius of 136 pm, resulting in a distance

between ions of 231 pm.  $\text{Ca}^{2+}$  has a radius of 99 pm and  $\text{O}^{2-}$  has a radius of 140 pm, resulting in a distance between ions of 239 pm. Even though the separation between the calcium and oxygen is slightly greater (which would tend to lower the lattice energy), the lattice energy for  $\text{CaO}$  is almost four times *greater*. The explanation lies in the charges of the ions. Recall from Coulomb's law that the magnitude of the potential energy of two interacting charges depends not only on the distance between the charges, but also on the product of the charges:

$$E = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r}$$

For  $\text{NaF}$ ,  $E$  is proportional to  $(1+)(1-) = 1-$ , while for  $\text{CaO}$ ,  $E$  is proportional to  $(2+)(2-) = 4-$ , so the relative stabilization for  $\text{CaO}$  relative to  $\text{NaF}$  is roughly four times greater, as observed in the lattice energy.

### **Summarizing Trends in Lattice Energies:**

- ▶ Lattice energies become less exothermic (less negative) with increasing ionic radius.
- ▶ Lattice energies become more exothermic (more negative) with increasing magnitude of ionic charge.

### **EXAMPLE 9.2 Predicting Relative Lattice Energies**

Arrange these ionic compounds in order of increasing *magnitude* of lattice energy:  
 $\text{CaO}$ ,  $\text{KBr}$ ,  $\text{KCl}$ ,  $\text{SrO}$ .

#### **SOLUTION**

$\text{KBr}$  and  $\text{KCl}$  should have lattice energies of smaller magnitude than  $\text{CaO}$  and  $\text{SrO}$  because of their lower ionic charges ( $1+$ ,  $1-$  compared to  $2+$ ,  $2-$ ). When you compare  $\text{KBr}$  and  $\text{KCl}$ , you expect  $\text{KBr}$  to have a lattice energy of lower magnitude due to the larger ionic radius of the bromide ion relative to the chloride ion. Between  $\text{CaO}$  and  $\text{SrO}$ , you expect  $\text{SrO}$  to have a lattice energy of lower magnitude due to the larger ionic radius of the strontium ion relative to the calcium ion.

Order of increasing *magnitude* of lattice energy:



Actual lattice energy values:

Compound	Lattice Energy (kJ/mol)
$\text{KBr}$	-671
$\text{KCl}$	-701
$\text{SrO}$	-3217
$\text{CaO}$	-3414

#### **FOR PRACTICE 9.2**

Arrange the following in order of increasing magnitude of lattice energy:  $\text{LiBr}$ ,  $\text{KI}$ , and  $\text{CaO}$ .

#### **FOR MORE PRACTICE 9.2**

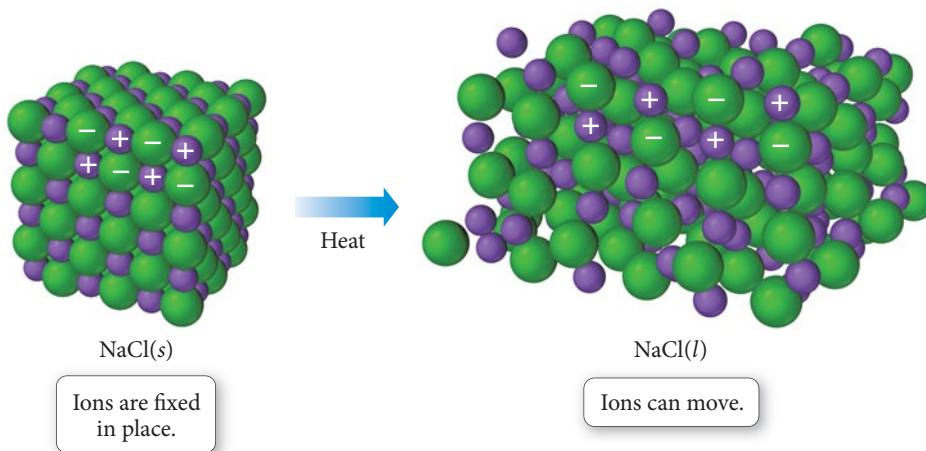
Which compound has a lattice energy of higher magnitude,  $\text{NaCl}$  or  $\text{MgCl}_2$ ?

### **Ionic Bonding: Models and Reality**

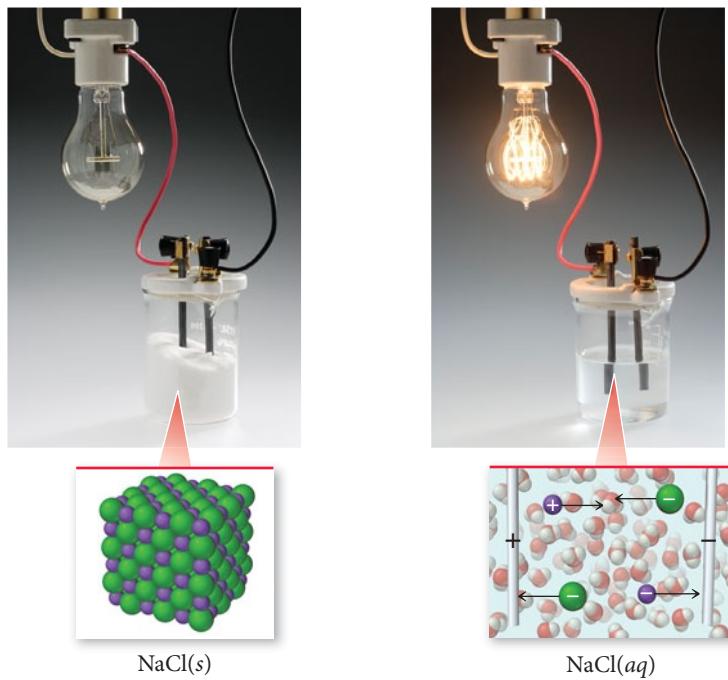
In this section, we have developed a model for ionic bonding. The value of a model is in how well it accounts for what we see in nature (through experiments). Does our ionic bonding model explain the properties of ionic compounds, including their high melting and boiling points, their tendency *not to conduct* electricity as solids, and their tendency *to conduct* electricity when dissolved in water?

We modeled an ionic solid as a lattice of individual ions held together by coulombic forces that are *nondirectional* (which means that, as you move away from the center of an ion, the forces are equally strong in all directions). To melt the solid, these forces must be overcome, which requires a significant amount of heat. Therefore, our model accounts for the high melting points of ionic solids. In the model, electrons are transferred from the metal to the nonmetal, but the transferred electrons remain localized on one atom. In other words, our model does not include any free electrons that might conduct electricity

► The melting of solid ionic compounds such as sodium chloride requires enough heat to overcome the electrical forces holding the anions and cations together in a lattice. Thus, the melting points of ionic compounds are relatively high.



(the movement or flow of electrons or other charged particles in response to an electric potential, or voltage, is electrical current). In addition, the ions themselves are fixed in place; therefore, our model accounts for the nonconductivity of ionic solids. When our idealized ionic solid dissolves in water, however, the cations and anions dissociate, forming free ions in solution. These ions can move in response to electrical forces, creating an electrical current. Thus, our model predicts that solutions of ionic compounds conduct electricity (which in fact they do).



▲ Solid sodium chloride does not conduct electricity.

▲ When sodium chloride dissolves in water, the resulting solution contains mobile ions that can create an electric current.

### Conceptual Connection 9.1 Melting Points of Ionic Solids

Use the ionic bonding model to determine which has the higher melting point, NaCl or MgO. Explain the relative ordering.



## Chemistry and Medicine

### Ionic Compounds in Medicine

Although most drugs are molecular compounds, a number of ionic compounds have medical uses. Consider the following partial list of ionic compounds used in medicine. Notice that many of these compounds contain polyatomic ions. The bonding between a metal and a polyatomic ion is ionic. However, the bonding within a polyatomic ion is covalent, the topic of our next section.



Formula	Name	Medical Use
$\text{AgNO}_3$	Silver nitrate	Topical anti-infective agent; in solution, used to treat and prevent eye infection, especially in newborn infants
$\text{BaSO}_4$	Barium sulfate	Given as a contrast medium—or image enhancer—in X-rays
$\text{CaSO}_4$	Calcium sulfate	Used to make plaster casts
$\text{KMnO}_4$	Potassium permanganate	Topical anti-infective agent; often used to treat fungal infections on the feet
$\text{KI}$	Potassium iodide	Antiseptic and disinfectant; given orally to prevent radiation sickness
$\text{Li}_2\text{CO}_3$	Lithium carbonate	Used to treat bipolar (manic-depressive) disorders
$\text{MgSO}_4$	Magnesium sulfate	Used to treat eclampsia (a condition that can occur during pregnancy in which elevated blood pressure leads to convulsions)
$\text{Mg(OH)}_2$	Magnesium hydroxide	Antacid and mild laxative
$\text{NaHCO}_3$	Sodium bicarbonate	Oral antacid used to treat heartburn and acid stomach; injected into blood to treat severe acidosis (acidification of the blood)
$\text{NaF}$	Sodium fluoride	Used to strengthen teeth
$\text{ZnO}$	Zinc oxide	Used as protection from ultraviolet light in sun

## 9.5 Covalent Bonding: Lewis Structures

The Lewis model provides us with a simple and useful model for covalent bonding. In this model, we represent molecular compounds with a *Lewis structure*, which depicts neighboring atoms as sharing some (or all) of their valence electrons in order to attain octets (or duets for hydrogen).

### Single Covalent Bonds

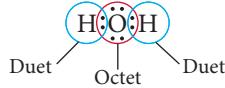
To see how covalent bonding is conceived in terms of the Lewis model, consider hydrogen and oxygen, which have the following Lewis symbols:



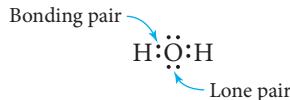
In water, these atoms share their unpaired valence electrons so that each hydrogen atom gets a duet and the oxygen atom gets an octet as represented with this Lewis structure:



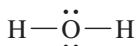
The shared electrons—those that appear in the space between the two atoms—count toward the octets (or duets) of *both of the atoms*.



A shared pair of electrons is called a **bonding pair**, while a pair that is associated with only one atom—and therefore not involved in bonding—is called a **lone pair**. Lone pair electrons are also called **nonbonding electrons**.



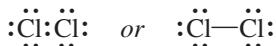
We often represent a bonding pair of electrons by a dash to emphasize that it constitutes a chemical bond.



The Lewis model also shows why the halogens form diatomic molecules. Consider the Lewis symbol for chlorine:



If two Cl atoms pair together, they can each get an octet:



Elemental chlorine does indeed exist as a diatomic molecule in nature, just as the Lewis model predicts. The same is true for the other halogens.

Similarly, the Lewis model predicts that hydrogen, which has the Lewis symbol



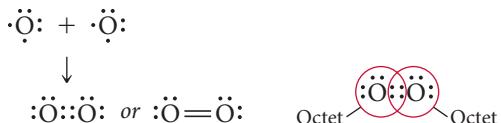
should exist as H<sub>2</sub>. When two hydrogen atoms share their valence electrons, each gets a duet, a stable configuration for hydrogen.



Again, the Lewis model is correct. In nature, elemental hydrogen exists as H<sub>2</sub> molecules.

## Double and Triple Covalent Bonds

In the Lewis model, two atoms may share more than one electron pair to get octets. For example, if we pair two oxygen atoms together, they share two electron pairs in order for each oxygen atom to have an octet.



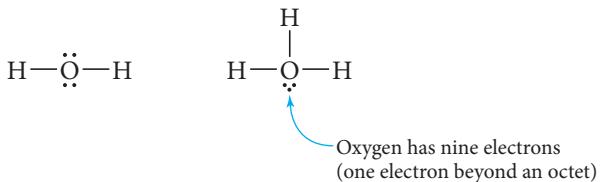
Each oxygen atom now has an octet because *the additional bonding pair counts toward the octet of both oxygen atoms*. When two electron pairs are shared between two atoms, the resulting bond is a **double bond**. In general, double bonds are shorter and stronger than single bonds. Atoms can also share three electron pairs. Consider the Lewis structure of N<sub>2</sub>. Since each N atom has five valence electrons, the Lewis structure for N<sub>2</sub> has 10 electrons. Both nitrogen atoms attain octets by sharing three electron pairs:



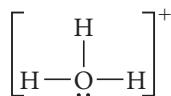
The bond is a **triple bond**. Triple bonds are even shorter and stronger than double bonds. When we examine nitrogen in nature, we find that it exists as a diatomic molecule with a very strong bond between the two nitrogen atoms. The bond is so strong that it is difficult to break, making N<sub>2</sub> a relatively unreactive molecule.

## Covalent Bonding: Models and Reality

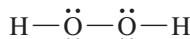
The Lewis model predicts the properties of molecular compounds in many ways. First, it accounts for why particular combinations of atoms form molecules and others do not. For example, why is water H<sub>2</sub>O and not H<sub>3</sub>O? We can write a good Lewis structure for H<sub>2</sub>O, but not for H<sub>3</sub>O.



In this way, the Lewis model predicts that  $\text{H}_2\text{O}$  should be stable, while  $\text{H}_3\text{O}$  should not be, and that is in fact the case. However, if we remove an electron from  $\text{H}_3\text{O}$ , we get  $\text{H}_3\text{O}^+$ , which should be stable (according to the Lewis model) because, when we remove the extra electron, oxygen gets an octet.



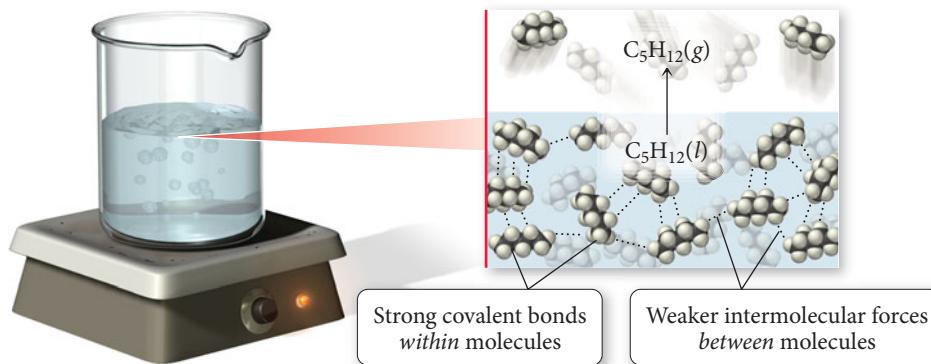
This ion, called the hydronium ion, is in fact stable in aqueous solutions (see Section 4.8). The Lewis model predicts other possible combinations for hydrogen and oxygen as well. For example, we can write a Lewis structure for  $\text{H}_2\text{O}_2$  as follows:



Indeed,  $\text{H}_2\text{O}_2$ , or hydrogen peroxide, exists and is often used as a disinfectant and a bleach.

The Lewis model also accounts for why covalent bonds are highly *directional*. The attraction between two covalently bonded atoms is due to the sharing of one or more electron pairs in the space between them. Thus, each bond links just one specific pair of atoms—in contrast to ionic bonds, which are nondirectional and hold together an entire array of ions. As a result, the fundamental units of covalently bonded compounds are individual molecules. These molecules can interact with one another in a number of different ways that we cover in Chapter 11. However, in covalently bonded molecular compounds the interactions *between* molecules (intermolecular forces) are generally much weaker than the bonding interactions within a molecule (intramolecular forces), as shown in Figure 9.5 ▼. When a molecular compound melts or boils, the molecules themselves remain intact—only the relatively weak interactions between molecules must be overcome. Consequently, molecular compounds tend to have lower melting and boiling points than ionic compounds.

### Molecular Compound



**▲ FIGURE 9.5 Intermolecular and Intramolecular Forces** The covalent bonds between atoms of a molecule are much stronger than the interactions between molecules. To boil a molecular substance, you simply have to overcome the relatively weak intermolecular forces, so molecular compounds generally have low boiling points.

### Conceptual Connection 9.2 Energy and the Octet Rule

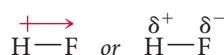
What is wrong with the following statement? *Atoms form bonds in order to satisfy the octet rule.*

## 9.6 Electronegativity and Bond Polarity

We know from Chapter 7 that representing electrons with dots, as we do in the Lewis model, is a drastic oversimplification. As we have already discussed, this does not invalidate the Lewis model—which is an extremely useful theory—but we must recognize and compensate for its inherent limitations. One limitation of representing electrons as dots, and covalent bonds as two dots shared between two atoms, is that the shared electrons always appear to be *equally* shared. Such is not the case. For example, consider the Lewis structure of hydrogen fluoride:



The two shared electron dots sitting between the H and the F atoms appear to be equally shared between hydrogen and fluorine. However, based on laboratory measurements, we know they are not. When HF is put in an electric field, the molecules orient as shown in Figure 9.6 ▶. From this observation, we know that the hydrogen side of the molecule must have a slight positive charge and the fluorine side of the molecule must have a slight negative charge. We represent this partial separation of charge as follows:

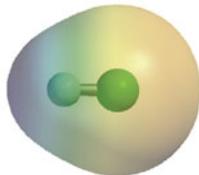
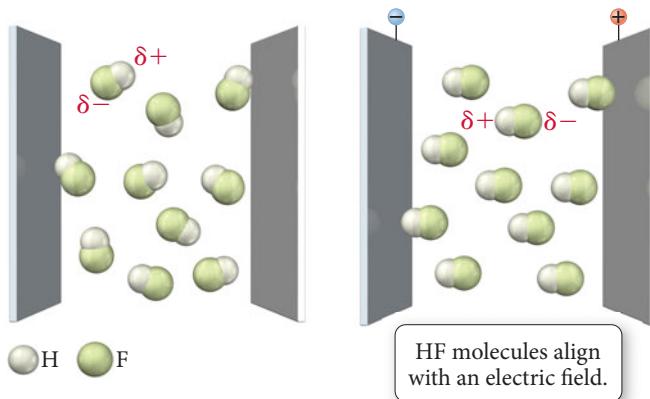


The red arrow on the left, with a positive sign on the tail, indicates that the left side of the molecule has a partial positive charge and that the right side of the molecule (the side the arrow is pointing *toward*) has a partial negative charge. Similarly, the  $\delta^+$  (delta plus) represents a partial positive charge and the  $\delta^-$  (delta minus) represents a partial negative charge. Does this make the bond ionic? No. In an ionic bond, the electron is essentially *transferred* from one atom to another. In HF, the electron is *unequally shared*. In other words, even though the Lewis structure of HF portrays the bonding electrons as residing *between* the two atoms, in reality the electron density is greater on the fluorine atom than on the hydrogen atom (Figure 9.7 ▶). The bond is said to be *polar*—having a positive pole and a negative pole. A **polar covalent bond** is intermediate in nature between a pure covalent bond and an ionic bond. In fact, the categories of pure covalent and ionic are really two extremes within a broad continuum. Most covalent bonds between dissimilar atoms are actually *polar covalent*, somewhere between the two extremes.

► FIGURE 9.6 Orientation of Gaseous

### Hydrogen Fluoride in an Electric Field

Because one side of the HF molecule has a slight positive charge and the other side a slight negative charge, the molecules align themselves with an external electric field.



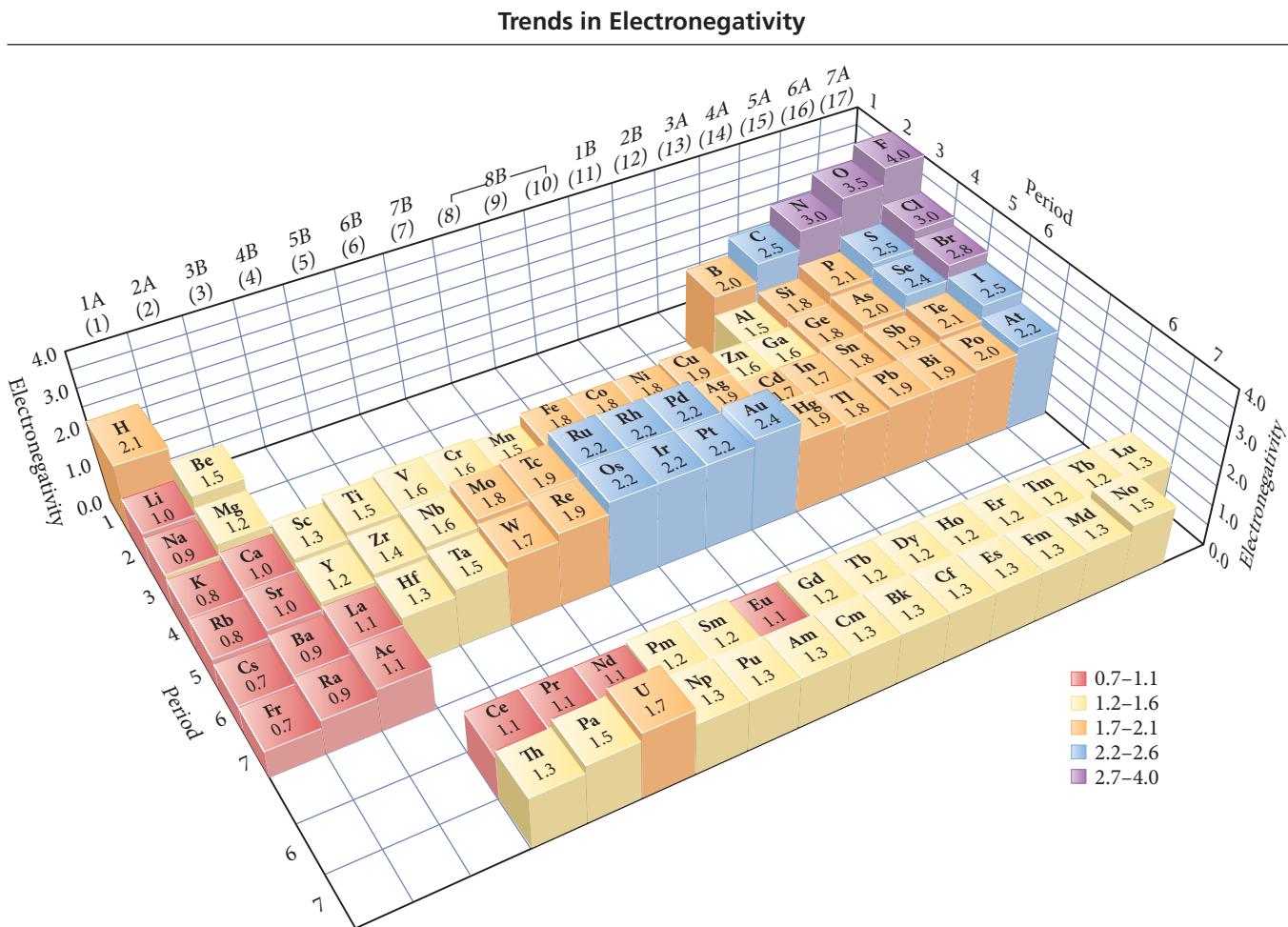
▲ FIGURE 9.7 Electrostatic Potential

Map for the HF Molecule The F end of the molecule, with its partial negative charge, is yellow/pink; the H end, with its partial positive charge, is blue.

## Electronegativity

The ability of an atom to attract electrons to itself in a chemical bond (which results in polar and ionic bonds) is called **electronegativity**. We say that fluorine is more *electronegative* than hydrogen because it takes a greater share of the electron density in HF.

Electronegativity was quantified by the American chemist Linus Pauling in his classic book, *The Nature of the Chemical Bond*. Pauling compared the bond energy—the energy required to break a bond—of a heteronuclear diatomic molecule such as HF with the bond energies of its homonuclear counterparts, in this case H<sub>2</sub> and F<sub>2</sub>. The bond energies of H<sub>2</sub> and F<sub>2</sub> are 436 kJ/mol and 155 kJ/mol, respectively. Pauling reasoned that if the HF bond



▲ FIGURE 9.8 Electronegativities of the Elements Electronegativity generally increases as we move across a row in the periodic table and decreases as we move down a column.

were purely covalent—that is, if the electrons were shared exactly equally—the bond energy of HF should simply be an average of the bond energies of H<sub>2</sub> and F<sub>2</sub>, which would be 296 kJ/mol. However, the bond energy of HF is experimentally measured to be 565 kJ/mol. Pauling suggested that the additional bond energy was due to the *ionic character* of the bond. Based on many such comparisons of bond energies, and by arbitrarily assigning an electronegativity of 4.0 to fluorine (the most electronegative element on the periodic table), Pauling developed the electronegativity values shown in Figure 9.8 ▲.

For main-group elements, notice the following periodic trends in electronegativity from Figure 9.8:

- Electronegativity generally increases across a period in the periodic table.
- Electronegativity generally decreases down a column in the periodic table.
- Fluorine is the most electronegative element.
- Francium is the least electronegative element (sometimes called the most *electropositive*).

The periodic trends in electronegativity are consistent with other periodic trends we have seen. In general, electronegativity is inversely related to atomic size—the larger the atom, the less ability it has to attract electrons to itself in a chemical bond.

We cover the concept of bond energy in more detail in Section 9.10.

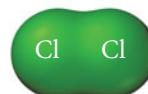
Pauling's “average” bond energy was actually calculated a little bit differently than the normal average shown here. He took the square root of the product of the bond energies of the homonuclear counterparts as the “average.”

### Conceptual Connection 9.3 Periodic Trends in Electronegativity

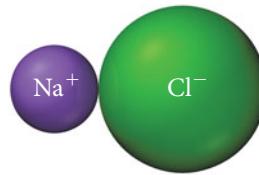
Arrange these elements in order of decreasing electronegativity: P, Na, N, Al.

## Bond Polarity, Dipole Moment, and Percent Ionic Character

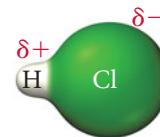
The degree of polarity in a chemical bond depends on the electronegativity difference (sometimes abbreviated  $\Delta\text{EN}$ ) between the two bonding atoms. The greater the electronegativity difference, the more polar the bond. If two atoms with identical electronegativities form a covalent bond, they share the electrons equally, and the bond is purely covalent or *nonpolar*. For example, the chlorine molecule, composed of two chlorine atoms (which necessarily have identical electronegativities), has a covalent bond in which electrons are evenly shared.



If there is a large electronegativity difference between the two atoms in a bond, such as normally occurs between a metal and a nonmetal, the electron from the metal is almost completely transferred to the nonmetal, and the bond is ionic. For example, sodium and chlorine form an ionic bond.



If there is an intermediate electronegativity difference between the two atoms, such as between two different nonmetals, then the bond is polar covalent. For example, HCl has a polar covalent bond.

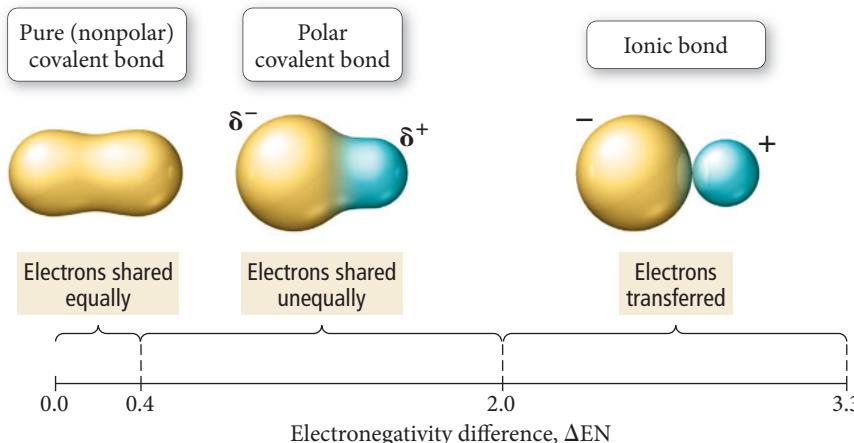


While all attempts to divide the bond polarity continuum into specific regions are necessarily arbitrary, it is helpful to classify bonds as covalent, polar covalent, and ionic, based on the electronegativity difference between the bonding atoms as shown in Table 9.1 and Figure 9.9 ▶.

**TABLE 9.1 The Effect of Electronegativity Difference on Bond Type**

Electronegativity Difference ( $\Delta\text{EN}$ )	Bond Type	Example
Small (0–0.4)	Covalent	$\text{Cl}_2$
Intermediate (0.4–2.0)	Polar covalent	HCl
Large (2.0+)	Ionic	NaCl

### The Continuum of Bond Types



▶ **FIGURE 9.9** Electronegativity Difference ( $\Delta\text{EN}$ ) and Bond Type

We quantify the polarity of a bond by the size of its dipole moment. A **dipole moment** ( $\mu$ ) occurs any time there is a separation of positive and negative charge. The magnitude of a dipole moment created by separating two particles of equal but opposite charges of magnitude  $q$  by a distance  $r$  is given by the equation:

$$\mu = qr \quad [9.1]$$

We can get a sense for the dipole moment of a completely ionic bond by calculating the dipole moment that results from separating a proton and an electron ( $q = 1.6 \times 10^{-19} \text{ C}$ ) by a distance of  $r = 130 \text{ pm}$  (the approximate length of a short chemical bond).

$$\begin{aligned} \mu &= qr \\ &= (1.6 \times 10^{-19} \text{ C})(130 \times 10^{-12} \text{ m}) \\ &= 2.1 \times 10^{-29} \text{ C} \cdot \text{m} \\ &= 6.2 \text{ D} \end{aligned}$$

The debye (D) is the unit commonly used for reporting dipole moments ( $1 \text{ D} = 3.34 \times 10^{-30} \text{ C} \cdot \text{m}$ ). Based on this calculation, we would expect the dipole moment of completely ionic bonds with bond lengths close to 130 pm to be about 6 D. The smaller the magnitude of the charge separation, and the smaller the distance between the charges, the smaller the dipole moment. Table 9.2 lists the dipole moments of several molecules along with the electronegativity differences of their atoms.

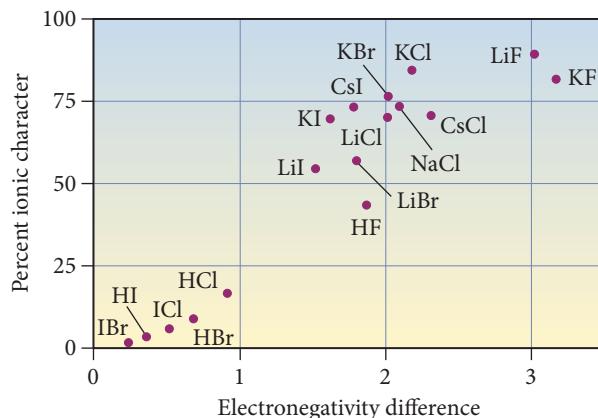
By comparing the *actual* dipole moment of a bond to what the dipole moment would be if the electron were completely transferred from one atom to the other, we can get a sense of the degree to which the electron is transferred (or the degree to which the bond is ionic). A quantity called the **percent ionic character** is the ratio of a bond's actual dipole moment to the dipole moment it would have if the electron were completely transferred from one atom to the other, multiplied by 100%:

$$\text{Percent ionic character} = \frac{\text{measured dipole moment of bond}}{\text{dipole moment if electron were completely transferred}} \times 100\%$$

For example, suppose a diatomic molecule with a bond length of 130 pm has a dipole moment of 3.5 D. We previously calculated that separating a proton and an electron by 130 pm results in a dipole moment of 6.2 D. Therefore, the percent ionic character of the bond is 56%:

$$\begin{aligned} \text{Percent ionic character} &= \frac{3.5 \text{ D}}{6.2 \text{ D}} \times 100\% \\ &= 56\% \end{aligned}$$

A bond in which an electron is completely transferred from one atom to another would have 100% ionic character (although even the most ionic bonds do not reach this ideal). Figure 9.10 ▶ shows the percent ionic character of a number of diatomic gas-phase molecules plotted against the electronegativity difference between the bonding atoms. As expected, the percent ionic character generally increases as the electronegativity difference increases. However, as we can see, no bond is 100% ionic. In general, bonds with greater than 50% ionic character are referred to as ionic bonds.



**TABLE 9.2 Dipole Moments of Several Molecules in the Gas Phase**

Molecule	$\Delta \text{EN}$	Dipole Moment (D)
$\text{Cl}_2$	0	0
$\text{ClF}$	1.0	0.88
$\text{HF}$	1.9	1.82
$\text{LiF}$	3.0	6.33

**◀ FIGURE 9.10** Percent Ionic Character versus Electronegativity Difference for Some Compounds

### EXAMPLE 9.3 Classifying Bonds as Pure Covalent, Polar Covalent, or Ionic

Determine whether the bond formed between each pair of atoms is covalent, polar covalent, or ionic.

(a) Sr and F

(b) N and Cl

(c) N and O

#### SOLUTION

- (a) In Figure 9.8, find the electronegativity of Sr (1.0) and of F (4.0). The electronegativity difference ( $\Delta\text{EN}$ ) is  $\Delta\text{EN} = 4.0 - 1.0 = 3.0$ . Using Table 9.1, classify this bond as ionic.
- (b) In Figure 9.8, find the electronegativity of N (3.0) and of Cl (3.0). The electronegativity difference ( $\Delta\text{EN}$ ) is  $\Delta\text{EN} = 3.0 - 3.0 = 0$ . Using Table 9.1, classify this bond as covalent.
- (c) In Figure 9.8, find the electronegativity of N (3.0) and of O (3.5). The electronegativity difference ( $\Delta\text{EN}$ ) is  $\Delta\text{EN} = 3.5 - 3.0 = 0.5$ . Using Table 9.1, classify this bond as polar covalent.

#### FOR PRACTICE 9.3

Determine whether the bond formed between each pair of atoms is pure covalent, polar covalent, or ionic.

(a) I and I

(b) Cs and Br

(c) P and O



### Conceptual Connection 9.4 Percent Ionic Character

The HCl(*g*) molecule has a bond length of 127 pm and a dipole moment of 1.08 D. Without doing detailed calculations, determine the best estimate for its percent ionic character.

(a) 5%

(b) 15%

(c) 50%

(d) 80%

## 9.7 Lewis Structures of Molecular Compounds and Polyatomic Ions

We now turn to the basic sequence of steps involved in actually writing Lewis structures for given combinations of atoms.

### Writing Lewis Structures for Molecular Compounds

To write a Lewis structure for a molecular compound, follow these steps:

Often, chemical formulas are written in a way that provides clues to how the atoms are bonded together. For example, CH<sub>3</sub>OH indicates that three hydrogen atoms and the oxygen atom are bonded to the carbon atom, but the fourth hydrogen atom is bonded to the oxygen atom.

There are a few exceptions to this rule, such as diborane (B<sub>2</sub>H<sub>6</sub>), which contains bridging hydrogens, but these are rare and cannot be adequately addressed by the Lewis model.

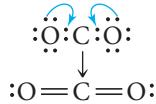
- 1. Write the correct skeletal structure for the molecule.** The Lewis structure of a molecule must have the atoms in the correct positions. For example, you could not write a Lewis structure for water if you started with the hydrogen atoms next to each other and the oxygen atom at the end (H H O). In nature, oxygen is the central atom and the hydrogen atoms are *terminal* (at the ends). The correct skeletal structure is H O H. The only way to determine the skeletal structure of a molecule with absolute certainty is to examine its structure experimentally. However, you can write likely skeletal structures by remembering two guidelines. First, *hydrogen atoms are always terminal*. Hydrogen does not ordinarily occur as a central atom because central atoms must form at least two bonds, and hydrogen, which has only a single valence electron to share and requires only a duet, can form just one. Second, *put the more electronegative elements in terminal positions* and the less electronegative elements (other than hydrogen) in the central position. Later in this section, you will learn how to distinguish between competing skeletal structures by applying the concept of formal charge.
- 2. Calculate the total number of electrons for the Lewis structure by summing the valence electrons of each atom in the molecule.** Remember that the number of valence

electrons for any main-group element is equal to its group number in the periodic table. If you are writing a Lewis structure for a polyatomic ion, you must consider the charge of the ion when calculating the total number of electrons. Add one electron for each negative charge and subtract one electron for each positive charge. Don't worry about which electron comes from which atom—only the total number is important.

- 3. Distribute the electrons among the atoms, giving octets (or duets in the case of hydrogen) to as many atoms as possible.** Begin by placing two electrons between every two atoms. These represent the minimum number of bonding electrons. Then distribute the remaining electrons as lone pairs, first to terminal atoms, and then to the central atom, giving octets (or duets for hydrogen) to as many atoms as possible.
- 4. If any atoms lack an octet, form double or triple bonds as necessary to give them octets.** Do this by moving lone electron pairs from terminal atoms into the bonding region with the central atom.

The left column that follows contains an abbreviated version of the procedure for writing Lewis structures; the center and right columns contain two examples of applying the procedure.

Sometimes distributing all the remaining electrons to the central atom results in more than an octet. This is called an expanded octet and is covered in Section 9.9.

PROCEDURE FOR...	EXAMPLE 9.4 Writing Lewis Structures for Covalent Compounds	EXAMPLE 9.5 Writing Lewis Structures Write the Lewis Structure for NH <sub>3</sub> .
1. Write the correct skeletal structure for the molecule.	<b>SOLUTION</b> Because carbon is the less electronegative atom, put it in the central position. $\text{O} \text{C} \text{O}$	<b>SOLUTION</b> Since hydrogen is always terminal, put nitrogen in the central position. $\text{H} \text{N} \text{H}$ $\text{H}$
2. Calculate the total number of electrons for the Lewis structure by summing the valence electrons of each atom in the molecule.	Total number of electrons for Lewis structure = $\begin{pmatrix} \text{number of} \\ \text{valence} \\ \text{e}^- \text{ for C} \end{pmatrix} + 2 \begin{pmatrix} \text{number of} \\ \text{valence} \\ \text{e}^- \text{ for O} \end{pmatrix}$ $= 4 + 2(6) = 16$	Total number of electrons for Lewis structure = $\begin{pmatrix} \text{number of} \\ \text{valence} \\ \text{e}^- \text{ for N} \end{pmatrix} + 3 \begin{pmatrix} \text{number of} \\ \text{valence} \\ \text{e}^- \text{ for H} \end{pmatrix}$ $= 5 + 3(1) = 8$
3. Distribute the electrons among the atoms, giving octets (or duets for hydrogen) to as many atoms as possible. Begin with the bonding electrons, and then proceed to lone pairs on terminal atoms, and finally to lone pairs on the central atom.	Bonding electrons are first. $\text{O:C:O}$ (4 of 16 electrons used)  Lone pairs on terminal atoms are next. $\ddot{\text{:O}}\text{:}\text{C}\text{:}\dot{\text{O}}\text{:}$ (16 of 16 electrons used)	Bonding electrons are first. $\text{H}:\ddot{\text{N}}:\text{H}$ $\text{H}$ (6 of 8 electrons used) Lone pairs on terminal atoms are next, but none is needed on hydrogen. Lone pairs on central atom are last. $\text{H}—\ddot{\text{N}}—\text{H}$ $\text{H}$ (8 of 8 electrons used)
4. If any atom lacks an octet, form double or triple bonds as necessary to give them octets.	Since carbon lacks an octet, move lone pairs from the oxygen atoms to bonding regions to form double bonds. 	Since all of the atoms have octets (or duets for hydrogen), the Lewis structure for NH <sub>3</sub> is complete as shown in the previous step.
	<b>FOR PRACTICE 9.4</b> Write the Lewis structure for CO.	<b>FOR PRACTICE 9.5</b> Write the Lewis structure for H <sub>2</sub> CO.

## Writing Lewis Structures for Polyatomic Ions

Write Lewis structures for polyatomic ions by following the same procedure, but pay special attention to the charge of the ion when calculating the number of electrons for the Lewis structure. Add one electron for each negative charge and subtract one electron for each positive charge. The Lewis structure for a polyatomic ion is usually written within brackets with the charge of the ion in the upper right-hand corner, outside the bracket.

### EXAMPLE 9.6 Writing Lewis Structures for Polyatomic Ions

Write the Lewis structure for the  $\text{NH}_4^+$  ion.

#### SOLUTION

Begin by writing the skeletal structure. Since hydrogen is always terminal, put the nitrogen atom in the central position.	$\begin{array}{c} \text{H} \\   \\ \text{H} \text{ N } \text{ H} \\   \\ \text{H} \end{array}$
Calculate the total number of electrons for the Lewis structure by summing the number of valence electrons for each atom and subtracting 1 for the $1^+$ charge.	<p>Total number of electrons for Lewis structure  <math>= (\text{number of valence } e^- \text{ in N}) + (\text{number of valence } e^- \text{ in H}) - 1</math>  <math>= 5 + 4(1) - 1</math>  <math>= 8</math></p> <p style="text-align: right;">↑ Subtract 1 <math>e^-</math> to account for <math>1^+</math> charge of ion.</p>
Place two bonding electrons between every two atoms. Since all of the atoms have complete octets, no double bonds are necessary.	$\begin{array}{c} \text{H} \\   \\ \text{H} \text{:} \ddot{\text{N}} \text{:} \text{H} \\   \\ \text{H} \\ \text{(8 of 8 electrons used)} \end{array}$
Lastly, write the Lewis structure in brackets with the charge of the ion in the upper right-hand corner.	$\left[ \begin{array}{c} \text{H} \\   \\ \text{H} \text{—} \text{N} \text{—} \text{H} \\   \\ \text{H} \end{array} \right]^+$

#### FOR PRACTICE 9.6

Write the Lewis structure for the hypochlorite ion,  $\text{ClO}^-$ .

## 9.8 Resonance and Formal Charge

We need two additional concepts to write the best possible Lewis structures for a large number of compounds. The concepts are *resonance*, used when two or more valid Lewis structures can be drawn for the same compound, and *formal charge*, an electron book-keeping system that allows us to discriminate between alternative Lewis structures.

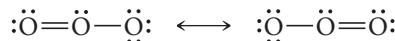
### Resonance

When writing Lewis structures, we may find that, for some molecules, we can write more than one valid Lewis structure. For example, consider writing a Lewis structure for  $\text{O}_3$ . The following two Lewis structures, with the double bond on alternate sides, are equally correct:



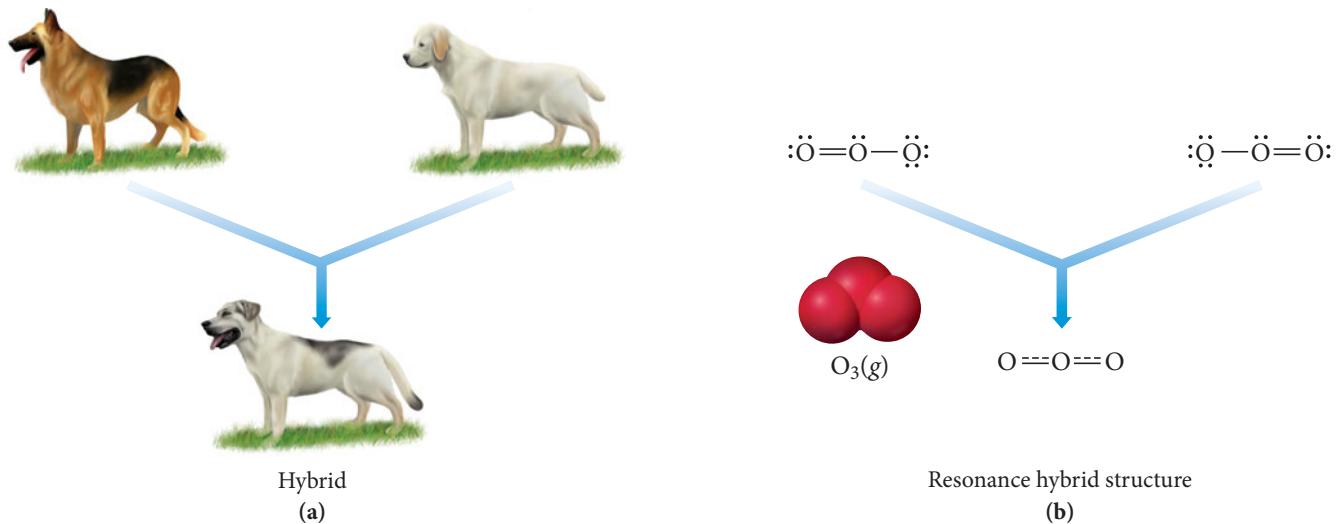
In cases such as this—where there are two or more valid Lewis structures for the same molecule—we find that, in nature, the molecule exists as an *average* of the two Lewis structures. Both of the two Lewis structures for  $\text{O}_3$  predict that  $\text{O}_3$  contains two different

bonds (one double bond and one single bond). However, when we experimentally examine the structure of  $O_3$ , we find that the bonds in the  $O_3$  molecule are equivalent and each is intermediate in strength and length between a double bond and single bond. We account for this by representing the molecule with both structures, called **resonance structures**, with a double-headed arrow between them:



A resonance structure is one of two or more Lewis structures that have the same skeletal formula (the atoms are in the same locations), but different electron arrangements. The actual structure of the molecule is intermediate between the two (or more) resonance structures and is called a **resonance hybrid**. The term *hybrid* comes from breeding and means the offspring of two animals or plants of different varieties or breeds. If we breed a Labrador retriever with a German shepherd, we get a *hybrid* that is intermediate between the two breeds (Figure 9.11(a) ▶). Similarly, the actual structure of a resonance hybrid is intermediate between the two resonance structures (Figure 9.11(b)). The only structure that actually exists is the hybrid structure—the individual resonance structures do not exist and are merely a convenient way to describe the actual structure. Notice that the actual structure of ozone has two equivalent bonds and a bent geometry (we will discuss molecular geometries in Chapter 10).

The concept of resonance is an adaptation of the Lewis model that helps account for the complexity of actual molecules. In the Lewis model, electrons are *localized* either on one atom (lone pair) or between atoms (bonding pair). However, in nature, the electrons in molecules are often *delocalized* over several atoms or bonds. The delocalization of electrons lowers their energy; it stabilizes them (for reasons that are beyond the scope of this book). Resonance depicts two or more structures with the electrons in different places in an attempt to more accurately reflect the delocalization of electrons. In the real hybrid structure, an average between the resonance structures, the electrons are more spread out (or delocalized) than in any of the resonance structures. The resulting stabilization of the electrons (that is, the lowering of their potential energy due to delocalization) is sometimes called *resonance stabilization*. Resonance stabilization makes an important contribution to the stability of many molecules.



▲ FIGURE 9.11 Hybridization Just as the offspring of two different dog breeds is a hybrid that is intermediate between the two breeds (a), the structure of a resonance hybrid is intermediate between that of the contributing resonance structures (b).

### EXAMPLE 9.7 Writing Resonance Structures

Write a Lewis structure for the  $\text{NO}_3^-$  ion. Include resonance structures.

#### SOLUTION

Begin by writing the skeletal structure. Since nitrogen is the least electronegative atom, put it in the central position.	O O N O
Calculate the total number of electrons for the Lewis structure by summing the number of valence electrons for each atom and adding 1 for the $1^-$ charge.	Total number of electrons for Lewis structure $= (\text{number of valence } e^- \text{ in N}) + 3(\text{number of valence } e^- \text{ in O}) + 1$ $= 5 + 3(6) + 1$ $= 24$
Place two bonding electrons between each pair of atoms.	O O:N:O (6 of 24 electrons used)
Distribute the remaining electrons, first to terminal atoms. There are not enough electrons to complete the octet on the central atom.	:O: :O:N:O: (24 of 24 electrons used)
Form a double bond by moving a lone pair from one of the oxygen atoms into the bonding region with nitrogen. Enclose the structure in brackets and include the charge.	$\left[ \begin{array}{c} :\ddot{\text{O}}: \\   \\ :\ddot{\text{O}}:\text{N}:\ddot{\text{O}}: \end{array} \right]^-$ <p style="text-align: center;">or</p> $\left[ \begin{array}{c} :\ddot{\text{O}}: \\   \\ :\ddot{\text{O}}-\text{N}=\ddot{\text{O}}: \end{array} \right]^-$
Since the double bond can form equally well with any of the three oxygen atoms, write all three structures as resonance structures.  (The actual space filling model of $\text{NO}_3^-$ is shown here for comparison. Note that all three bonds are equal in length.)	$\left[ \begin{array}{c} :\ddot{\text{O}}: \\   \\ :\ddot{\text{O}}-\text{N}=\ddot{\text{O}}: \end{array} \right]^- \longleftrightarrow \left[ \begin{array}{c} :\ddot{\text{O}}: \\   \\ :\ddot{\text{O}}-\text{N}-\ddot{\text{O}}: \end{array} \right]^- \longleftrightarrow \left[ \begin{array}{c} :\ddot{\text{O}}: \\   \\ :\ddot{\text{O}}=\text{N}-\ddot{\text{O}}: \end{array} \right]^-$  <p style="text-align: center;"><math>\text{NO}_3^-</math></p>

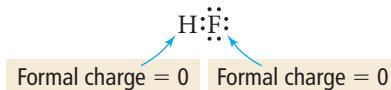
#### FOR PRACTICE 9.7

Write a Lewis structure for the  $\text{NO}_2^-$  ion. Include resonance structures.

In the examples of resonance hybrids that we have examined so far, the contributing structures have been equivalent (or equally valid) Lewis structures. In these cases, the true structure is an equally weighted average of the resonance structures. In some cases, however, we can write resonance structures that are not equivalent. For reasons we cover in the material that follows—such as formal charge—one possible resonance structure may be somewhat better than another. In such cases, the true structure is still an average of the resonance structures, but the better resonance structure contributes more to the true structure. In other words, multiple nonequivalent resonance structures may be weighted differently in their contributions to the true overall structure of a molecule (see Example 9.8).

## Formal Charge

*Formal charge* is a fictitious charge assigned to each atom in a Lewis structure that helps us to distinguish among competing Lewis structures. The **formal charge** of an atom in a Lewis structure is *the charge it would have if all bonding electrons were shared equally between the bonded atoms*. In other words, formal charge is the calculated charge for an atom if we completely ignore the effects of electronegativity. For example, we know that because fluorine is more electronegative than hydrogen, HF has a dipole moment—the hydrogen atom has a slight positive charge and the fluorine atom has a slight negative charge. However, the *formal charges* of hydrogen and fluorine in HF (the calculated charges if we ignore their differences in electronegativity) are both zero.



We can calculate the formal charge on any atom as the difference between the number of valence electrons in the atom and the number of electrons that it “owns” in a Lewis structure. An atom in a Lewis structure can be thought of as “owning” all of its nonbonding electrons and one-half of its bonding electrons.

$$\text{Formal charge} = \text{number of valence electrons} -$$

$$(\text{number of nonbonding electrons} + \frac{1}{2} \text{ number of bonding electrons})$$

So the formal charge of hydrogen in HF is 0:

$$\text{Formal charge} = 1 - [0 + \frac{1}{2}(2)] = 0$$

Number of valence electrons for H    
 Number of electrons that H “owns” in the Lewis structure

Similarly, we calculate the formal charge of fluorine in HF as 0:

$$\text{Formal charge} = 7 - [6 + \frac{1}{2}(2)] = 0$$

Number of valence electrons for F    
 Number of electrons that F “owns” in the Lewis structure

The concept of formal charge is useful because it can help us distinguish between competing skeletal structures or competing resonance structures. In general, these four rules apply:

1. The sum of all formal charges in a neutral molecule must be zero.
2. The sum of all formal charges in an ion must equal the charge of the ion.
3. Small (or zero) formal charges on individual atoms are better than large ones.
4. When formal charge cannot be avoided, negative formal charge should reside on the most electronegative atom.

We can use formal charge to determine which of the competing skeletal structures for hydrogen cyanide shown here is best (or most stable). Notice that both skeletal structures satisfy the octet rule equally. The formal charge of each atom in the structure is calculated below it.

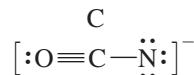
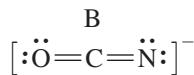
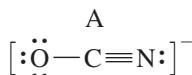
	Structure A				Structure B				
H	—	C	≡	N:	H	—	N	≡	C:
number of valence e <sup>-</sup>	1		4	5	1		5		4
— number of nonbonding e <sup>-</sup>	—0		—0	—2	—0		—0		—2
— $\frac{1}{2}$ (number of bonding e <sup>-</sup> )	— $\frac{1}{2}(2)$		— $\frac{1}{2}(8)$	— $\frac{1}{2}(6)$	— $\frac{1}{2}(2)$		— $\frac{1}{2}(8)$		— $\frac{1}{2}(6)$
<b>Formal charge</b>	<b>0</b>		<b>0</b>	<b>0</b>	<b>0</b>		<b>+1</b>		<b>—1</b>

As required, the sum of the formal charges for each of these structures is zero (as it always must be for neutral molecules). However, structure B has formal charges on both the N atom and the C atom, while structure A has no formal charges on any atom. Furthermore, in structure B, the negative formal charge is not on the most electronegative element (nitrogen is more electronegative than carbon). Consequently, structure A is the best Lewis structure. Since atoms in the middle of a molecule tend to have more bonding electrons and fewer nonbonding electrons, they also tend to have more positive formal charges. Consequently, the best skeletal structure usually has the least electronegative atom in the central position, as we learned in step 1 of our procedure for writing Lewis structures.

Both HCN and HNC exist, but—as predicted by formal charge—HCN is more stable than HNC.

### EXAMPLE 9.8 Assigning Formal Charges

Assign formal charges to each atom in the resonance forms of the cyanate ion ( $\text{OCN}^-$ ). Which resonance form is likely to contribute most to the correct structure of  $\text{OCN}^-$ ?



#### SOLUTION

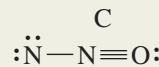
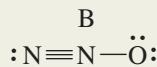
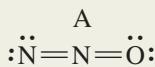
Calculate the formal charge on each atom by finding the number of valence electrons and subtracting the number of nonbonding electrons and one-half the number of bonding electrons.

	A			B			C		
	$[\ddot{\text{O}}-\text{C}\equiv\text{N}:]^-$			$[\ddot{\text{O}}=\text{C}=\ddot{\text{N}}:]^-$			$[\ddot{\text{O}}\equiv\text{C}-\ddot{\text{N}}:]^-$		
Number of valence $e^-$	6	4	5	6	4	5	6	4	5
—number of nonbonding $e^-$	-6	-0	-2	-4	-0	-4	-2	-0	-6
$-\frac{1}{2}$ (number of bond $e^-$ )	-1	-4	-3	-2	-4	-2	-3	-4	-1
Formal charge	-1	0	0	0	0	-1	+1	0	-2

The sum of all formal charges for each structure is  $-1$ , as it should be for a  $1-$  ion. Structures A and B have the least amount of formal charge and are therefore to be preferred over structure C. Structure A is preferable to B because it has the negative formal charge on the more electronegative atom. You therefore expect structure A to make the biggest contribution to the resonance forms of the cyanate ion.

#### FOR PRACTICE 9.8

Assign formal charges to each atom in the resonance forms of  $\text{N}_2\text{O}$ . Which resonance form is likely to contribute most to the correct structure of  $\text{N}_2\text{O}$ ?



#### FOR MORE PRACTICE 9.8

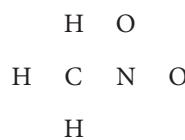
Assign formal charges to each of the atoms in the nitrate ion ( $\text{NO}_3^-$ ). The Lewis structure for the nitrate ion is shown in Example 9.7.

### EXAMPLE 9.9 Drawing Resonance Structures and Assigning Formal Charge for Organic Compounds

Draw the Lewis structure (including resonance structures) for nitromethane ( $\text{CH}_3\text{NO}_2$ ). For each resonance structure, assign formal charges to all atoms that have formal charge.

#### SOLUTION

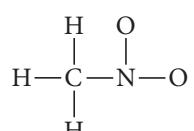
Begin by writing the skeletal structure. For organic compounds, the condensed structural formula (in this case  $\text{CH}_3\text{NO}_2$ ) indicates how the atoms are connected.



Calculate the total number of electrons for the Lewis structure by summing the number of valence electrons for each atom.

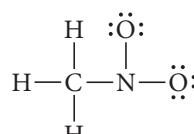
$$\begin{aligned} \text{Total number of electrons for Lewis structure} \\ = & (\# \text{ valence } e^- \text{ in C}) + 3(\# \text{ valence } e^- \text{ in H}) + (\# \text{ valence } e^- \text{ in N}) \\ & + 2(\# \text{ valence } e^- \text{ in O}) \\ = & 4 + 3(1) + 5 + 2(6) \\ = & 24 \end{aligned}$$

Place a dash between each pair of atoms to indicate a bond. Each dash counts for two electrons.



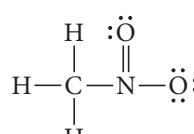
(12 of 24 electrons used)

Distribute the remaining electrons, first to terminal atoms then to interior atoms.

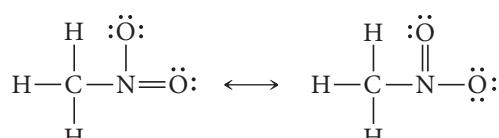


(24 of 24 electrons used)

If there are not enough electrons to complete the octets on the interior atoms, form double bonds by moving lone pair electrons from terminal atoms into the bonding region with interior atoms.

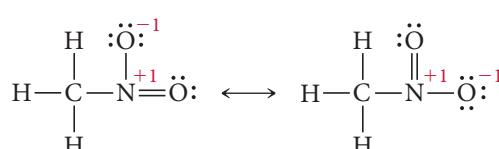


Draw any necessary resonance structures by moving only electron dots. (In this case, you can form a double bond between the nitrogen atom and the other oxygen atom.)



Assign formal charges (FC) to each atom.

$$\text{FC} = \# \text{ valence } e^- - (\# \text{ nonbonding } e^- + \frac{1}{2} \# \text{ bonding } e^-)$$



Carbon, hydrogen, and the doubly-bonded oxygen atoms have no formal charge. Nitrogen has a +1 formal charge [ $5 - \frac{1}{2}(8)$ ] and the singly bonded oxygen atom in each resonance structure has a -1 formal charge [ $6 - (6 + \frac{1}{2}(2))$ ].

#### FOR PRACTICE 9.9

Draw the Lewis structure (including resonance structures) for diazomethane ( $\text{CH}_2\text{N}_2$ ).

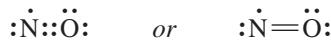
For each resonance structure, assign formal charges to all atoms that have formal charge.

## 9.9 Exceptions to the Octet Rule: Odd-Electron Species, Incomplete Octets, and Expanded Octets

The octet rule in the Lewis model has some exceptions, which we examine in this section of the chapter. They include (1) *odd-electron species*, molecules or ions with an odd number of electrons; (2) *incomplete octets*, molecules or ions with *fewer than eight electrons* around an atom; and (3) *expanded octets*, molecules or ions with *more than eight electrons* around an atom.

### Odd-Electron Species

Molecules and ions with an odd number of electrons in their Lewis structures are called **free radicals** (or simply *radicals*). For example, nitrogen monoxide—a pollutant found in motor vehicle exhaust—has 11 electrons. If we try to write a Lewis structure for nitrogen monoxide, we can't achieve octets for both atoms:



The nitrogen atom does not have an octet, so this Lewis structure does not satisfy the octet rule. Yet, nitrogen monoxide exists, especially in polluted air. Why? As with any simple theory, the Lewis model is not sophisticated enough to handle every single case. It is impossible to write good Lewis structures for free radicals, nevertheless, some of these molecules exist in nature. Perhaps it is a testament to the Lewis model, however, that *relatively few* such molecules exist and that, in general, they tend to be somewhat unstable and reactive. NO, for example, reacts with oxygen in the air to form NO<sub>2</sub>, another odd-electron molecule represented with the following 17-electron resonance structures:



In turn, NO<sub>2</sub> reacts with water to form nitric acid (a component of acid rain) and also reacts with other atmospheric pollutants to form peroxyacetyl nitrate (PAN), an active component of photochemical smog. For free radicals, such as NO and NO<sub>2</sub>, we simply write the best Lewis structure that we can.

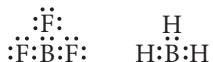
### Conceptual Connection 9.5 Odd-Electron Species

Which molecule would you expect to be a free radical?

- (a) CO      (b) CO<sub>2</sub>      (c) N<sub>2</sub>O      (d) NO<sub>2</sub>

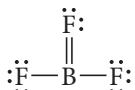
### Incomplete Octets

Another significant exception to the octet rule involves those elements that tend to form *incomplete octets*. The most important of these is boron, which forms compounds with only six electrons around B, rather than eight. For example, BF<sub>3</sub> and BH<sub>3</sub> lack an octet for B.



Beryllium compounds, such as BeH<sub>2</sub>, also have incomplete octets.

You might be wondering why we don't just form double bonds to increase the number of electrons around B. For BH<sub>3</sub>, of course, we can't, because there are no additional electrons to move into the bonding region. For BF<sub>3</sub>, however, we could attempt to give B an octet by moving a lone pair from an F atom into the bonding region with B.



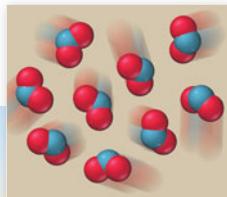
**The unpaired electron in nitrogen monoxide is put on the nitrogen rather than the oxygen in order to minimize formal charges.**



## Chemistry in the Environment

### Free Radicals and the Atmospheric Vacuum Cleaner

Free radicals play a key role in much of the chemistry of the atmosphere. The free radical that is most important to atmospheric reactions is the hydroxyl radical:

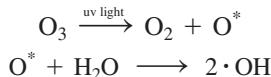


▲  $\text{NO}_2(g)$  is a pollutant found in urban air.

Many free radical structures are abbreviated by writing a single dot with the formula. Thus, the hydroxyl radical is often abbreviated as:

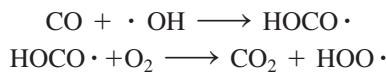


In the atmosphere, the hydroxyl radical forms when excited oxygen atoms—formed from the photodecomposition of ozone—react with water vapor.



The \* next to the O indicates that the oxygen atom has excess energy.

The resulting hydroxyl radical reacts with a wide variety of molecules from both natural sources and from air pollution that are present in the atmosphere. For example, the hydroxyl radical reacts with carbon monoxide, an atmospheric pollutant that we first encountered in Chapter 1, in the following two-step process:

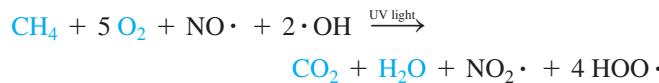


We can see from this reaction that the hydroxyl radical converts toxic CO into relatively nontoxic  $\text{CO}_2$ .

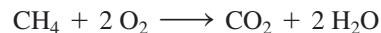
The  $\text{HOO}\cdot$  free radical generated by the second reaction is converted back into the hydroxyl radical when it reacts with other atmospheric substances, and the process repeats itself. Therefore, a single hydroxyl radical can convert a lot of CO into  $\text{CO}_2$ .

Do you ever wonder what happens to the hydrocarbons you accidentally spill when filling your car's gas tank or to the

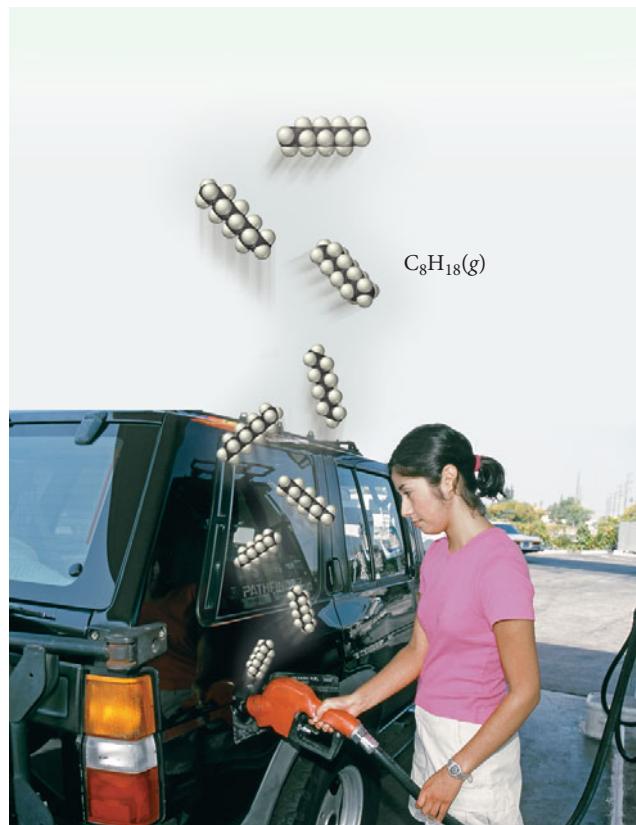
natural gas that is released into the atmosphere as you light your kitchen stove? Hydrocarbons released into the atmosphere are converted to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in a series of steps initiated by the hydroxyl free radical. Consider the following representative reaction of methane, the main hydrocarbon in natural gas:



Notice the similarity between this reaction and the direct combustion (or burning) of methane:



As you can see, the free radical reaction initiates a slow “burning” of  $\text{CH}_4$  in a series of steps that produce carbon dioxide and water and some additional free radicals. The hydroxyl radical initiates similar reactions with other pollutants as well as undesirable naturally occurring atmospheric gases. Without the hydroxyl free radical—sometimes called *the atmospheric vacuum cleaner*—our atmosphere would be a much dirtier place.

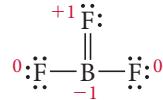


▲ Hydrocarbons such as octane evaporate into the atmosphere when a motor vehicle is fueled. What happens to them?

#### Question

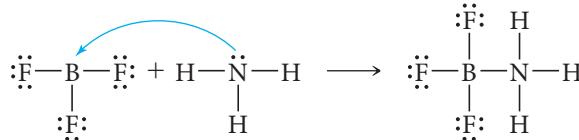
Draw the best possible Lewis structures for the free radicals important in atmospheric chemistry:  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{HOO}\cdot$ ,  $\text{OH}$ ,  $\text{CH}_3\cdot$

This Lewis structure has octets for all atoms, including boron. However, when we assign formal charges to this structure, we get a negative formal charge on B and a positive formal charge on F:



The positive formal charge on fluorine—the most electronegative element in the periodic table—makes this an unfavorable structure. This leaves us with some questions. Do we complete the octet on B at the expense of giving fluorine a positive formal charge? Or do we leave B without an octet in order to avoid the positive formal charge on fluorine? The answers to these kinds of questions are not always clear because we are pushing the limits of the Lewis model. In the case of boron, we usually accept the incomplete octet as the better Lewis structure. However, doing so does not rule out the possibility that the doubly bonded Lewis structure might be a minor contributing resonance structure. The ultimate answers to these kinds of questions must be determined from experiments. Experimental measurements of the B—F bond length in  $\text{BF}_3$  suggest that the bond may be slightly shorter than expected for a single B—F bond, indicating that it may indeed have a small amount of double-bond character.

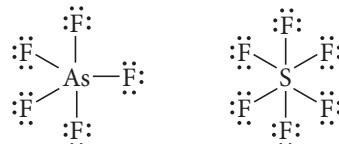
$\text{BF}_3$  can complete its octet in another way—via a chemical reaction. The Lewis model predicts that  $\text{BF}_3$  might react in ways that would complete its octet, and indeed it does. For example,  $\text{BF}_3$  reacts with  $\text{NH}_3$  as follows:



The product has complete octets for all atoms in the structure.

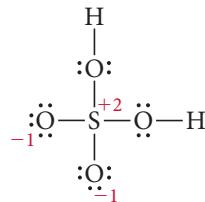
## Expanded Octets

Elements in the third row of the periodic table and beyond often exhibit *expanded octets* of up to 12 (and occasionally 14) electrons. Consider the Lewis structures of arsenic pentafluoride and sulfur hexafluoride.



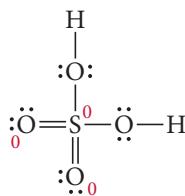
In  $\text{AsF}_5$  arsenic has an expanded octet of 10 electrons, and in  $\text{SF}_6$  sulfur has an expanded octet of 12 electrons. Both of these compounds exist and are stable. In third-period elements and beyond, 10 and 12-electron expanded octets are common because the *d* orbitals in these elements are energetically accessible (they are not much higher in energy than the orbitals occupied by the valence electrons) and can accommodate the extra electrons (see Section 8.3). Expanded octets *never* occur in second-period elements.

In some Lewis structures, we must decide whether or not to expand an octet in order to lower formal charge. For example, consider the Lewis structure of  $\text{H}_2\text{SO}_4$ :



Notice that both of the oxygen atoms have a  $-1$  formal charge and that sulfur has a  $+2$  formal charge. While this amount of formal charge is acceptable, especially since the

negative formal charge resides on the more electronegative atom, it is possible to eliminate the formal charge by expanding the octet on sulfur:



Which of these two Lewis structures for  $\text{H}_2\text{SO}_4$  is better? Again, the answer is not straightforward. Experiments show that the sulfur–oxygen bond lengths in the two sulfur–oxygen bonds without the hydrogen atoms are shorter than expected for sulfur–oxygen single bonds, indicating that the double-bonded Lewis structure plays an important role in describing the bonding in  $\text{H}_2\text{SO}_4$ . In general, we expand octets in third-row (or beyond) elements in order to lower formal charge. However, we should *never* expand the octets of second-row elements. Second-row elements do not have energetically accessible *d* orbitals and therefore never exhibit expanded octets.

### EXAMPLE 9.10 Writing Lewis Structures for Compounds Having Expanded Octets

Write the Lewis structure for  $\text{XeF}_2$ .

#### SOLUTION

Begin by writing the skeletal structure. Since xenon is the less electronegative atom, put it in the central position.

$\text{F Xe F}$

Calculate the total number of electrons for the Lewis structure by summing the number of valence electrons for each atom.

$$\begin{aligned} \text{Total number of electrons for Lewis structure} &= (\text{number of valence } e^- \text{ in Xe}) + 2(\text{number of valence } e^- \text{ in F}) \\ &= 8 + 2(7) \\ &= 22 \end{aligned}$$

Place two bonding electrons between the atoms of each pair of atoms.

$\text{F:Xe:F}$   
(4 of 22 electrons used)

Distribute the remaining electrons to give octets to as many atoms as possible, beginning with terminal atoms and finishing with the central atom. Arrange additional electrons around the central atom, giving it an expanded octet of up to 12 electrons.

$\begin{array}{c} \cdot\ddot{\text{F}}: \text{Xe} \cdot\ddot{\text{F}}: \\ \cdot\ddot{\text{F}}:\cdot\ddot{\text{F}}: \\ \text{(16 of 22 electrons used)} \end{array}$   
 $\begin{array}{c} \cdot\ddot{\text{F}}:\cdot\ddot{\text{F}}: \\ \cdot\ddot{\text{F}}:\text{Xe}:\cdot\ddot{\text{F}}: \text{ or } \cdot\ddot{\text{F}}:-\text{Xe}-:\ddot{\text{F}}: \\ \text{(22 of 22 electrons used)} \end{array}$

#### FOR PRACTICE 9.10

Write the Lewis structure for  $\text{XeF}_4$ .

#### FOR MORE PRACTICE 9.10

Write the Lewis structure for  $\text{H}_3\text{PO}_4$ . If necessary, expand the octet on any appropriate atoms to lower formal charge.

### Conceptual Connection 9.6 Expanded Octets

Which molecule could have an expanded octet?

- (a)  $\text{H}_2\text{CO}_3$       (b)  $\text{H}_3\text{PO}_4$       (c)  $\text{HNO}_2$

## 9.10 Bond Energies and Bond Lengths

In Chapter 6, we discussed how to calculate the standard enthalpy change for a chemical reaction ( $\Delta H^\circ_{\text{rxn}}$ ) from tabulated standard enthalpies of formation. However, sometimes we may not easily find standard enthalpies of formation for all of the reactants and

products of a reaction. In such cases, we can use individual *bond energies* to estimate enthalpy changes of reaction. In this section, we examine the concept of bond energy and how we can use bond energies to calculate enthalpy changes of reaction. We also look at average bond lengths for a number of commonly encountered bonds.

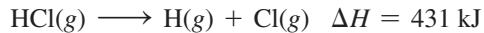
## Bond Energy

Bond energy is also called bond enthalpy or bond dissociation energy.

The **bond energy** of a chemical bond is the energy required to break 1 mole of the bond in the gas phase. For example, the bond energy of the Cl—Cl bond in Cl<sub>2</sub> is 243 kJ/mol.



The bond energy of HCl is 431 kJ/mol.



Bond energies are always positive, because it always takes energy to break a bond. We say that the HCl bond is *stronger* than the Cl<sub>2</sub> bond because it requires more energy to break it. In general, compounds with stronger bonds tend to be more chemically stable, and therefore less chemically reactive, than compounds with weaker bonds. The triple bond in N<sub>2</sub> has a bond energy of 946 kJ/mol.

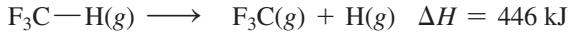


It is a very strong and stable bond, which explains nitrogen's relative inertness.

The bond energy of a particular bond in a polyatomic molecule is a little more difficult to determine because a particular type of bond can have different bond energies in different molecules. For example, consider the C—H bond. In CH<sub>4</sub>, the energy required to break one C—H bond is 438 kJ/mol.



However, the energy required to break a C—H bond in other molecules varies slightly, as shown here:



We can calculate an *average bond energy* for a chemical bond, which is an average of the bond energies for that bond in a large number of compounds. For the limited number of compounds listed, we calculate an average C—H bond energy of 422 kJ/mol. Table 9.3 lists average bond energies for a number of common chemical bonds averaged over a large number of compounds. Notice that the C—H bond energy listed is 414 kJ/mol, which is not too different from the value we calculated from our limited number of compounds. Notice also that bond energies depend, not only on the kind of atoms involved in the bond, but also on the type of bond: single, double, or triple. In general, for a given pair of atoms, triple bonds are stronger than double bonds, which are, in turn, stronger than single bonds. For example, consider the bond energies of carbon–carbon triple, double, and single bonds listed in Table 9.3 (middle of left column).

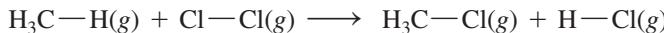
**TABLE 9.3 Average Bond Energies**

Bond	Bond Energy (kJ/mol)	Bond	Bond Energy (kJ/mol)	Bond	Bond Energy (kJ/mol)
H—H	436	N—N	163	Br—F	237
H—C	414	N=N	418	Br—Cl	218
H—N	389	N≡N	946	Br—Br	193
H—O	464	N—O	222	I—Cl	208
H—S	368	N=O	590	I—Br	175
H—F	565	N—F	272	I—I	151
H—Cl	431	N—Cl	200	Si—H	323
H—Br	364	N—Br	243	Si—Si	226
H—I	297	N—I	159	Si—C	301
C—C	347	O—O	142	S—O	265
C=C	611	O=O	498	Si=O	368
C≡C	837	O—F	190	S=O	523
C—N	305	O—Cl	203	Si—Cl	464
C=N	615	O—I	234	S=S	418
C≡N	891	F—F	159	S—F	327
C—O	360	Cl—F	253	S—Cl	253
C=O	736*	Cl—Cl	243	S—Br	218
C≡O	1072			S—S	266
C—Cl	339				

\*799 in CO<sub>2</sub>.

## Using Average Bond Energies to Estimate Enthalpy Changes for Reactions

We can use average bond energies to *estimate* the enthalpy change of a reaction. For example, consider the reaction between methane and chlorine:



We can imagine this reaction occurring by the breaking of a C—H bond and a Cl—Cl bond and the forming of a C—Cl bond and an H—Cl bond. We know that when bonds break, the process is endothermic (positive bond energy) and when bonds form, the process is exothermic (negative bond energy). So we can calculate the overall enthalpy change as a sum of the enthalpy changes associated with breaking the required bonds in the reactants and forming the required bonds in the products, as shown in Figure 9.12 ▼.



Bonds Broken		Bonds Formed	
C—H break	+414 kJ	C—Cl form	-339 kJ
Cl—Cl break	+243 kJ	H—Cl form	-431 kJ
<i>Sum (<math>\Sigma</math>) ΔH's bonds broken: +657 kJ</i>		<i>Sum (<math>\Sigma</math>) ΔH's bonds formed: -770 kJ</i>	

$$\begin{aligned}\Delta H_{rxn} &= \Sigma(\Delta H's \text{ bonds broken}) + \Sigma(\Delta H's \text{ bonds formed}) \\ &= +657 \text{ kJ} - 770 \text{ kJ} \\ &= -113 \text{ kJ}\end{aligned}$$

We find that  $\Delta H_{rxn} = -113 \text{ kJ}$ . Calculating  $\Delta H^\circ_{rxn}$  from tabulated enthalpies of formation—as we learned in Chapter 6—gives  $\Delta H^\circ_{rxn} = -101 \text{ kJ}$ , fairly close to the value we obtained from average bond energies. In general, we can calculate  $\Delta H_{rxn}$  from average bond energies by summing the changes in enthalpy for all of the bonds that are broken and adding the sum of the enthalpy changes for all of the bonds that are formed. Remember that  $\Delta H$  is positive for breaking bonds and negative for forming them:

$$\Delta H_{rxn} = \underbrace{\sum(\Delta H's \text{ bonds broken})}_{\text{Positive}} + \underbrace{\sum(\Delta H's \text{ bonds formed})}_{\text{Negative}}$$

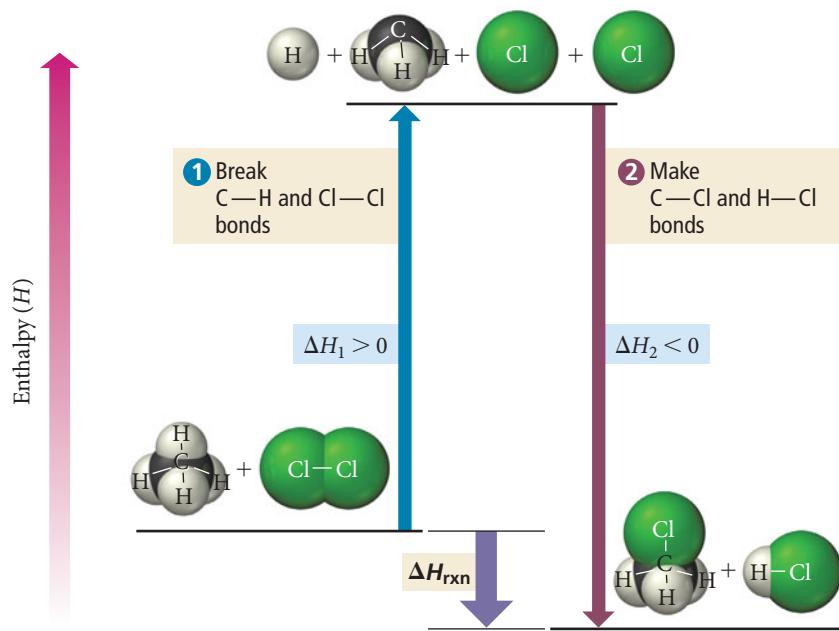
As you can see from the equation:

- A reaction is *exothermic* when weak bonds break and strong bonds form.
- A reaction is *endothermic* when strong bonds break and weak bonds form.

Scientists sometimes say that “energy is stored in chemical bonds or in a chemical compound,” which may make it sound as if breaking the bonds in the compound releases energy. For example, in biology we often hear that energy is stored in glucose or in ATP. However, *breaking a chemical bond always requires energy*. When we say that energy is stored in a compound, or that a compound is energy rich, we mean that the compound can undergo a reaction in which weak bonds break and strong bonds form, thereby releasing energy in the overall process. However, *it is always the forming of chemical bonds that releases energy*.

▼ FIGURE 9.12 Estimating  $\Delta H_{rxn}$  from Bond Energies We can approximate the enthalpy change of a reaction by summing up the enthalpy changes involved in breaking old bonds and forming new ones.

### Estimating the Enthalpy Change of a Reaction from Bond Energies



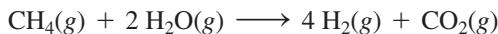
**Conceptual Connection 9.7**
**Bond Energies and  $\Delta H_{rxn}$** 

The reaction between hydrogen and oxygen to form water is highly exothermic. Which statement is true of the energies of the bonds that break and form during the reaction?

- The energy needed to break the required bonds is greater than the energy released when the new bonds form.
- The energy needed to break the required bonds is less than the energy released when the new bonds form.
- The energy needed to break the required bonds is about the same as the energy released when the new bonds form.

**EXAMPLE 9.11 Calculating  $\Delta H_{rxn}$  from Bond Energies**

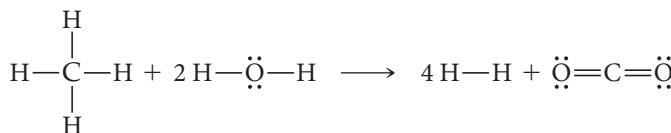

Hydrogen gas, a potential fuel, can be made by the reaction of methane gas and steam.



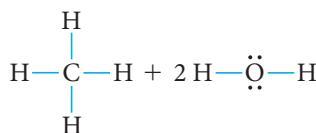
Use bond energies to calculate  $\Delta H_{rxn}$  for this reaction.

**SOLUTION**

Begin by rewriting the reaction using the Lewis structures of the molecules involved.

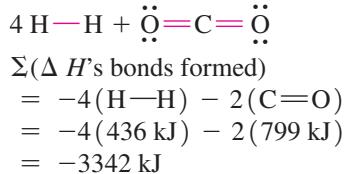


Determine which bonds are broken in the reaction and sum the bond energies of these.



$$\begin{aligned} \Sigma(\Delta H's \text{ bonds broken}) &= 4(\text{C-H}) + 4(\text{O-H}) \\ &= 4(414 \text{ kJ}) + 4(464 \text{ kJ}) \\ &= 3512 \text{ kJ} \end{aligned}$$

Determine which bonds are formed in the reaction and sum the negatives of their bond energies.



Find  $\Delta H_{rxn}$  by summing the results of the previous two steps.

$$\begin{aligned} \Delta H_{rxn} &= \Sigma(\Delta H's \text{ bonds broken}) + \Sigma(\Delta H's \text{ bonds formed}) \\ &= 3512 - 3342 \\ &= 1.70 \times 10^2 \text{ kJ} \end{aligned}$$

**FOR PRACTICE 9.11**

Another potential future fuel is methanol ( $\text{CH}_3\text{OH}$ ). Write a balanced equation for the combustion of gaseous methanol and use bond energies to calculate the enthalpy of combustion of methanol in  $\text{kJ/mol}$ .

**FOR MORE PRACTICE 9.11**

Use bond energies to calculate  $\Delta H_{rxn}$  for this reaction:  $\text{N}_2(g) + 3 \text{H}_2(g) \longrightarrow 2 \text{NH}_3(g)$ .

**Bond Lengths**

Just as we can tabulate average bond energies, which represent the average energy of a bond between two particular atoms in a large number of compounds, we can tabulate average bond lengths (Table 9.4). The average **bond length** represents the average

**TABLE 9.4 Average Bond Lengths**

Bond	Bond Length (pm)	Bond	Bond Length (pm)	Bond	Bond Length (pm)
H—H	74	C—C	154	N—N	145
H—C	110	C=C	134	N=N	123
H—N	100	C≡C	120	N≡N	110
H—O	97	C—N	147	N—O	136
H—S	132	C=N	128	N=O	120
H—F	92	C≡N	116	O—O	145
H—Cl	127	C—O	143	O=O	121
H—Br	141	C=O	120	F—F	143
H—I	161	C—Cl	178	Cl—Cl	199
				Br—Br	228
				I—I	266

length of a bond between two particular atoms in a large number of compounds. Like bond energies, bond lengths depend not only on the kind of atoms involved in the bond, but also on the type of bond: single, double, or triple. In general, for a particular pair of atoms, triple bonds are shorter than double bonds, which are in turn shorter than single bonds. For example, consider the bond lengths (shown here with bond strengths) of carbon–carbon triple, double, and single bonds:

Bond	Bond Length (pm)	Bond Strength (kJ/mol)
C≡C	120 pm	837 kJ/mol
C=C	134 pm	611 kJ/mol
C—C	154 pm	347 kJ/mol

Notice that, as the bond gets longer, it also becomes weaker. This relationship between the length of a bond and the strength of a bond does not necessarily hold true for all bonds. Consider the following series of nitrogen–halogen single bonds:

Bond	Bond Length (pm)	Bond Strength (kJ/mol)
N—F	139	272
N—Cl	191	200
N—Br	214	243
N—I	222	159

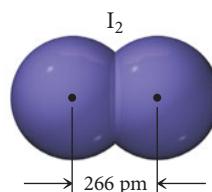
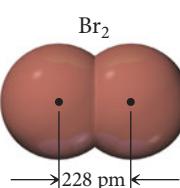
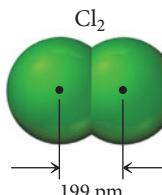
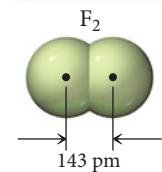
Although the bonds generally get weaker as they get longer, the trend is not a smooth one.

## 9.11 Bonding in Metals: The Electron Sea Model

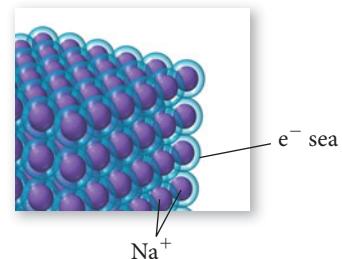
So far, we have developed simple models for bonding between a metal and a nonmetal (ionic bonding) and for bonding between two nonmetals (covalent bonding). We have seen how these models account for and predict the properties of ionic and molecular compounds. The last type of bonding that we examine in this chapter is metallic bonding, which occurs between metals.

As we have already discussed, metals have a tendency to lose electrons, which means that they have relatively low ionization energies. When metal atoms bond together to form a solid, each metal atom donates one or more electrons to an *electron sea*. For example, we can think of sodium metal as an array of positively charged  $\text{Na}^+$  ions immersed in a sea of negatively charged electrons ( $e^-$ ), as shown in Figure 9.13 ►.

Bond Lengths



▲ Bond lengths in the diatomic halogen molecules.



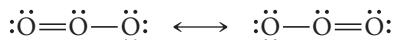
▲ **FIGURE 9.13** The Electron Sea Model for Sodium In this model of metallic bonding,  $\text{Na}^+$  ions are immersed in a “sea” of electrons.



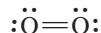
## Chemistry in the Environment

### The Lewis Structure of Ozone

Ozone is a form of oxygen in which three oxygen atoms bond together. Its Lewis structure consists of the following resonance structures:



Compare the Lewis structure of ozone to the Lewis structure of  $\text{O}_2$ :



Since double bonds are stronger and shorter than single bonds,  $\text{O}_2$  must have a stronger bond because it is a double bond.  $\text{O}_3$ , on the other hand, has bonds that are intermediate between single and double, which are weaker bonds. The effects of this are significant. As we discussed in Section 6.10,  $\text{O}_3$  absorbs harmful ultraviolet light entering Earth's atmosphere. Ozone is ideally suited to do this because photons at wavelengths of 280–320 nm (the most harmful components

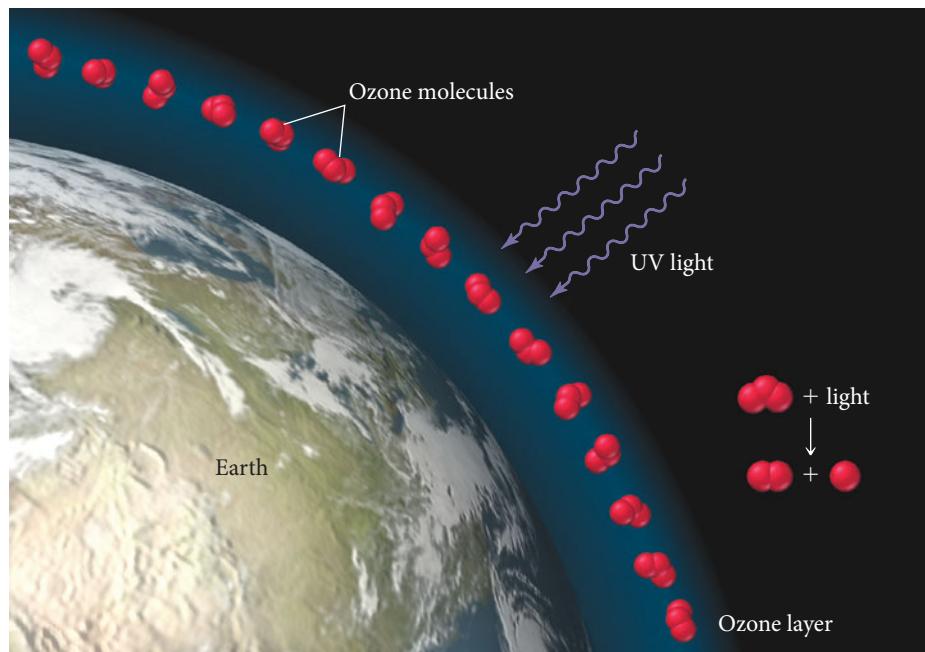
of sunlight) are just strong enough to break the bonds in the  $\text{O}_3$  molecule:



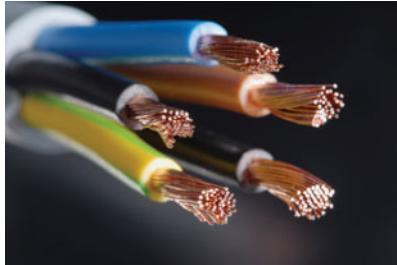
In this process, the photon is absorbed.  $\text{O}_2$  and  $\text{O}$  then recombine to re-form  $\text{O}_3$ , which can in turn absorb more UV light. The same wavelengths of UV light, however, do not have sufficient energy to break the stronger double bond of  $\text{O}_2$ . No other molecules in our atmosphere can do the job that ozone does. Consequently, we should continue, and even strengthen, the ban on ozone-depleting compounds.

### Question

Calculate the average bond energy of one  $\text{O}_3$  bond. What wavelength of light has just the right amount of energy to break this bond?



▲ Ozone protects life on Earth from harmful ultraviolet light.



▲ Copper can easily be drawn into fine strands like those used in household electrical cords.

Each sodium atom donates its one valence electron to the “sea” and becomes a sodium ion. The sodium cations are held together by their attraction to the sea of electrons.

Although this model is simple, it accounts for many of the properties of metals. For example, metals conduct electricity because—in contrast to ionic solids, in which electrons are localized on an ion—the electrons in a metal are free to move. The movement or flow of electrons in response to an electric potential (or voltage) is an electric current. Metals are also excellent conductors of heat, again because of the highly mobile electrons, which help to disperse thermal energy throughout the metal.

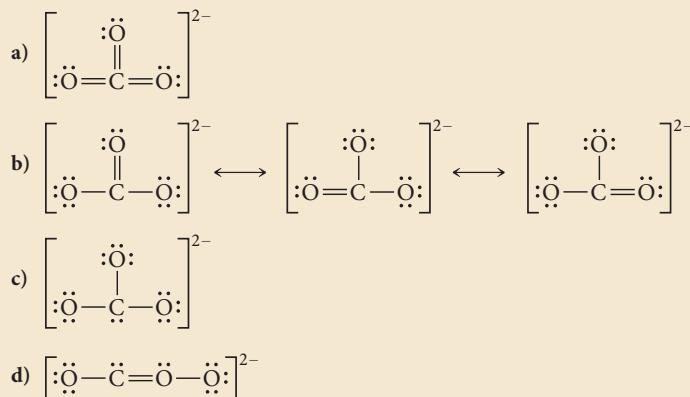
The electron sea model also accounts for the *malleability* of metals (their capacity to be pounded into sheets) and the *ductility* of metals (their capacity to be drawn into wires). Since there are no localized or specific “bonds” in a metal, we can deform it relatively easily by forcing the metal ions to slide past one another. The electron sea easily accommodates deformations by flowing into the new shape.

# CHAPTER IN REVIEW

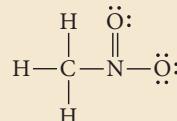
## Self Assessment Quiz

- Q1.** Which pair of elements is most likely to form an ionic bond?
- nitrogen and oxygen
  - carbon and hydrogen
  - sulfur and oxygen
  - calcium and oxygen
- Q2.** Which set of elements is arranged in order of increasing electronegativity?
- $O < S < As < Ge$
  - $Ge < As < S < O$
  - $S < O < As < Ge$
  - $As < O < Ge < S$
- Q3.** Which is the correct Lewis structure for magnesium bromide?
- $2 \text{Mg}^{2+} \left[ :\ddot{\text{Br}}: \right]^-$
  - $\text{Mg}^+ \ddot{\text{Br}}:$
  - $\text{Mg}^{2+} 2 \left[ :\ddot{\text{Br}}: \right]^-$
  - $:\ddot{\text{Mg}}:\ddot{\text{Br}}:$
- Q4.** Which compound is likely to have an incomplete octet?
- $\text{NH}_3$
  - $\text{SO}_3$
  - $\text{N}_2\text{O}$
  - $\text{BH}_3$
- Q5.** Which compound has the highest magnitude of lattice energy?
- $\text{MgS}$
  - $\text{CaS}$
  - $\text{SrS}$
  - $\text{BaS}$
- Q6.** Which set of compounds is arranged in order of increasing magnitude of lattice energy?
- $\text{CsI} < \text{NaCl} < \text{MgS}$
  - $\text{NaCl} < \text{CsI} < \text{MgS}$
  - $\text{MgS} < \text{NaCl} < \text{CsI}$
  - $\text{CsI} < \text{MgS} < \text{NaCl}$
- Q7.** Which pair of atoms forms the most polar bond?
- N and O
  - C and O
  - C and F
  - N and F
- Q8.** Which pair of atoms forms a nonpolar covalent bond?
- C and S
  - C and O
  - B and O
  - Na and Cl
- Q9.** Which is the correct Lewis structure for nitrogen trifluoride?
- $:\ddot{\text{F}}=\ddot{\text{N}}-\ddot{\text{F}}:$   
           $:\ddot{\text{F}}:$
  - $:\ddot{\text{F}}-\ddot{\text{N}}-\ddot{\text{F}}:$   
           $:\ddot{\text{F}}:$
  - $:\ddot{\text{F}}-\ddot{\text{N}}-\ddot{\text{F}}:$   
           $:\ddot{\text{F}}:$
  - $:\ddot{\text{F}}-\ddot{\text{N}}-\ddot{\text{F}}-\ddot{\text{F}}:$

- Q10.** Which is the correct Lewis structure for  $\text{CO}_3^{2-}$ ?

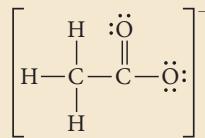


- Q11.** Determine the formal charge of nitrogen in this structure.

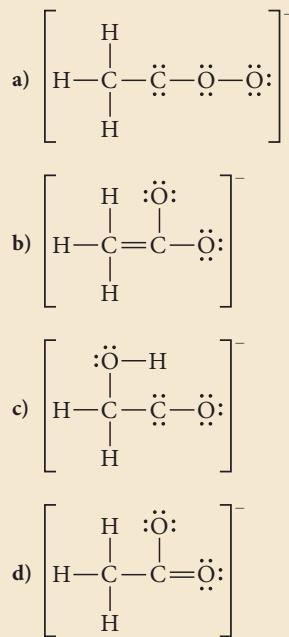


- +1
- +2
- 1
- 2

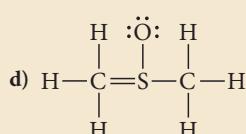
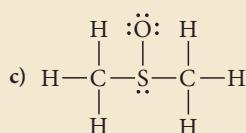
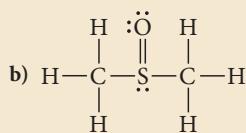
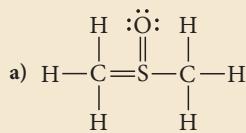
- Q12.** A Lewis structure for the acetate ion is shown here:



Which structure is the best resonance structure for the acetate ion?



- Q13.** Use formal charge to choose the best Lewis structure for  $\text{CH}_3\text{SOCH}_3$ .

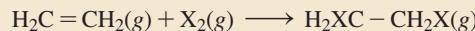


- Q14.** Use bond energies to determine  $\Delta H_{\text{rxn}}$  for the reaction between ethanol and hydrogen chloride.



- a)  $-1549 \text{ kJ}$   
 b)  $1549 \text{ kJ}$   
 c)  $-12 \text{ kJ}$   
 d)  $12 \text{ kJ}$

- Q15.** Consider the halogenation of ethene, where X is a generic halogen:



Use bond energies to determine which halogen produces the most exothermic halogenation reaction with ethene. The C—F, C—Br, and C—I bond energies are 552 kJ/mol, 280 kJ/mol, and 209 kJ/mol, respectively. Find all other necessary bond energies in Table 9.3.

- a) fluorine  
 b) chlorine  
 c) bromine  
 d) iodine

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

## Key Terms

### Section 9.1

Lewis model (382)  
 Lewis electron-dot structures (Lewis structures) (382)

### Section 9.2

ionic bond (382)  
 covalent bond (383)  
 metallic bonding (383)

### Section 9.3

Lewis symbol (384)  
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### Section 9.9

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## Key Concepts

### Bonding Models and AIDS Drugs (9.1)

- Theories that predict how and why atoms bond together are central to chemistry because they explain compound stability and molecule shape.
- Bonding theories have been useful in combating HIV because they help in the design of molecules that bind to the active site of a protein crucial for the development of AIDS.

### Types of Chemical Bonds (9.2)

- We can divide chemical bonds into three general types: ionic bonds, which occur between a metal and a nonmetal; covalent bonds, which occur between two nonmetals; and metallic bonds, which occur within metals.
- In an ionic bond, an electron transfers from the metal to the nonmetal and the resultant ions attract each other by coulombic forces.

- In a covalent bond, nonmetals share electrons that interact with the nuclei of both atoms via coulombic forces, holding the atoms together.
- In a metallic bond, the atoms form a lattice in which each metal loses electrons to an “electron sea.” The attraction of the positively charged metal ions to the electron sea holds the metal together.

### The Lewis Model and Electron Dots (9.3)

- In the Lewis model, chemical bonds are formed when atoms transfer (ionic bonding) or share (covalent bonding) valence electrons to attain noble gas electron configurations.
- The Lewis model represents valence electrons as dots surrounding the symbol for an element. When two or more elements bond together, the dots are transferred or shared so that every atom gets eight dots, an octet (or two dots, a duet, in the case of hydrogen).

### Ionic Lewis Structures and Lattice Energy (9.4)

- In an ionic Lewis structure involving main-group metals, the metal transfers its valence electrons (dots) to the nonmetal.
- The formation of most ionic compounds is exothermic because of lattice energy, the energy released when metal cations and nonmetal anions coalesce to form the solid; the smaller the radius of the ions and the greater their charge, the more exothermic the lattice energy.

### Covalent Lewis Structures, Electronegativity, and Polarity (9.5, 9.6, 9.7)

- In a covalent Lewis structure, neighboring atoms share valence electrons to attain octets (or duets).
- A single shared electron pair constitutes a single bond, while two or three shared pairs constitute double or triple bonds, respectively.
- The shared electrons in a covalent bond are not always *equally* shared; when two dissimilar nonmetals form a covalent bond, the electron density is greater on the more electronegative element. The result is a polar bond, with one element carrying a partial positive charge and the other a partial negative charge.
- Electronegativity—the ability of an atom to attract electrons to itself in chemical bonding—increases as we move to the right across a period in the periodic table and decreases as we move down a column.
- Elements with very dissimilar electronegativities form ionic bonds, those with very similar electronegativities form nonpolar covalent bonds, and those with intermediate electronegativity differences form polar covalent bonds.

---

## Key Equations and Relationships

Dipole Moment ( $\mu$ ): Separation of Two Particles of Equal but Opposite Charges of Magnitude  $q$  by a Distance  $r$  (9.6)

$$\mu = qr$$

Percent Ionic Character (9.6)

Percent ionic character =

$$\frac{\text{measured dipole moment of bond}}{\text{dipole moment if electron were completely transferred}} \times 100\%$$

### Resonance and Formal Charge (9.8)

- Some molecules are best represented not by a single Lewis structure, but by two or more resonance structures. The actual structure of these molecules is a resonance hybrid: a combination or average of the contributing structures.
- The formal charge of an atom in a Lewis structure is the charge the atom would have if all bonding electrons were shared equally between bonding atoms.
- In general, the best Lewis structures will have the fewest atoms with formal charge and any negative formal charge will be on the most electronegative atom.

### Exceptions to the Octet Rule (9.9)

- Although the octet rule is normally used in drawing Lewis structures, some exceptions occur.
- These exceptions include odd-electron species, which necessarily have Lewis structures with only seven electrons around an atom. Such molecules, called free radicals, tend to be unstable and chemically reactive.
- Other exceptions to the octet rule include molecules with incomplete octets—usually totaling 6 electrons (especially important in compounds containing boron)—and molecules with expanded octets—usually 10 or 12 electrons (which can occur in compounds containing elements from the third row of the periodic table and below). Expanded octets never occur in second-period elements.

### Bond Energies and Bond Lengths (9.10)

- The bond energy of a chemical bond is the energy required to break 1 mole of the bond in the gas phase.
- Average bond energies for a number of different bonds are tabulated and can be used to calculate enthalpies of reaction.
- Average bond lengths are also tabulated.
- In general, triple bonds are shorter and stronger than double bonds, which are in turn shorter and stronger than single bonds.

### Bonding in Metals (9.11)

- When metal atoms bond together to form a solid, each metal atom donates one or more electrons to an *electron sea*. The metal cations are then held together by their attraction to the sea of electrons.
- The *electron sea* model accounts for the electrical conductivity, thermal conductivity, malleability, and ductility of metals.

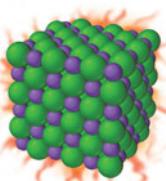
### Formal Charge (9.8)

Formal charge = number of valence electrons – (number of nonbonding electrons +  $\frac{1}{2}$  number of shared electrons)

Enthalpy Change of a Reaction ( $\Delta H_{rxn}$ ): Relationship of Bond Energies (9.10)

$$\Delta H_{rxn} = \Sigma (\Delta H^{\circ}\text{'s bonds broken}) + \Sigma (\Delta H^{\circ}\text{'s bonds formed})$$

## Key Learning Outcomes

Chapter Objectives	Assessment
Predicting Chemical Formulas of an Ionic Compound (9.4)	Example 9.1 For Practice 9.1 Exercises 41–42
Predicting Relative Lattice Energies (9.4) 	Example 9.2 For Practice 9.2 For More Practice 9.2 Exercise 46
Classifying Bonds: Pure Covalent, Polar Covalent, or Ionic (9.6)	Example 9.3 For Practice 9.3 Exercises 55–56
Writing Lewis Structures for Covalent Compounds (9.7)	Example 9.4–9.5 For Practice 9.4–9.5 Exercises 51–52
Writing Lewis Structures for Polyatomic Ions (9.7)	Example 9.6 For Practice 9.6 Exercises 59–64
Writing Resonance Lewis Structures (9.8) 	Example 9.7 For Practice 9.7 Exercises 63–64
Assigning Formal Charges to Assess Competing Resonance Structures (9.8)	Example 9.8 For Practice 9.8 For More Practice 9.8 Exercises 65–66
Drawing Resonance Structures and Assigning Formal Charge for Organic Compounds (9.8)	Example 9.9 For Practice 9.9 Exercises 69–72
Writing Lewis Structures for Compounds Having Expanded Octets (9.9)	Example 9.9 For Practice 9.9 For More Practice 9.9 Exercises 77–78
Calculating $\Delta H_{rxn}$ from Bond Energies (9.10)	Example 9.10 For Practice 9.10 For More Practice 9.10 Exercises 81–83

## EXERCISES

### Review Questions

- Why are bonding theories important? Provide some examples of what bonding theories can predict.
- Why do chemical bonds form? What basic forces are involved in bonding?
- What are the three basic types of chemical bonds? What happens to electrons in the bonding atoms in each type?
- How do you determine how many dots to put around the Lewis symbol of an element?
- Describe the octet rule in the Lewis model.
- According to the Lewis model, what is a chemical bond?
- How do you draw an ionic Lewis structure?
- How can Lewis structures be used to determine the formula of ionic compounds? Give an example.
- What is lattice energy?
- Why is the formation of solid sodium chloride from solid sodium and gaseous chlorine exothermic, even though it takes more energy to form the  $\text{Na}^+$  ion than the amount of energy released upon formation of  $\text{Cl}^-$ ?
- What is the Born–Haber cycle? List each of the steps in the cycle and show how the cycle is used to calculate lattice energy.
- How does lattice energy relate to ionic radii? To ion charge?
- How does the ionic bonding model explain the relatively high melting points of ionic compounds?
- How does the ionic bonding model explain the nonconductivity of ionic solids, and at the same time the conductivity of ionic solutions?

15. Within a covalent Lewis structure, what is the difference between lone pair and bonding pair electrons?
16. In what ways are double and triple covalent bonds different from single covalent bonds?
17. How does the Lewis model for covalent bonding account for why certain combinations of atoms are stable while others are not?
18. How does the Lewis model for covalent bonding account for the relatively low melting and boiling points of molecular compounds (compared to ionic compounds)?
19. What is electronegativity? What are the periodic trends in electronegativity?
20. Explain the difference between a pure covalent bond, a polar covalent bond, and an ionic bond.
21. Explain what is meant by the percent ionic character of a bond. Do any bonds have 100% ionic character?
22. What is a dipole moment?
23. What is the magnitude of the dipole moment formed by separating a proton and an electron by 100 pm? 200 pm?
24. What is the basic procedure for writing a covalent Lewis structure?
25. How do you determine the number of electrons that go into the Lewis structure of a molecule? A polyatomic ion?
26. What are resonance structures? What is a resonance hybrid?
27. Do resonance structures always contribute equally to the overall structure of a molecule? Explain.
28. What is formal charge? How is formal charge calculated? How is it helpful?
29. Why does the octet rule have exceptions? Give the three major categories of exceptions and an example of each.
30. What elements can have expanded octets? What elements should never have expanded octets?
31. What is bond energy? How can you use average bond energies to calculate enthalpies of reaction?
32. Explain the difference between endothermic reactions and exothermic reactions with respect to the bond energies of the bonds broken and formed.
33. What is the electron sea model for bonding in metals?
34. How does the electron sea model explain the conductivity of metals? The malleability and ductility of metals?

## Problems by Topic

### Valence Electrons and Dot Structures

35. Write an electron configuration for N. Then write a Lewis symbol for N and show which electrons from the electron configuration are included in the Lewis symbol.
36. Write an electron configuration for Ne. Then write a Lewis symbol for Ne and show which electrons from the electron configuration are included in the Lewis symbol.
37. Write a Lewis symbol for each atom or ion.
- |       |                  |       |                  |
|-------|------------------|-------|------------------|
| a. Al | b. $\text{Na}^+$ | c. Cl | d. $\text{Cl}^-$ |
|-------|------------------|-------|------------------|
38. Write a Lewis symbol for each atom or ion.
- |                    |       |                     |      |
|--------------------|-------|---------------------|------|
| a. $\text{S}^{2-}$ | b. Mg | c. $\text{Mg}^{2+}$ | d. P |
|--------------------|-------|---------------------|------|

### Ionic Lewis Symbols and Lattice Energy

39. Write the Lewis symbols that represent the ions in each ionic compound.
- |        |        |                    |                         |
|--------|--------|--------------------|-------------------------|
| a. NaF | b. CaO | c. $\text{SrBr}_2$ | d. $\text{K}_2\text{O}$ |
|--------|--------|--------------------|-------------------------|
40. Write the Lewis symbols that represent the ions in each ionic compound.
- |        |                          |                   |        |
|--------|--------------------------|-------------------|--------|
| a. SrO | b. $\text{Li}_2\text{S}$ | c. $\text{CaI}_2$ | d. RbF |
|--------|--------------------------|-------------------|--------|
41. Use Lewis symbols to determine the formula for the compound that forms between each pair of elements.
- |              |              |
|--------------|--------------|
| a. Sr and Se | b. Ba and Cl |
| c. Na and S  | d. Al and O  |
42. Use Lewis symbols to determine the formula for the compound that forms between each pair of elements:
- |             |             |
|-------------|-------------|
| a. Ca and N | b. Mg and I |
| c. Ca and S | d. Cs and F |
43. Explain the trend in the lattice energies of the alkaline earth metal oxides.

Metal Oxide	Lattice Energy (kJ/mol)
MgO	-3795
CaO	-3414
SrO	-3217
BaO	-3029

44. Rubidium iodide has a lattice energy of -617 kJ/mol, while potassium bromide has a lattice energy of -671 kJ/mol. Why is the lattice energy of potassium bromide more exothermic than the lattice energy of rubidium iodide?
45. The lattice energy of CsF is -744 kJ/mol, whereas that of BaO is -3029 kJ/mol. Explain this large difference in lattice energy.
46. Arrange these compounds in order of increasing magnitude of lattice energy: KCl, SrO, RbBr, CaO.
47. Use the Born–Haber cycle and data from Appendix IIB, and Chapter 8 and this chapter to calculate the lattice energy of KCl. ( $\Delta H_{\text{sub}}$  for potassium is 89.0 kJ/mol.)
48. Use the Born–Haber cycle and data from Appendix IIB and Table 9.3 to calculate the lattice energy of CaO. ( $\Delta H_{\text{sub}}$  for calcium is 178 kJ/mol;  $\text{IE}_1$  and  $\text{IE}_2$  for calcium are 590 kJ/mol and 1145 kJ/mol, respectively;  $\text{EA}_1$  and  $\text{EA}_2$  for O are -141 kJ/mol and 744 kJ/mol, respectively.)

### Simple Covalent Lewis Structures, Electronegativity, and Bond Polarity

49. Use covalent Lewis structures to explain why each element (or family of elements) occurs as diatomic molecules.
- |             |                 |
|-------------|-----------------|
| a. hydrogen | b. the halogens |
| c. oxygen   | d. nitrogen     |
50. Use covalent Lewis structures to explain why the compound that forms between nitrogen and hydrogen has the formula  $\text{NH}_3$ . Show why  $\text{NH}_2$  and  $\text{NH}_4$  are not stable.
51. Write the Lewis structure for each molecule.
- |                  |                   |       |                  |
|------------------|-------------------|-------|------------------|
| a. $\text{PH}_3$ | b. $\text{SCl}_2$ | c. HI | d. $\text{CH}_4$ |
|------------------|-------------------|-------|------------------|
52. Write the Lewis structure for each molecule.
- |                  |        |                   |                   |
|------------------|--------|-------------------|-------------------|
| a. $\text{NF}_3$ | b. HBr | c. $\text{SBr}_2$ | d. $\text{CCl}_4$ |
|------------------|--------|-------------------|-------------------|
53. Write the Lewis structure for each molecule.
- |  |   |
|--|---|
| a. $\text{SF}_2$                       | b. $\text{SiH}_4$                           |
| c. $\text{HCOOH}$ (both O bonded to C) | d. $\text{CH}_3\text{SH}$ (C and S central) |

54. Write the Lewis structure for each molecule.

- a.  $\text{CH}_2\text{O}$
- b.  $\text{C}_2\text{Cl}_4$
- c.  $\text{CH}_3\text{NH}_2$
- d.  $\text{CFCl}_3$  (C central)

55. Determine whether a bond between each pair of atoms would be pure covalent, polar covalent, or ionic.

- a. Br and Br
- b. C and Cl
- c. C and S
- d. Sr and O

56. Determine whether a bond between each pair of atoms would be pure covalent, polar covalent, or ionic.

- a. C and N
- b. N and S
- c. K and F
- d. N and N

57. Draw the Lewis structure for CO with an arrow representing the dipole moment. Use Figure 9.10 to estimate the percent ionic character of the CO bond.

58. Draw the Lewis structure for  $\text{BrF}$  with an arrow representing the dipole moment. Use Figure 9.10 to estimate the percent ionic character of the  $\text{BrF}$  bond.

### Covalent Lewis Structures, Resonance, and Formal Charge

59. Write the Lewis structure for each molecule or ion.

- a.  $\text{Cl}_4^-$
- b.  $\text{N}_2\text{O}$
- c.  $\text{SiH}_4$
- d.  $\text{Cl}_2\text{CO}$

60. Write the Lewis structure for each molecule or ion.

- a.  $\text{H}_3\text{COH}$
- b.  $\text{OH}^-$
- c.  $\text{BrO}^-$
- d.  $\text{O}_2^{2-}$

61. Write the Lewis structure for each molecule or ion.

- a.  $\text{N}_2\text{H}_2$
- b.  $\text{N}_2\text{H}_4$
- c.  $\text{C}_2\text{H}_2$
- d.  $\text{C}_2\text{H}_4$

62. Write the Lewis structure for each molecule or ion.

- a.  $\text{H}_3\text{COCH}_3$
- b.  $\text{CN}^-$
- c.  $\text{NO}_2^-$
- d.  $\text{ClO}^-$

63. Write a Lewis structure that obeys the octet rule for each molecule or ion. Include resonance structures if necessary and assign formal charges to each atom.

- a.  $\text{SeO}_2$
- b.  $\text{CO}_3^{2-}$
- c.  $\text{ClO}^-$
- d.  $\text{NO}_2^-$

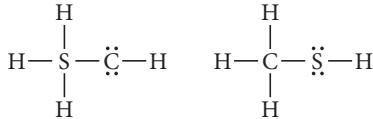
64. Write a Lewis structure that obeys the octet rule for each ion. Include resonance structures if necessary and assign formal charges to each atom.

- a.  $\text{ClO}_3^-$
- b.  $\text{ClO}_4^-$
- c.  $\text{NO}_3^-$
- d.  $\text{NH}_4^+$

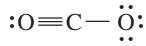
65. Use formal charge to determine which Lewis structure is better:



66. Use formal charge to determine which Lewis structure is better:



67. How important is this resonance structure to the overall structure of carbon dioxide? Explain.

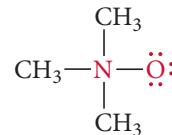


68. In  $\text{N}_2\text{O}$ , nitrogen is the central atom and the oxygen atom is terminal. In  $\text{OF}_2$ , however, oxygen is the central atom. Use formal charges to explain why.

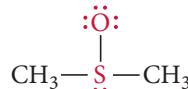
69. Draw the Lewis structure (including resonance structures) for the acetate ion ( $\text{CH}_3\text{COO}^-$ ). For each resonance structure, assign formal charges to all atoms that have formal charge.

70. Draw the Lewis structure (including resonance structures) for methyl azide ( $\text{CH}_3\text{N}_3$ ). For each resonance structure, assign formal charges to all atoms that have formal charge.

71. What are the formal charges of the atoms shown in red?



72. What are the formal charges of the atoms shown in red?



### Odd-Electron Species, Incomplete Octets, and Expanded Octets

73. Write the Lewis structure for each molecule (octet rule not followed).

- a.  $\text{BCl}_3$
- b.  $\text{NO}_2$
- c.  $\text{BH}_3$

74. Write the Lewis structure for each molecule (octet rule not followed).

- a.  $\text{BBr}_3$
- b.  $\text{NO}$
- c.  $\text{ClO}_2$

75. Write the Lewis structure for each ion. Include resonance structures if necessary and assign formal charges to all atoms. If necessary, expand the octet on the central atom to lower formal charge.

- a.  $\text{PO}_4^{3-}$
- b.  $\text{CN}^-$
- c.  $\text{SO}_3^{2-}$
- d.  $\text{ClO}_2^-$

76. Write Lewis structures for each molecule or ion. Include resonance structures if necessary and assign formal charges to all atoms. If necessary, expand the octet on the central atom to lower formal charge.

- a.  $\text{SO}_4^{2-}$
- b.  $\text{HSO}_4^-$
- c.  $\text{SO}_3$
- d.  $\text{BrO}_2^-$

77. Write Lewis structures for each molecule or ion. Use expanded octets as necessary.

- a.  $\text{PF}_5$
- b.  $\text{I}_3^-$
- c.  $\text{SF}_4$
- d.  $\text{GeF}_4$

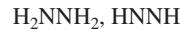
78. Write Lewis structures for each molecule or ion. Use expanded octets as necessary.

- a.  $\text{ClF}_5$
- b.  $\text{AsF}_6^-$
- c.  $\text{Cl}_3\text{PO}$
- d.  $\text{IF}_5$

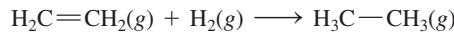
### Bond Energies and Bond Lengths

79. Order these compounds in order of increasing carbon–carbon bond strength and in order of decreasing carbon–carbon bond length:  $\text{HCCH}$ ,  $\text{H}_2\text{CCH}_2$ ,  $\text{H}_3\text{CCH}_3$ .

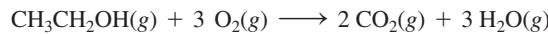
80. Which of these compounds has the stronger nitrogen–nitrogen bond? The shorter nitrogen–nitrogen bond?



81. Hydrogenation reactions are used to add hydrogen across double bonds in hydrocarbons and other organic compounds. Use average bond energies to calculate  $\Delta H_{\text{rxn}}$  for the hydrogenation reaction.



82. Ethanol is a possible fuel. Use average bond energies to calculate  $\Delta H_{\text{rxn}}$  for the combustion of ethanol.



83. Hydrogen, a potential future fuel, can be produced from carbon (from coal) and steam by this reaction:



Use average bond energies to calculate  $\Delta H_{\text{rxn}}$  for the reaction.

84. In the *Chemistry and the Environment* box on free radicals in this chapter, we discussed the importance of the hydroxyl radical in reacting with and eliminating many atmospheric pollutants.

However, the hydroxyl radical does not clean up everything. For example, chlorofluorocarbons—which destroy stratospheric ozone—are not attacked by the hydroxyl radical. Consider the hypothetical reaction by which the hydroxyl radical might react with a chlorofluorocarbon:



Use bond energies to explain why this reaction is improbable.

## Cumulative Problems

85. Write an appropriate Lewis structure for each compound. Make certain to distinguish between ionic and molecular compounds.

- a.  $\text{BI}_3$       b.  $\text{K}_2\text{S}$       c.  $\text{HCFO}$       d.  $\text{PBr}_3$

86. Write an appropriate Lewis structure for each compound. Make certain to distinguish between ionic and molecular compounds.

- a.  $\text{Al}_2\text{O}_3$       b.  $\text{ClF}_5$       c.  $\text{MgI}_2$       d.  $\text{XeO}_4$

87. Each compound contains both ionic and covalent bonds. Write ionic Lewis structures for each of them, including the covalent structure for the ion in brackets. Write resonance structures if necessary.

- a.  $\text{BaCO}_3$       b.  $\text{Ca}(\text{OH})_2$   
c.  $\text{KNO}_3$       d.  $\text{LiIO}$

88. Each compound contains both ionic and covalent bonds. Write ionic Lewis structures for each of them, including the covalent structure for the ion in brackets. Write resonance structures if necessary.

- a.  $\text{RbIO}_2$       b.  $\text{NH}_4\text{Cl}$       c.  $\text{KOH}$       d.  $\text{Sr}(\text{CN})_2$

89. Carbon ring structures are common in organic chemistry. Draw a Lewis structure for each carbon ring structure, including any necessary resonance structures.

- a.  $\text{C}_4\text{H}_8$       b.  $\text{C}_4\text{H}_4$       c.  $\text{C}_6\text{H}_{12}$       d.  $\text{C}_6\text{H}_6$

90. Amino acids are the building blocks of proteins. The simplest amino acid is glycine ( $\text{H}_2\text{NCH}_2\text{COOH}$ ). Draw a Lewis structure for glycine. (Hint: the central atoms in the skeletal structure are nitrogen bonded to carbon, which is bonded to another carbon. The two oxygen atoms are bonded directly to the right-most carbon atom.)

91. Formic acid is responsible for the sting of ant bites. By mass, formic acid is 26.10% C, 4.38% H, and 69.52% O. The molar mass of formic acid is 46.02 g/mol. Find the molecular formula of formic acid and draw its Lewis structure.

92. Diazomethane is a highly poisonous, explosive compound because it readily evolves  $\text{N}_2$ . Diazomethane has the following composition by mass: 28.57% C; 4.80% H; and 66.64% N. The molar mass of diazomethane is 42.04 g/mol. Find the molecular formula of diazomethane, draw its Lewis structure, and assign formal charges to each atom. Why is diazomethane not very stable? Explain.

93. The reaction of  $\text{Fe}_2\text{O}_3(s)$  with  $\text{Al}(s)$  to form  $\text{Al}_2\text{O}_3(s)$  and  $\text{Fe}(s)$  is called the thermite reaction and is highly exothermic. What role does lattice energy play in the exothermicity of the reaction?

94.  $\text{NaCl}$  has a lattice energy of  $-787 \text{ kJ/mol}$ . Consider a hypothetical salt  $\text{XY}$ .  $\text{X}^{3+}$  has the same radius of  $\text{Na}^+$  and  $\text{Y}^{3-}$  has the same radius as  $\text{Cl}^-$ . Estimate the lattice energy of  $\text{XY}$ .

95. Draw the Lewis structure for nitric acid (the hydrogen atom is attached to one of the oxygen atoms). Include all three resonance structures by alternating the double bond among the

three oxygen atoms. Use formal charge to determine which of the resonance structures is most important to the structure of nitric acid.

96. Phosgene ( $\text{Cl}_2\text{CO}$ ) is a poisonous gas used as a chemical weapon during World War I. It is a potential agent for chemical terrorism today. Draw the Lewis structure of phosgene. Include all three resonance forms by alternating the double bond among the three terminal atoms. Which resonance structure is the best?

97. The cyanate ion ( $\text{OCN}^-$ ) and the fulminate ion ( $\text{CNO}^-$ ) share the same three atoms but have vastly different properties. The cyanate ion is stable, while the fulminate ion is unstable and forms explosive compounds. The resonance structures of the cyanate ion were explored in Example 9.8. Draw Lewis structures for the fulminate ion—including possible resonance forms—and use formal charge to explain why the fulminate ion is less stable (and therefore more reactive) than the cyanate ion.

98. Draw the Lewis structure for each organic compound from its condensed structural formula.

- |                               |                              |
|-------------------------------|------------------------------|
| a. $\text{C}_3\text{H}_8$     | b. $\text{CH}_3\text{OCH}_3$ |
| c. $\text{CH}_3\text{COCH}_3$ | d. $\text{CH}_3\text{COOH}$  |
| e. $\text{CH}_3\text{CHO}$    |                              |

99. Draw the Lewis structure for each organic compound from its condensed structural formula.

- |                           |                                      |
|---------------------------|--------------------------------------|
| a. $\text{C}_2\text{H}_4$ | b. $\text{CH}_3\text{NH}_2$          |
| c. $\text{HCHO}$          | d. $\text{CH}_3\text{CH}_2\text{OH}$ |
| e. $\text{HCOOH}$         |                                      |

100. Use Lewis structures to explain why  $\text{Br}_3^-$  and  $\text{I}_3^-$  are stable, while  $\text{F}_3^-$  is not.

101. Draw the Lewis structure for  $\text{HCSNH}_2$ . (The carbon and nitrogen atoms are bonded together and the sulfur atom is bonded to the carbon atom.) Label each bond in the molecule as polar or nonpolar.

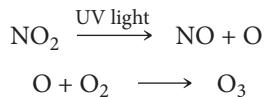
102. Draw the Lewis structure for urea,  $\text{H}_2\text{NCONH}_2$ , one of the compounds responsible for the smell of urine. (The central carbon atom is bonded to both nitrogen atoms and to the oxygen atom.) Does urea contain polar bonds? Which bond in urea is most polar?

103. Some theories of aging suggest that free radicals cause certain diseases and perhaps aging in general. As you know from the Lewis model, such molecules are not chemically stable and will quickly react with other molecules. According to certain theories, free radicals may attack molecules within the cell, such as DNA, changing them and causing cancer or other diseases. Free radicals may also attack molecules on the surfaces of cells, making them appear foreign to the body's immune system. The immune system then attacks the cells and destroys them, weak-

ening the body. Draw Lewis structures for each free radical implicated in this theory of aging.

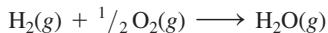
- $\text{O}_2^-$
- $\text{O}^-$
- $\text{OH}$
- $\text{CH}_3\text{OO}$  (unpaired electron on terminal oxygen)

- 104.** Free radicals are important in many environmentally significant reactions (see the *Chemistry in the Environment* box on free radicals in this chapter). For example, photochemical smog—smog that results from the action of sunlight on air pollutants—forms in part by these two steps:



The product of this reaction, ozone, is a pollutant in the lower atmosphere. (Upper atmospheric ozone is a natural part of the atmosphere that protects life on Earth from ultraviolet light.) Ozone is an eye and lung irritant and also accelerates the weathering of rubber products. Rewrite the given reactions using the Lewis structure of each reactant and product. Identify the free radicals.

- 105.** If hydrogen were used as a fuel, it could be burned according to this reaction:



Use average bond energies to calculate  $\Delta H_{\text{rxn}}$  for this reaction and also for the combustion of methane ( $\text{CH}_4$ ). Which fuel yields more energy per mole? Per gram?

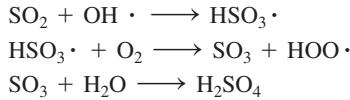
- 106.** Calculate  $\Delta H_{\text{rxn}}$  for the combustion of octane ( $\text{C}_8\text{H}_{18}$ ), a component of gasoline, by using average bond energies and then

calculate it using enthalpies of formation from Appendix II.B. What is the percent difference between your results? Which result would you expect to be more accurate?

- 107.** Draw Lewis structures for each compound.
- $\text{Cl}_2\text{O}_7$  (no Cl—Cl bond)
  - $\text{H}_3\text{PO}_3$  (two OH bonds)
  - $\text{H}_3\text{AsO}_4$
- 108.** The azide ion,  $\text{N}_3^-$ , is a symmetrical ion, all of whose contributing resonance structures have formal charges. Draw three important contributing structures for this ion.
- 109.** List the following gas-phase ion pairs in order of the quantity of energy released when they form from separated gas-phase ions. Start with the pair that releases the least energy.  $\text{Na}^+\text{F}^-$ ,  $\text{Mg}^{2+}\text{F}^-$ ,  $\text{Na}^+\text{O}^{2-}$ ,  $\text{Mg}^{2+}\text{O}^{2-}$ ,  $\text{Al}^{3+}\text{O}^{2-}$ .
- 110.** Calculate  $\Delta H^\circ$  for the reaction  $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \longrightarrow 2 \text{HBr}(\text{g})$  using the bond energy values. The  $\Delta H^\circ$  of  $\text{HBr}(\text{g})$  is not equal to one-half of the value calculated. Account for the difference.
- 111.** The heat of atomization is the heat required to convert a molecule in the gas phase into its constituent atoms in the gas phase. The heat of atomization is used to calculate average bond energies. Without using any tabulated bond energies, calculate the average C—Cl bond energy from the following data: the heat of atomization of  $\text{CH}_4$  is 1660 kJ/mol and of  $\text{CH}_2\text{Cl}_2$  is 1495 kJ/mol.
- 112.** Calculate the heat of atomization (see previous problem) of  $\text{C}_2\text{H}_3\text{Cl}$ , using the average bond energies in Table 9.3.
- 113.** A compound composed of only carbon and hydrogen is 7.743% hydrogen by mass. Propose a Lewis structure for the compound.
- 114.** A compound composed of only carbon and chlorine is 85.5% chlorine by mass. Propose a Lewis structure for the compound.

## Challenge Problems

- 115.** The main component of acid rain ( $\text{H}_2\text{SO}_4$ ) forms from  $\text{SO}_2$  pollutant in the atmosphere via these steps:



Draw the Lewis structure for each of the species in these steps and use bond energies and Hess's law to estimate  $\Delta H_{\text{rxn}}$  for the overall process. (Use 265 kJ/mol for the S—O single bond energy.)

- 116.** A 0.167 g sample of an unknown acid requires 27.8 mL of 0.100 M NaOH to titrate to the equivalence point. Elemental analysis of the acid gives the following percentages by mass: 40.00% C, 6.71% H, 53.29% O. Determine the molecular formula, molar mass, and Lewis structure of the unknown acid.

- 117.** Use the dipole moments of HF and HCl (given at the end of the problem) together with the percent ionic character of each bond (Figure 9.10) to estimate the bond length in each molecule. How well does your estimated bond length agree with the bond length in Table 9.4?

$$\text{HCl } \mu = 1.08 \text{ D}$$

$$\text{HF } \mu = 1.82 \text{ D}$$

- 118.** Use average bond energies together with the standard enthalpy of formation of  $\text{C}(\text{g})$  (718.4 kJ/mol) to estimate the standard enthalpy of formation of gaseous benzene,  $\text{C}_6\text{H}_6(\text{g})$ . (Remember that average bond energies apply to the gas phase only.) Compare the value you obtain using average bond energies to the actual standard enthalpy of formation of gaseous benzene, 82.9 kJ/mol. What does the difference between these two values tell you about the stability of benzene?

- 119.** The standard state of phosphorus at 25°C is  $\text{P}_4$ . This molecule has four equivalent P atoms, no double or triple bonds, and no expanded octets. Draw its Lewis structure.

- 120.** The standard heat of formation of  $\text{CaBr}_2$  is  $-675 \text{ kJ/mol}$ . The first ionization energy of Ca is  $590 \text{ kJ/mol}$  and its second ionization energy is  $1145 \text{ kJ/mol}$ . The heat of sublimation of  $\text{Ca}[\text{Ca}(\text{s}) \longrightarrow \text{Ca}(\text{g})]$  is  $178 \text{ kJ/mol}$ . The bond energy of  $\text{Br}_2$  is  $193 \text{ kJ/mol}$ , the heat of vaporization of  $\text{Br}_2(\text{l})$  is  $31 \text{ kJ/mol}$ , and the electron affinity of Br is  $-325 \text{ kJ/mol}$ . Calculate the lattice energy of  $\text{CaBr}_2$ .

- 121.** The standard heat of formation of  $\text{PI}_3(\text{s})$  is  $-24.7 \text{ kJ/mol}$  and the PI bond energy in this molecule is  $184 \text{ kJ/mol}$ . The standard heat of formation of  $\text{P}(\text{g})$  is  $334 \text{ kJ/mol}$  and that of  $\text{I}_2(\text{g})$  is  $62 \text{ kJ/mol}$ . The  $\text{I}_2$  bond energy is  $151 \text{ kJ/mol}$ . Calculate the heat of sublimation of  $\text{PI}_3[\text{PI}_3(\text{s}) \longrightarrow \text{PI}_3(\text{g})]$ .

122. A compound has the formula C<sub>8</sub>H<sub>8</sub> and does not contain any double or triple bonds. All the carbon atoms are chemically identical and all the hydrogen atoms are chemically identical. Draw the Lewis structure for this molecule.
123. Find the oxidation number of each sulfur in the molecule H<sub>2</sub>S<sub>4</sub>, which has a linear arrangement of its atoms.

124. Ionic solids of the O<sup>-</sup> and O<sup>3-</sup> anions do not exist, while ionic solids of the O<sup>2-</sup> anion are common. Explain.
125. The standard state of sulfur is solid rhombic sulfur. Use the appropriate standard heats of formation given in Appendix II to find the average bond energy of the S = O in SO<sub>2</sub>.

## Conceptual Problems

126. Which statement is true of an endothermic reaction?
- Strong bonds break and weak bonds form.
  - Weak bonds break and strong bonds form.
  - The bonds that break and those that form are of approximately the same strength.
127. When a firecracker explodes, energy is obviously released. The compounds in the firecracker can be viewed as being “energy rich.” What does this mean? Explain the source of the energy in terms of chemical bonds.

128. A fundamental difference between compounds containing ionic bonds and those containing covalent bonds is the existence of molecules. Explain why molecules exist in solid covalent compounds but do not exist in solid ionic compounds.
129. In the very first chapter of this book, we described the scientific approach and put a special emphasis on scientific models or theories. In this chapter, we looked carefully at a model for chemical bonding (the Lewis model). Why is this theory successful? What are some of the limitations of the theory?

## Answers to Conceptual Connections

### Melting Points of Ionic Solids

- 9.1 You would expect MgO to have the higher melting point because, in our bonding model, the magnesium and oxygen ions are held together in a crystalline lattice by charges of 2+ for magnesium and 2- for oxygen. In contrast, the NaCl lattice is held together by charges of 1+ for sodium and 1- for chlorine. The experimentally measured melting points of these compounds are 801 °C for NaCl and 2852 °C for MgO, in accordance with our model.

### Energy and the Octet Rule

- 9.2 The reasons that atoms form bonds are complex. One contributing factor is the lowering of their potential energy. The octet rule is just a handy way to predict the combinations of atoms that will have a lower potential energy when they bond together.

### Periodic Trends in Electronegativity

- 9.3 N > P > Al > Na

### Percent Ionic Character

- 9.4 (b) You are given that the dipole moment of the HCl bond is about 1 D and that the bond length is 127 pm. Previously

we calculated the dipole moment for a 130 pm bond that is 100% ionic to be about 6.2 D. You can therefore estimate the bond's ionic character as  $1/6 \times 100$ , which is closest to 15%.

### Odd-Electron Species

- 9.5 (d) NO<sub>2</sub> because the sum of the valence electrons of its atoms is an odd number.

### Expanded Octets

- 9.6 (b) The only molecule in this group that could have an expanded octet is H<sub>3</sub>PO<sub>4</sub> because phosphorus is a third-period element. Expanded octets *never* occur in second-period elements such as carbon and nitrogen.

### Bond Energies and $\Delta H_{rxn}$

- 9.7 (b) In a highly exothermic reaction, the energy needed to break bonds is less than the energy released when the new bonds form, resulting in a net release of energy.

# 10

## Chemical Bonding II: Molecular Shapes, Valence Bond Theory, and Molecular Orbital Theory

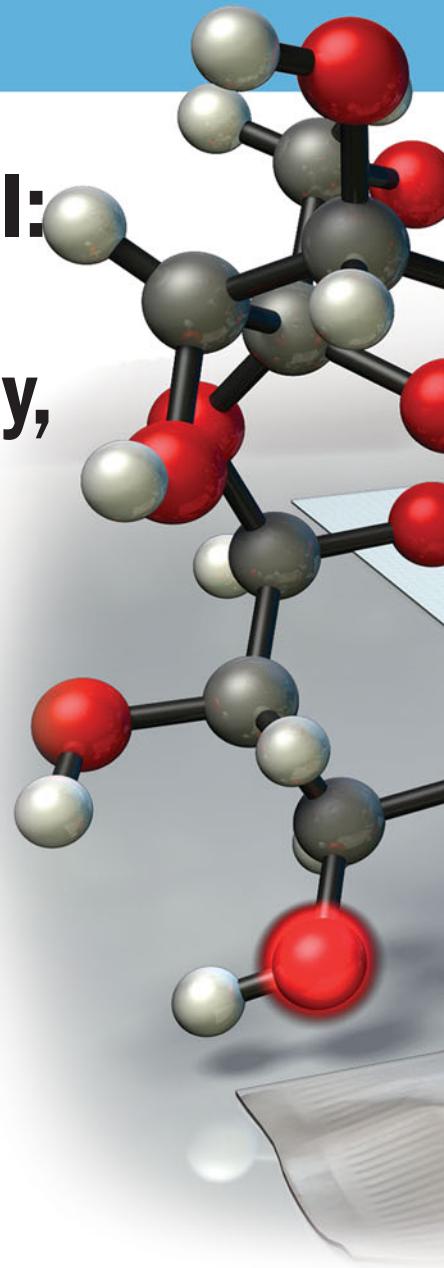
*No theory ever solves all the puzzles with which it is confronted at a given time; nor are the solutions already achieved often perfect.*

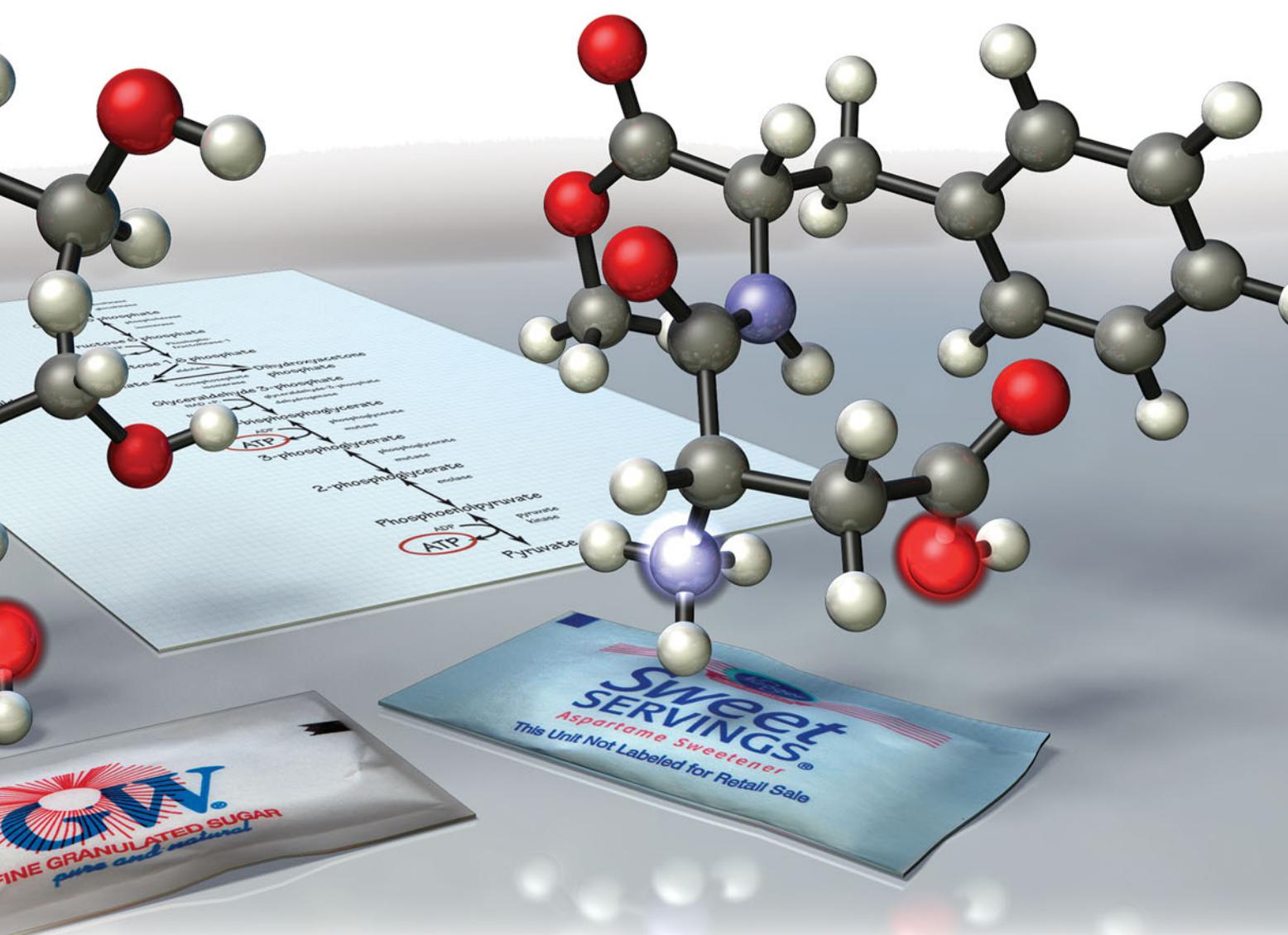
—Thomas Kuhn (1922–1996)

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**Key Learning Outcomes** 473

In Chapter 9, we examined a simple model for chemical bonding called the Lewis model. We saw how this model helps us to explain and predict the combinations of atoms that form stable molecules. When we combine the Lewis model with the idea that valence electron groups repel one another—the basis of an approach known as VSEPR theory—we can predict the general shape of a molecule from its Lewis structure. We address molecular shapes and their importance in the first part of this chapter. We then move on to explore two additional bonding theories—called valence bond theory and molecular orbital theory—that are progressively more sophisticated, but at the cost of being more complex, than the Lewis model. As you work through this chapter, our second on chemical bonding, keep in mind the importance of this topic. In our universe, elements join together to form compounds, and that makes many things possible, including our own existence.

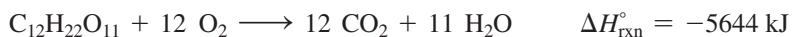




*Similarities in the shape of sucrose and aspartame give both molecules the ability to stimulate a sweet taste sensation.*

## 10.1 Artificial Sweeteners: Fooled by Molecular Shape

Artificial sweeteners, such as aspartame (NutraSweet), taste sweet but have few or no calories. Why? *Because taste and caloric value are independent properties of foods.* The caloric value of a food depends on the amount of energy released when the food is metabolized. For example, sucrose (table sugar) is metabolized by oxidation to carbon dioxide and water:



When your body metabolizes a mole of sucrose, it obtains 5644 kJ of energy. Some artificial sweeteners, such as saccharin, for example, are not metabolized at all—they just pass through the body unchanged—and therefore have no caloric value. Other artificial sweeteners, such as aspartame, are metabolized but have a much lower caloric content (for a given amount of sweetness) than sucrose.

The *taste* of a food, however, is independent of its metabolism. The sensation of taste originates in the tongue, where specialized taste cells act as highly sensitive and specific molecular detectors. These cells can discern sugar molecules from the thousands of different types of molecules present in a mouthful of food. The main factors for this discrimination are the sugar molecule's shape and charge distribution.

The surface of a taste cell contains specialized protein molecules called taste receptors. A particular *tastant*—a molecule that we can taste—fits snuggly into a special pocket (just as a key fits into a lock) on the taste receptor protein called the *active site*. A sugar molecule precisely fits into the active site of the sugar receptor protein called T1r3. When the sugar molecule (the key) enters the active site (the lock), the different subunits of the T1r3 protein split apart. This split causes ion channels in the cell membrane to open, resulting in nerve signal transmission (see Section 8.1). The nerve signal reaches the brain and registers a sweet taste.

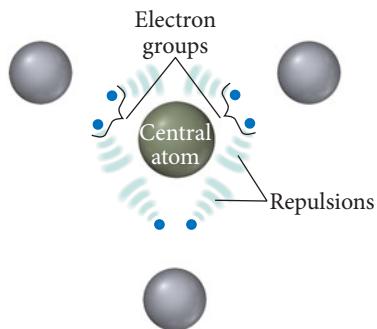
Artificial sweeteners taste sweet because they fit into the receptor pocket that normally binds sucrose. In fact, both aspartame and saccharin bind to the active site in the T1r3 protein more strongly than does sugar! For this reason, artificial sweeteners are “sweeter than sugar.” Aspartame, for example, is 200 times sweeter than sugar, meaning that it takes 200 times as much sugar as aspartame to trigger the same amount of nerve signal transmission from taste cells.

The lock-and-key fit between the active site of a protein and a particular molecule is important not only to taste but to many other biological functions as well. Immune response, the sense of smell, and many types of drug action all depend on shape-specific interactions between molecules and proteins. In fact, our ability to determine the shapes of key biological molecules is largely responsible for the revolution in biology that has occurred over the last 50 years.

In this chapter, we look at ways to predict and account for the shapes of molecules. The molecules we examine are much smaller than the protein molecules we just discussed, but the same principles apply to both. The simple model we examine to account for molecular shape is called *valence shell electron pair repulsion* (VSEPR) theory, and we will use it in conjunction with the Lewis model. We will then proceed to explore two additional bonding theories: valence bond theory and molecular orbital theory. These bonding theories are more complex, but also more powerful, than the Lewis model. They predict and account for molecular shape as well as other properties of molecules.

## 10.2 VSEPR Theory: The Five Basic Shapes

**Valence shell electron pair repulsion (VSEPR) theory** is based on the simple idea that **electron groups**—which we define as lone pairs, single bonds, multiple bonds, and even single electrons—repel one another through coulombic forces. The electron groups, of course, are also attracted to the nucleus (otherwise the molecule would fall apart), but VSEPR theory focuses on the repulsions. According to VSEPR theory, the repulsions between electron groups on *interior atoms* of a molecule determine the geometry of the molecule (Figure 10.1 ▲). The preferred geometry of a molecule is the one in which the electron groups have the maximum separation (and therefore the minimum energy) possible. Consequently, for molecules having just one interior atom (the central atom), molecular geometry depends on (a) the number of electron groups around the central atom and (b) how many of those electron groups are bonding groups and how many are lone pairs. We first look at the molecular geometries associated with two to six electron groups around the central atom when all of those groups are bonding groups (single or multiple bonds). The resulting geometries constitute the five basic shapes of molecules. We will then consider how these basic shapes are modified if one or more of the electron groups are lone pairs.



▲ **FIGURE 10.1** Repulsion between Electron Groups The basic idea of VSEPR theory is that repulsions between electron groups determine molecular geometry.

### Two Electron Groups: Linear Geometry

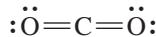
Consider the Lewis structure of  $\text{BeCl}_2$ , which has two electron groups (two single bonds) about the central atom:



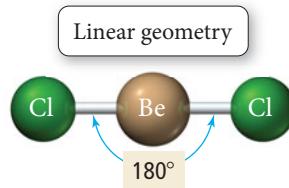
Beryllium often forms incomplete octets, as it does in this structure.

According to VSEPR theory, the geometry of  $\text{BeCl}_2$  is determined by the repulsion between these two electron groups, which maximize their separation by assuming a  $180^\circ$  bond angle or a **linear geometry**. Experimental measurements of the geometry of  $\text{BeCl}_2$  indicate that the molecule is indeed linear, as predicted by the theory.

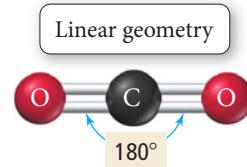
Molecules that form only two single bonds, with no lone pairs, are rare because they do not follow the octet rule. However, the same geometry is observed in all molecules that have two electron groups (and no lone pairs). Consider the Lewis structure of  $\text{CO}_2$ , which has two electron groups (the double bonds) around the central carbon atom:



According to VSEPR theory, the two double bonds repel each other (just as the two single bonds in  $\text{BeCl}_2$  repel each other), resulting in a linear geometry for  $\text{CO}_2$ . Experimental observations confirm that  $\text{CO}_2$  is indeed a linear molecule.



A double bond counts as one electron group.



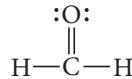
### Three Electron Groups: Trigonal Planar Geometry

The Lewis structure of  $\text{BF}_3$  (another molecule with an incomplete octet) has three electron groups around the central atom:



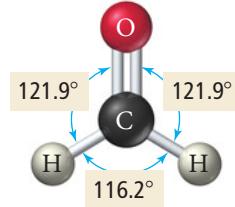
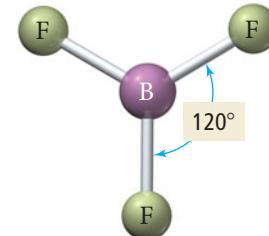
These three electron groups can maximize their separation by assuming  $120^\circ$  bond angles in a plane—a **trigonal planar geometry**. Experimental observations of the structure of  $\text{BF}_3$  again confirm the predictions of VSEPR theory.

Another molecule with three electron groups, formaldehyde, has one double bond and two single bonds around the central atom:



Since formaldehyde has three electron groups around the central atom, we initially predict that the bond angles should also be  $120^\circ$ . However, experimental observations show that the HCO bond angles are  $121.9^\circ$  and the HCH bond angle is  $116.2^\circ$ . These bond angles are close to the idealized  $120^\circ$  that we originally predicted, but the HCO bond angles are slightly greater than the HCH bond angle because the double bond contains more electron density than the single bond and therefore exerts a slightly greater repulsion on the single bonds. In general, *different types of electron groups exert slightly different repulsions*—the resulting bond angles reflect these differences.

Trigonal planar geometry

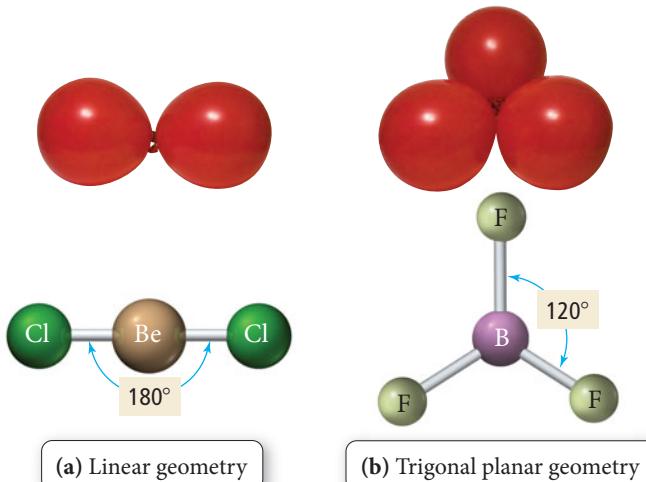


### Conceptual Connection 10.1 Electron Groups and Molecular Geometry

In determining electron geometry, why do we consider only the electron groups on the central atom? In other words, why don't we consider electron groups on terminal atoms?

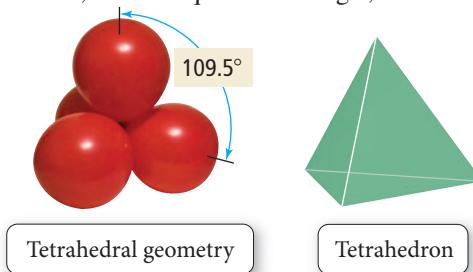
### Four Electron Groups: Tetrahedral Geometry

The VSEPR geometries of molecules with two or three electron groups around the central atom are two-dimensional and therefore easily visualized and represented on paper. For molecules with four or more electron groups around the central atom, the geometries are three-dimensional and therefore more difficult to imagine and draw. One common way to help visualize these basic shapes is by analogy to balloons tied together. In this analogy, each electron group around a central atom is like a balloon tied to a central point. The bulkiness of

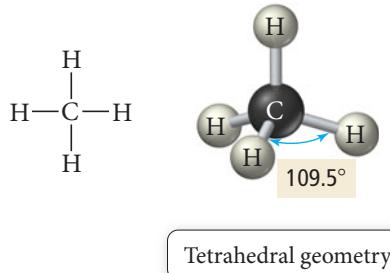


**▲ FIGURE 10.2** Representing Electron Geometry with Balloons (a) The bulkiness of balloons causes them to assume a linear arrangement when two of them are tied together. Similarly, the repulsion between two electron groups produces a linear geometry. (b) Like three balloons tied together, three electron groups adopt a trigonal planar geometry.

the balloons causes them to spread out as much as possible, much as the repulsion between electron groups causes them to position themselves as far apart as possible. For example, if you tie two balloons together, they assume a roughly linear arrangement, as shown in Figure 10.2a ▲, analogous to the linear geometry of  $\text{BeCl}_2$  that we just examined. Notice that the balloons do not represent atoms, but *electron groups*. Similarly, if you tie three balloons together—in analogy to three electron groups—they assume a trigonal planar geometry, as shown in Figure 10.2b ▲, much like the  $\text{BF}_3$  molecule. If you tie *four* balloons together, however, they assume a three-dimensional **tetrahedral geometry** with  $109.5^\circ$  angles between the balloons. That is, the balloons point toward the vertices of a **tetrahedron**—a geometrical shape with four identical faces, each an equilateral triangle, as shown here.



Methane is an example of a molecule with four electron groups around the central atom:



For four electron groups, the tetrahedron is the three-dimensional shape that allows the maximum separation among the groups. The repulsions among the four electron groups in the C—H bonds cause the molecule to assume the tetrahedral shape. When we write the Lewis structure of  $\text{CH}_4$  on paper, it may seem that the molecule should be square planar, with bond angles of  $90^\circ$ . However, in three dimensions, the electron groups can get farther away from each other by forming the tetrahedral geometry, as shown by our balloon analogy.

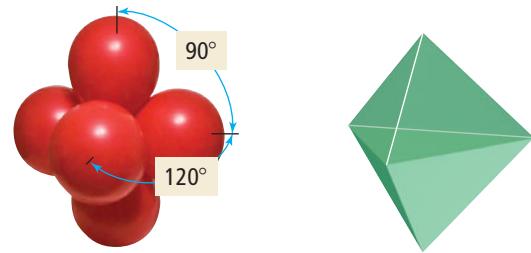
## Conceptual Connection 10.2 Molecular Geometry

What is the geometry of the HCN molecule? The Lewis structure of HCN is H—C≡N.

- (a) linear (b) trigonal planar (c) tetrahedral

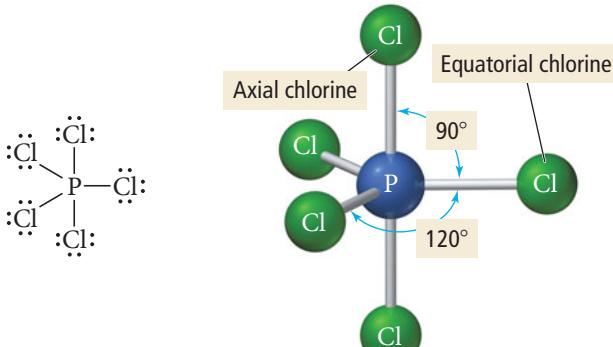
### Five Electron Groups: Trigonal Bipyramidal Geometry

Five electron groups around a central atom assume a **trigonal bipyramidal geometry**, like that of five balloons tied together. In this structure, three of the groups lie in a single plane, as in the trigonal planar configuration, while the other two are positioned above and below this plane. The angles in the trigonal bipyramidal structure are not all the same. The angles between the *equatorial positions* (the three bonds in the trigonal plane) are  $120^\circ$ , while the angle between the *axial positions* (the two bonds on either side of the trigonal plane) and the trigonal plane is  $90^\circ$ . As an example of a molecule with five electron groups around the central atom, consider  $\text{PCl}_5$ :



Trigonal bipyramidal geometry

Trigonal bipyramidal

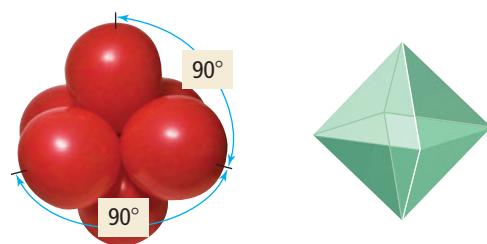


Trigonal bipyramidal geometry

The three equatorial chlorine atoms are separated by  $120^\circ$  bond angles and the two axial chlorine atoms are separated from the equatorial atoms by  $90^\circ$  bond angles.

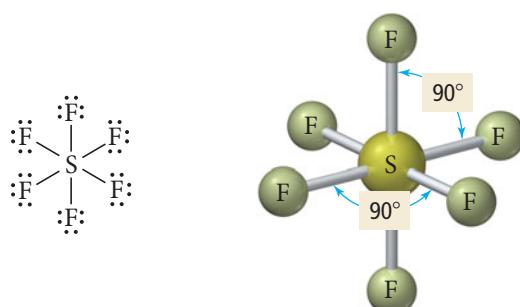
### Six Electron Groups: Octahedral Geometry

Six electron groups around a central atom assume an **octahedral geometry**, like that of six balloons tied together. In this structure—named after the eight-sided geometrical shape called the octahedron—four of the groups lie in a single plane, with a fifth group above the plane and another below it. The angles in this geometry are all  $90^\circ$ . As an example of a molecule with six electron groups around the central atom, consider  $\text{SF}_6$ :



Octahedral geometry

Octahedron



Octahedral geometry

The structure of this molecule is highly symmetrical; all six bonds are equivalent.

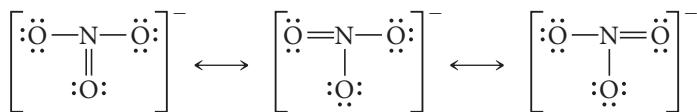
### EXAMPLE 10.1 VSEPR Theory and the Basic Shapes

Determine the molecular geometry of  $\text{NO}_3^-$ .

#### SOLUTION

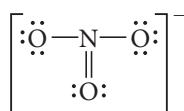
The molecular geometry of  $\text{NO}_3^-$  is determined by the number of electron groups around the central atom (N). Begin by drawing a Lewis structure of  $\text{NO}_3^-$ .

$\text{NO}_3^-$  has  $5 + 3(6) + 1 = 24$  valence electrons. The Lewis structure has three resonance structures:



The hybrid structure is intermediate between these three and has three equivalent bonds.

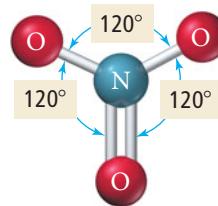
Use any one of the resonance structures to determine the number of electron groups around the central atom.



The nitrogen atom has three electron groups.

Based on the number of electron groups, determine the geometry that minimizes the repulsions between the groups.

The electron geometry that minimizes the repulsions between three electron groups is trigonal planar.



Since the three bonds are equivalent (because of the resonance structures), they each exert the same repulsion on the other two and the molecule has three equal bond angles of  $120^\circ$ .

#### FOR PRACTICE 10.1

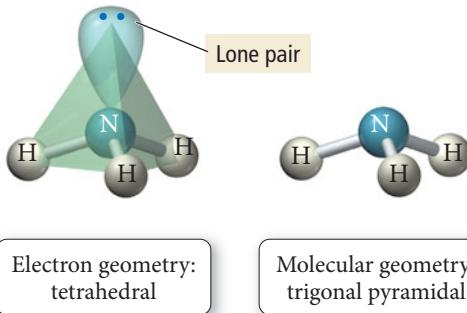
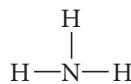
Determine the molecular geometry of  $\text{CCl}_4$ .

## 10.3 VSEPR Theory: The Effect of Lone Pairs

Each of the examples we have just seen has only bonding electron groups around the central atom. What happens in molecules that have lone pairs around the central atom as well? The lone pairs also repel other electron groups, as we see in the examples that follow.

### Four Electron Groups with Lone Pairs

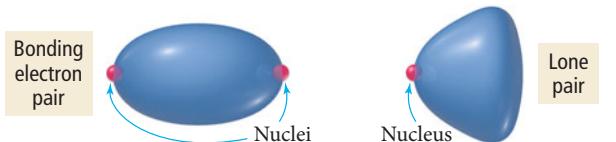
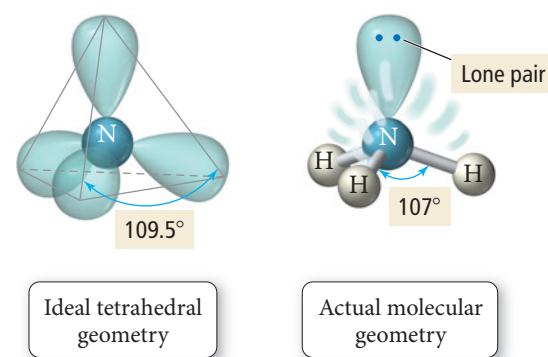
Consider the Lewis structure of ammonia:



The central nitrogen atom has four electron groups (one lone pair and three bonding pairs) that repel one another. If we do not distinguish between bonding electron groups and lone pairs, we find that the **electron geometry**—the geometrical arrangement of the *electron groups*—is still tetrahedral, as we expect for four electron groups. However, the **molecular geometry**—the geometrical arrangement of the atoms—is **trigonal pyramidal**, as shown at left.

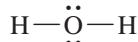
Notice that although the electron geometry and the molecular geometry are different, *the electron geometry is relevant to the molecular geometry*. The lone pair exerts its influence on the bonding pairs.

As we noted previously, different kinds of electron groups generally result in different amounts of repulsion. Lone pair electrons generally exert slightly greater repulsions than bonding electrons. If all four electron groups in  $\text{NH}_3$  exerted equal repulsions on one another, the bond angles in the molecule would all be the ideal tetrahedral angle,  $109.5^\circ$ . However, the actual angle between N—H bonds in ammonia is slightly smaller,  $107^\circ$ . A lone electron pair is more spread out in space than a bonding electron pair because a lone pair is attracted to only one nucleus while a bonding pair is attracted to two (Figure 10.3 ▼). The lone pair occupies more of the angular space around a nucleus, exerting a greater repulsive force on neighboring electrons and compressing the N—H bond angles.



**▲ FIGURE 10.3** Nonbonding versus Bonding Electron Pairs A lone electron pair occupies more space than a bonding pair.

A water molecule's Lewis structure is:



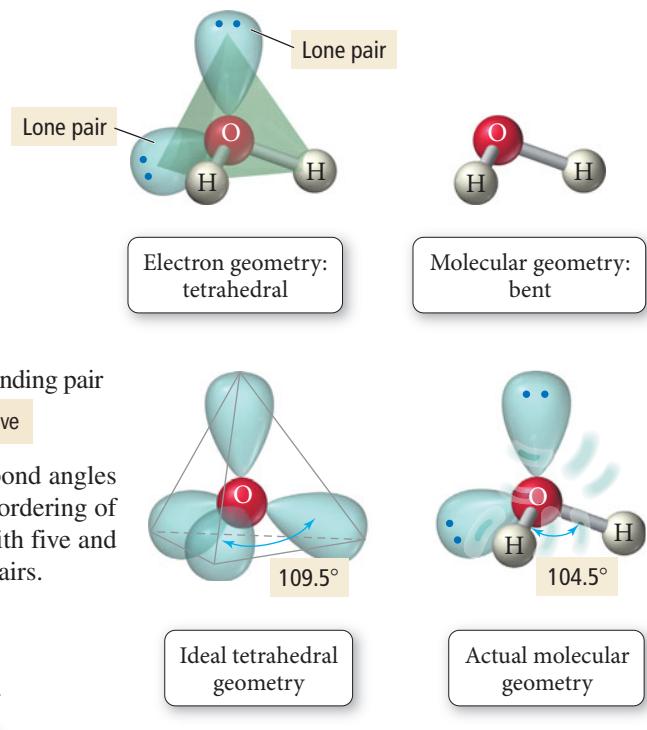
Since it has four electron groups (two bonding pairs and two lone pairs), its *electron geometry* is also tetrahedral, but its *molecular geometry* is **bent**, as shown at right. As in  $\text{NH}_3$ , the bond angles in  $\text{H}_2\text{O}$  are smaller ( $104.5^\circ$ ) than the ideal tetrahedral bond angles because of the greater repulsion exerted by the lone pair electrons. The bond angle in  $\text{H}_2\text{O}$  is even smaller than in  $\text{NH}_3$  because  $\text{H}_2\text{O}$  has *two* lone pairs of electrons on the central oxygen atom. These lone pairs compress the  $\text{H}_2\text{O}$  bond angle to a greater extent than in  $\text{NH}_3$ . In general, electron group repulsions vary as follows:

Lone pair–lone pair > Lone pair–bonding pair > Bonding pair–bonding pair

Most repulsive

Least repulsive

We see the effects of this ordering in the progressively smaller bond angles of  $\text{CH}_4$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$ , as shown in Figure 10.4 ▼. The relative ordering of repulsions also helps to determine the geometry of molecules with five and six electron groups when one or more of those groups are lone pairs.

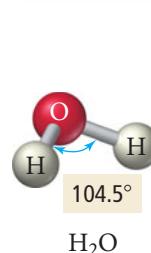
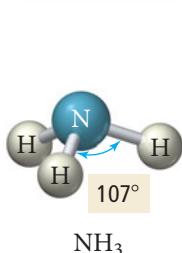
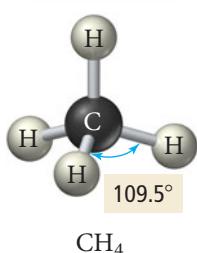


### Effect of Lone Pairs on Molecular Geometry

No lone pairs

One lone pair

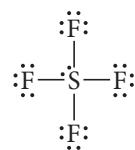
Two lone pairs



**◀ FIGURE 10.4** The Effect of Lone Pairs on Molecular Geometry The bond angles get progressively smaller as the number of lone pairs on the central atom increases from zero in  $\text{CH}_4$  to one in  $\text{NH}_3$  to two in  $\text{H}_2\text{O}$ .

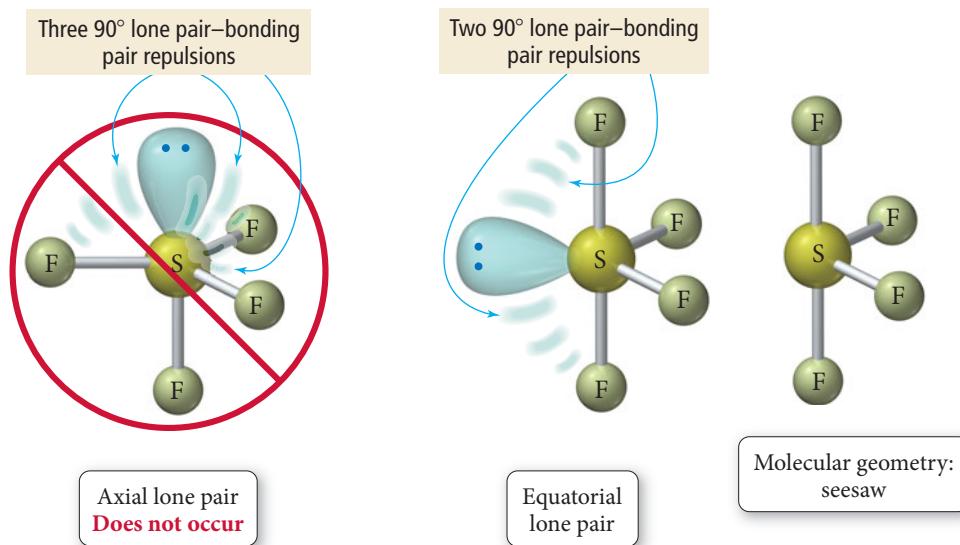
## Five Electron Groups with Lone Pairs

Consider the Lewis structure of SF<sub>4</sub>:

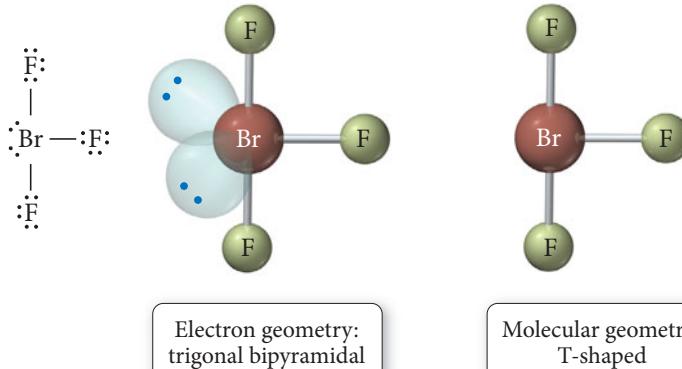


The central sulfur atom has five electron groups (one lone pair and four bonding pairs). The *electron geometry*, due to the five electron groups, is trigonal bipyramidal. To determine the molecular geometry, notice that the lone pair could occupy either an equatorial position or an axial position within the trigonal bipyramidal electron geometry. Which position is most favorable? To answer this question, we must consider that, as we have just seen, lone pair–bonding pair repulsions are greater than bonding pair–bonding pair repulsions. Therefore, the lone pair occupies the position that minimizes its interaction with the bonding pairs. If the lone pair were in an axial position, it would have three 90° interactions with bonding pairs. In an equatorial position, however, it has only two 90° interactions. Consequently, the lone pair occupies an equatorial position. The resulting molecular geometry is called **seesaw** because it resembles a seesaw (or teeter-totter).

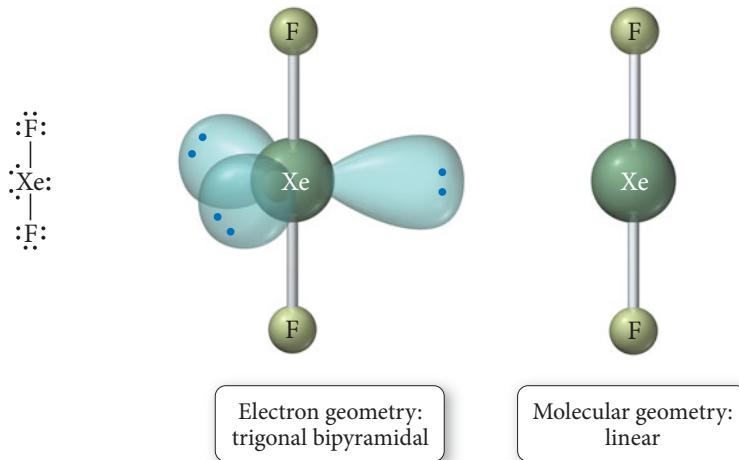
The seesaw molecular geometry is sometimes called an *irregular tetrahedron*.



When two of the five electron groups around the central atom are lone pairs, as in BrF<sub>3</sub>, the lone pairs occupy two of the three equatorial positions—again minimizing 90° interactions with bonding pairs and also avoiding a lone pair–lone pair 90° repulsion. The resulting molecular geometry is **T-shaped**.

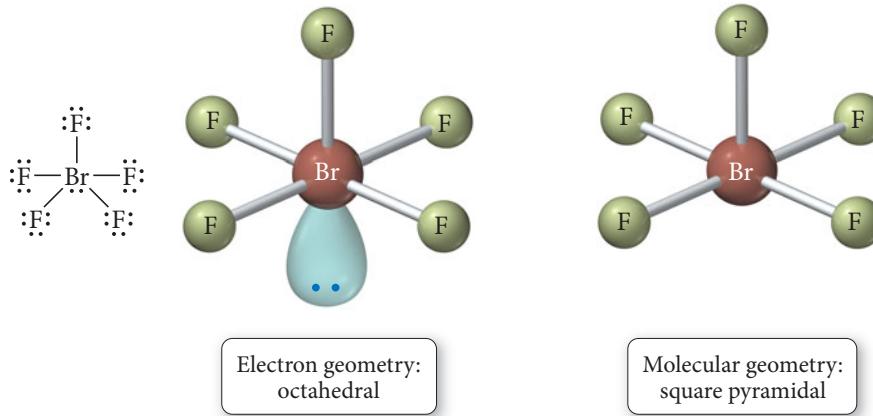


When three of the five electron groups around the central atom are lone pairs, as in  $\text{XeF}_2$ , the lone pairs occupy all three of the equatorial positions, and the resulting molecular geometry is linear.

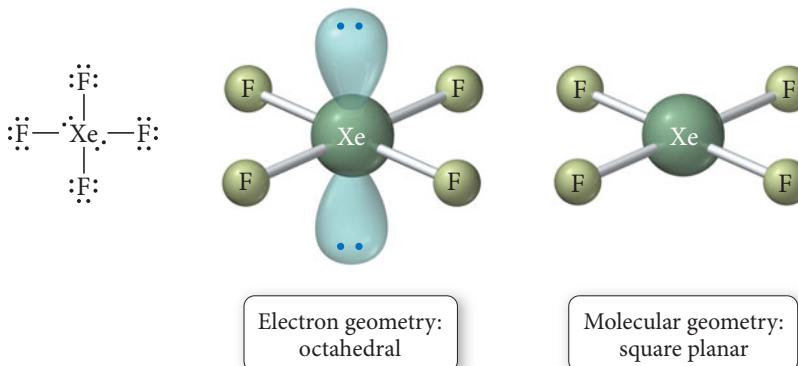


## Six Electron Groups with Lone Pairs

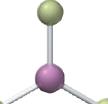
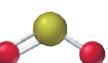
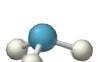
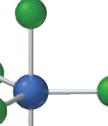
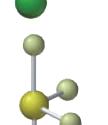
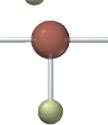
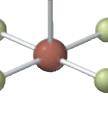
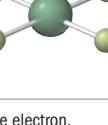
The Lewis structure of  $\text{BrF}_5$  is shown next. The central bromine atom has six electron groups (one lone pair and five bonding pairs). The electron geometry, due to the six electron groups, is octahedral. Since all six positions in the octahedral geometry are equivalent, the lone pair can be situated in any one of these positions. The resulting molecular geometry is **square pyramidal**.



When two of the six electron groups around the central atom are lone pairs, as in  $\text{XeF}_4$ , the lone pairs occupy positions across from one another (to minimize lone pair–lone pair repulsions), and the resulting molecular geometry is **square planar**.



**TABLE 10.1** Electron and Molecular Geometries

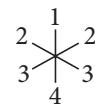
Electron Groups*	Bonding Groups	Lone Pairs	Electron Geometry	Molecular Geometry	Approximate Bond Angles	Example
2	2	0	Linear	Linear	180°	$\ddot{\text{O}} = \text{C} = \ddot{\text{O}}$ 
3	3	0	Trigonal planar	Trigonal planar	120°	$\begin{array}{c} \text{:F:} \\   \\ \text{:F---B---F:} \\   \\ \text{:F:} \end{array}$ 
3	2	1	Trigonal planar	Bent	<120°	$\ddot{\text{O}} = \text{S} = \ddot{\text{O}}$ 
4	4	0	Tetrahedral	Tetrahedral	109.5°	$\begin{array}{c} \text{H} \\   \\ \text{H---C---H} \\   \\ \text{H} \end{array}$ 
4	3	1	Tetrahedral	Trigonal pyramidal	<109.5°	$\begin{array}{c} \text{H} \\   \\ \text{H---N---H} \\   \\ \text{H} \end{array}$ 
4	2	2	Tetrahedral	Bent	<109.5°	$\text{H---}\ddot{\text{O}}\text{---H}$ 
5	5	0	Trigonal bipyramidal	Trigonal bipyramidal	120° (equatorial) 90° (axial)	$\begin{array}{ccccc} \text{:Cl:} & & \text{:Cl:} & & \text{:Cl:} \\ & \diagdown & & \diagup & \\ & \text{P} & & \text{P} & \\ & \diagup & & \diagdown & \\ \text{:Cl:} & & \text{:Cl:} & & \text{:Cl:} \end{array}$ 
5	4	1	Trigonal bipyramidal	Seesaw	<120° (equatorial) <90° (axial)	$\begin{array}{ccccc} \text{:F:} & & \text{:F:} & & \text{:F:} \\ & \diagdown & & \diagup & \\ & \text{S} & & \text{S} & \\ & \diagup & & \diagdown & \\ \text{:F:} & & \text{:F:} & & \text{:F:} \end{array}$ 
5	3	2	Trigonal bipyramidal	T-shaped	<90°	$\begin{array}{ccccc} \text{:F:} & & \text{:F:} & & \text{:F:} \\ & \diagdown & & \diagup & \\ & \text{Br} & & \text{Br} & \\ & \diagup & & \diagdown & \\ \text{:F:} & & \text{:F:} & & \text{:F:} \end{array}$ 
5	2	3	Trigonal bipyramidal	Linear	180°	$\begin{array}{ccccc} \text{:F:} & & \text{:Xe:} & & \text{:F:} \\ & \diagdown & & \diagup & \\ & \text{Xe} & & \text{Xe} & \\ & \diagup & & \diagdown & \\ \text{:F:} & & \text{:F:} & & \text{:F:} \end{array}$ 
6	6	0	Octahedral	Octahedral	90°	$\begin{array}{ccccc} \text{:F:} & & \text{:F:} & & \text{:F:} \\ & \diagdown & & \diagup & \\ & \text{S} & & \text{S} & \\ & \diagup & & \diagdown & \\ \text{:F:} & & \text{:F:} & & \text{:F:} \end{array}$ 
6	5	1	Octahedral	Square pyramidal	<90°	$\begin{array}{ccccc} \text{:F:} & & \text{:F:} & & \text{:F:} \\ & \diagdown & & \diagup & \\ & \text{Br} & & \text{Br} & \\ & \diagup & & \diagdown & \\ \text{:F:} & & \text{:F:} & & \text{:F:} \end{array}$ 
6	4	2	Octahedral	Square planar	90°	$\begin{array}{ccccc} \text{:F:} & & \text{:F:} & & \text{:F:} \\ & \diagdown & & \diagup & \\ & \text{Xe} & & \text{Xe} & \\ & \diagup & & \diagdown & \\ \text{:F:} & & \text{:F:} & & \text{:F:} \end{array}$ 

\*Count only electron groups around the central atom. Each of the following is considered one electron group: a lone pair, a single bond, a double bond, a triple bond, or a single electron.


**Connection 10.3 Lone Pair Electrons and Molecular Geometry**

Suppose that a molecule with six electron groups were confined to two dimensions and therefore had a hexagonal planar electron geometry. If two of the six groups were lone pairs, where would they be located?

- (a) positions 1 and 2   (b) positions 1 and 3   (c) positions 1 and 4


**Summarizing VSEPR Theory:**

- ▶ The geometry of a molecule is determined by the number of electron groups on the central atom (or on all interior atoms, if there is more than one).
- ▶ The number of electron groups is determined from the Lewis structure of the molecule. If the Lewis structure contains resonance structures, use any one of the resonance structures to determine the number of electron groups.
- ▶ Each of the following counts as a single electron group: a lone pair, a single bond, a double bond, a triple bond, or a single electron (as in a free radical).
- ▶ The geometry of the electron groups is determined by their repulsions as summarized in Table 10.1. In general, electron group repulsions vary as follows:

Lone pair–lone pair > lone pair–bonding pair > bonding pair–bonding pair

- ▶ Bond angles can vary from the idealized angles because double and triple bonds occupy more space than single bonds (they are bulkier even though they are shorter), and lone pairs occupy more space than bonding groups. The presence of lone pairs usually makes bond angles smaller than the ideal angle for the particular geometry.

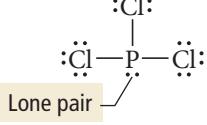
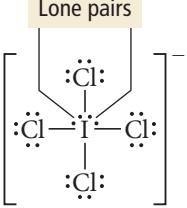
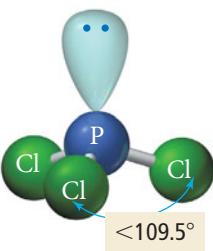
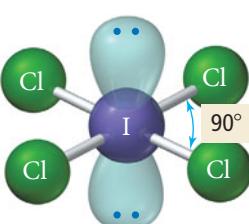

**Connection 10.4 Molecular Geometry and Electron Group Repulsions**

Which statement is *always* true according to VSEPR theory?

- (a) The shape of a molecule is determined only by repulsions among bonding electron groups.  
 (b) The shape of a molecule is determined only by repulsions among nonbonding electron groups.  
 (c) The shape of a molecule is determined by the polarity of its bonds.  
 (d) The shape of a molecule is determined by repulsions among all electron groups on the central atom (or interior atoms, if there is more than one).

## 10.4 VSEPR Theory: Predicting Molecular Geometries

To determine the geometry of a molecule, follow the procedure presented here. As in other examples, we provide the steps in the left column and provide two examples of applying the steps in the center and right columns.

PROCEDURE FOR...	EXAMPLE 10.2	EXAMPLE 10.3
<b>Predicting Molecular Geometries</b>	<b>Predicting Molecular Geometries</b> Predict the geometry and bond angles of $\text{PCl}_3$ .	Predict the geometry and bond angles of $\text{ICl}_4^-$ .
<b>1. Draw the Lewis structure for the molecule.</b>	$\text{PCl}_3$ has 26 valence electrons.	$\text{ICl}_4^-$ has 36 valence electrons.
<b>2. Determine the total number of electron groups around the central atom.</b> Lone pairs, single bonds, double bonds, triple bonds, and single electrons each count as one group.	The central atom (P) has four electron groups.	The central atom (I) has six electron groups.
<b>3. Determine the number of bonding groups and the number of lone pairs around the central atom.</b> These should sum to your result from step 2. Bonding groups include single bonds, double bonds, and triple bonds.	 Three of the four electron groups around P are bonding groups and one is a lone pair.	 Four of the six electron groups around I are bonding groups and two are lone pairs.
<b>4. Refer to Table 10.1 to determine the electron geometry and molecular geometry.</b> If no lone pairs are present around the central atom, the bond angles will be that of the ideal geometry. If lone pairs are present, the bond angles may be smaller than the ideal geometry.	The electron geometry is tetrahedral (four electron groups) and the molecular geometry—the shape of the molecule—is <i>trigonal pyramidal</i> (three bonding groups and one lone pair). Because of the presence of a lone pair, the bond angles are less than $109.5^\circ$ .  Trigonal pyramidal	The electron geometry is octahedral (six electron groups) and the molecular geometry—the shape of the molecule—is <i>square planar</i> (four bonding groups and two lone pairs). Even though lone pairs are present, the bond angles are $90^\circ$ because the lone pairs are symmetrically arranged and do not compress the I–Cl bond angles.  Square planar
	<b>FOR PRACTICE 10.2</b> Predict the molecular geometry and bond angle of $\text{ClNO}$ .	<b>FOR PRACTICE 10.3</b> Predict the molecular geometry of $\text{I}_3^-$ .



## Representing Molecular Geometries on Paper

Since molecular geometries are three-dimensional, they are often difficult to represent on two-dimensional paper. Many

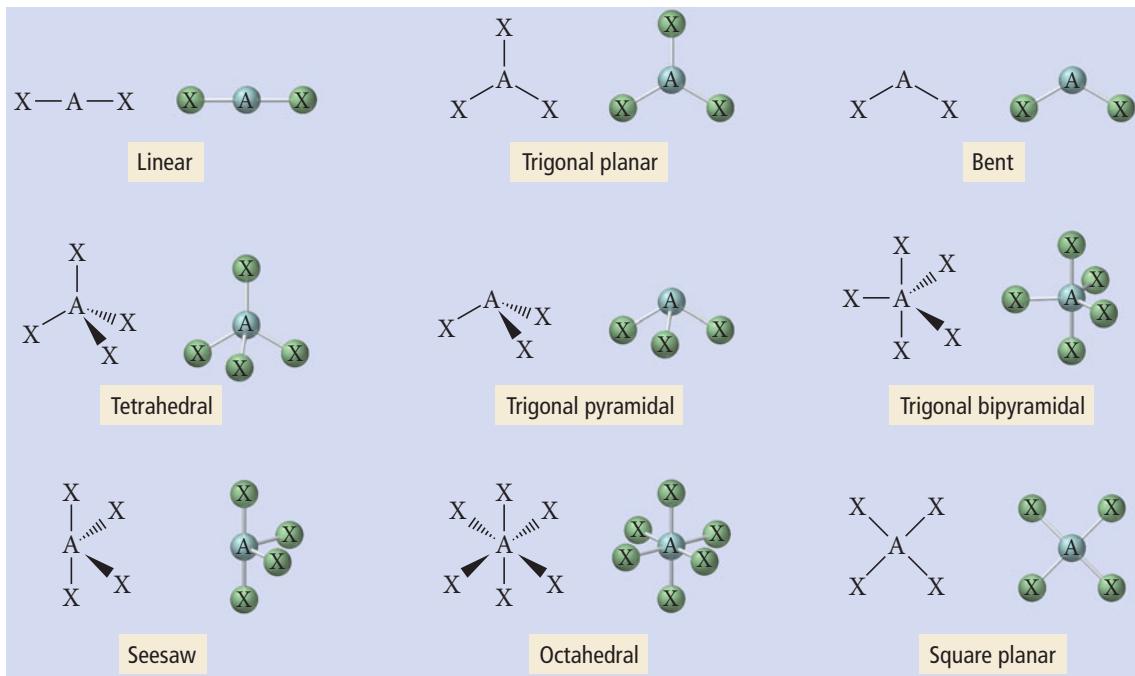
chemists use the notation shown here for bonds to indicate three-dimensional structures on two-dimensional paper.

 Straight line  
Bond in plane of paper

 Hatched wedge  
Bond going into the page

 Solid wedge  
Bond coming out of the page

Some examples of the molecular geometries used in this book are shown below using this notation.

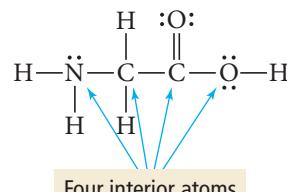


## Predicting the Shapes of Larger Molecules

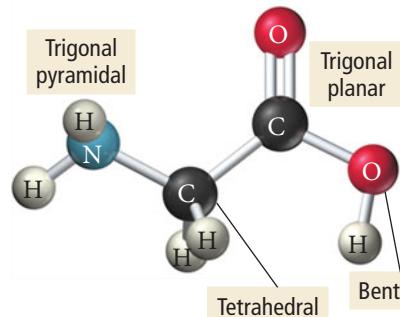
Larger molecules may have two or more *interior* atoms. When predicting the shapes of these molecules, we apply the principles we just covered to each interior atom. Consider glycine, an amino acid found in many proteins (such as those involved in taste discussed in Section 10.1). Glycine, shown at right, contains four interior atoms: one nitrogen atom, two carbon atoms, and an oxygen atom. To determine the shape of glycine, we determine the geometry about each interior atom as follows:

Atom	Number of Electron Groups	Number of Lone Pairs	Molecular Geometry
Nitrogen	4	1	Trigonal pyramidal
Leftmost carbon	4	0	Tetrahedral
Rightmost carbon	3	0	Trigonal planar
Oxygen	4	2	Bent

Using the geometries of each of these, we can determine the entire three-dimensional shape of the molecule as shown at right.



Glycine

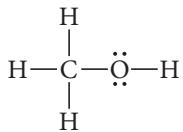


### EXAMPLE 10.4 Predicting the Shape of Larger Molecules

Predict the geometry about each interior atom in methanol ( $\text{CH}_3\text{OH}$ ) and make a sketch of the molecule.

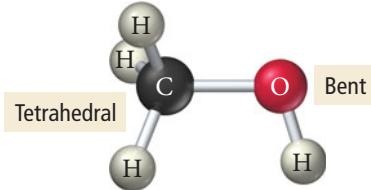
#### SOLUTION

Begin by drawing the Lewis structure of  $\text{CH}_3\text{OH}$ .  $\text{CH}_3\text{OH}$  contains two interior atoms: one carbon atom and one oxygen atom. To determine the shape of methanol, determine the geometry about each interior atom as follows:



Atom	Number of Electron Groups	Number of Lone Pairs	Molecular Geometry
Carbon	4	0	Tetrahedral
Oxygen	4	2	Bent

Using the geometries of each of these, draw a three-dimensional sketch of the molecule as shown here:



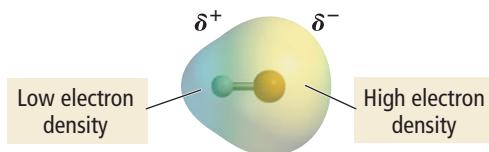
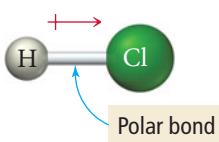
#### FOR PRACTICE 10.4

Predict the geometry about each interior atom in acetic acid ( $\text{H}_3\text{C}-\text{C}(=\text{O})-\text{OH}$ ) and make a sketch of the molecule.

## 10.5 Molecular Shape and Polarity

In Chapter 9, we discussed polar bonds. Entire molecules can also be polar, depending on their shape and the nature of their bonds. For example, if a diatomic molecule has a polar bond, the molecule as a whole will be polar:

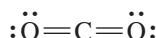
Net dipole moment



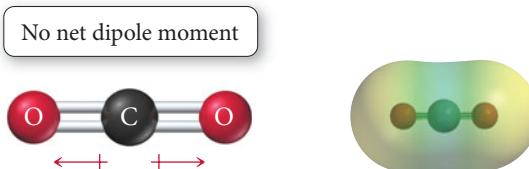
The figure on the right is an electrostatic potential map of  $\text{HCl}$ . In these maps, red areas indicate electron rich regions in the molecule and the blue areas indicate electron poor regions. Yellow indicates moderate electron density. Notice that the region around the more electronegative atom (chlorine) is more electron rich than the region around the hydrogen atom. Thus the molecule itself is polar. If the bond in a diatomic molecule is *nonpolar*, the molecule as a whole will be *nonpolar*.

In polyatomic molecules, the presence of polar bonds may or may not result in a polar molecule, depending on the molecular geometry. If the molecular geometry is such that the dipole moments of individual polar bonds sum together to a net dipole moment,

then the molecule will be polar. But, if the molecular geometry is such that the dipole moments of the individual polar bonds cancel each other (that is, sum to zero), then the molecule will be nonpolar. It all depends on the geometry of the molecule. Consider carbon dioxide:

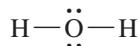


Each C=O bond in CO<sub>2</sub> is polar because oxygen and carbon have significantly different electronegativities (3.5 and 2.5, respectively). However, since CO<sub>2</sub> is a linear molecule, the polar bonds directly oppose one another and the dipole moment of one bond exactly opposes the dipole moment of the other—the two dipole moments sum to zero and the *molecule* is nonpolar. Dipole moments cancel each other because they are *vector quantities*; they have both a magnitude and a direction. Think of each polar bond as a vector, pointing in the direction of the more electronegative atom. The length of the vector is proportional to the electronegativity difference between the bonding atoms. In CO<sub>2</sub>, we have two identical vectors pointing in exactly opposite directions—the vectors sum to zero, much as +1 and -1 sum to zero:

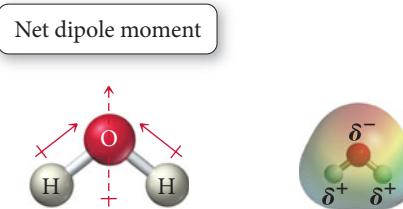


Notice that the electrostatic potential map shows regions of moderately high electron density (yellow with slight red) positioned symmetrically on either end of the molecule with a region of low electron density (blue) located in the middle.

In contrast, consider water:



The O—H bonds in water are also polar; oxygen and hydrogen have electronegativities of 3.5 and 2.1, respectively. However, the water molecule is not linear but bent, so the two dipole moments do not sum to zero. If we imagine each bond as a vector pointing toward oxygen (the more electronegative atom) we see that, because of the angle between the vectors, they do not cancel, but sum to an overall vector or a net dipole moment (shown by the dashed arrow).



See the box on p. 440 for an explanation of how to add vectors.

The electrostatic potential map shows an electron rich region at the oxygen end of the molecule. Consequently, water is a polar molecule. Table 10.2 summarizes common geometries and molecular polarity.

#### **Summarizing Molecular Shape and Polarity:**

- ▶ **Draw the Lewis structure for the molecule and determine its molecular geometry.**
- ▶ **Determine if the molecule contains polar bonds.** A bond is polar if the two bonding atoms have sufficiently different electronegativities (see Figure 9.8). If the molecule contains polar bonds, superimpose a vector, pointing toward the more electronegative atom, on each bond. Make the length of the vector proportional to the electronegativity difference between the bonding atoms.
- ▶ **Determine if the polar bonds add together to form a net dipole moment.** Sum the vectors corresponding to the polar bonds together. If the vectors sum to zero, the molecule is nonpolar. If the vectors sum to a net vector, the molecule is polar.



## Vector Addition

As discussed previously, we can determine whether a molecule is polar by summing the vectors associated with the dipole moments of all the polar bonds in the molecule. If the vectors sum to zero, the molecule will be nonpolar. If they sum to a net vector, the molecule will be polar. In this box, we demonstrate how to add vectors together in one dimension and in two or more dimensions.

### One Dimension

To add two vectors that lie on the same line, assign one direction as positive. Vectors pointing in that direction have positive magnitudes. Consider vectors pointing in the opposite direction to have negative magnitudes. Then sum the vectors (always remembering to include their signs), as shown in Examples 1 and 2.

**Example 1**

$$\begin{array}{ccc} +5 & & +5 \\ \text{---} & & \text{---} \\ \vec{A} & & \vec{B} \end{array} = \begin{array}{c} +10 \\ \text{---} \\ \vec{R} = \vec{A} + \vec{B} \end{array}$$

**Example 2**

$$\begin{array}{ccc} -5 & & +10 \\ \text{---} & & \text{---} \\ \vec{A} & & \vec{B} \end{array} = \begin{array}{c} +5 \\ \text{---} \\ \vec{R} = \vec{A} + \vec{B} \end{array}$$

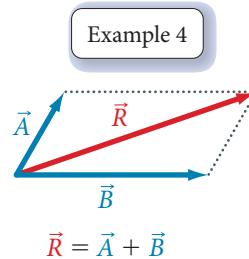
To add three or more vectors, add two of them together first, and then add the third vector to the result.

**Example 3**

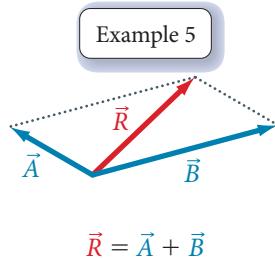
$$\begin{array}{ccc} -5 & & +5 \\ \text{---} & & \text{---} \\ \vec{A} & & \vec{B} \end{array} = \begin{array}{c} 0 \\ \vec{R} = \vec{A} + \vec{B} \\ (\text{the vectors exactly cancel}) \end{array}$$

### Two or More Dimensions

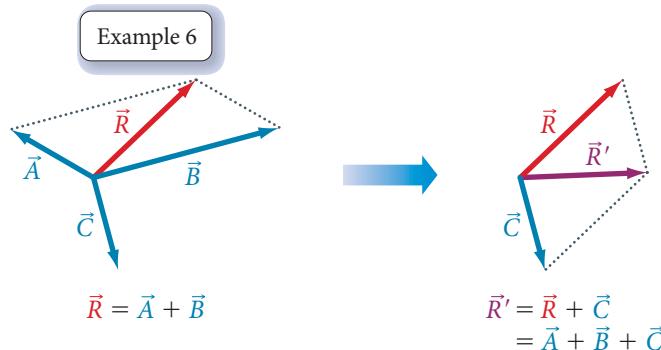
To add two vectors, draw a parallelogram in which the two vectors form two adjacent sides. Draw the other two sides of the parallelogram parallel to and the same length as the two original vectors. Draw the resultant vector beginning at the origin and extending to the far corner of the parallelogram.



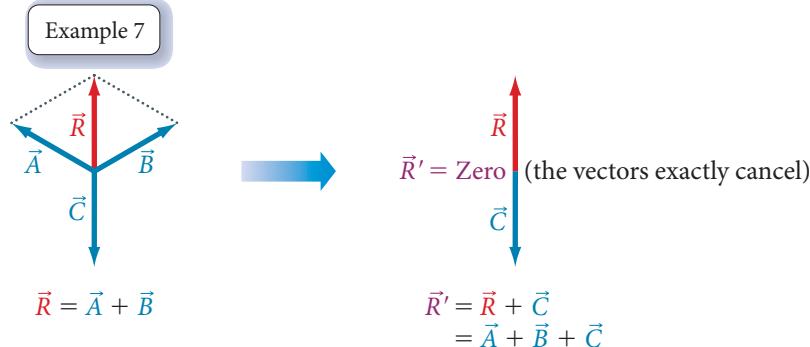
$$\vec{R} = \vec{A} + \vec{B}$$



$$\vec{R} = \vec{A} + \vec{B}$$



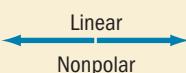
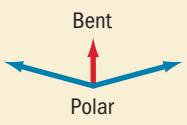
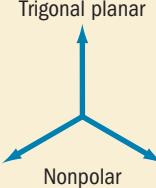
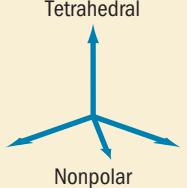
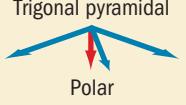
$$\begin{aligned} \vec{R}' &= \vec{R} + \vec{C} \\ &= \vec{A} + \vec{B} + \vec{C} \end{aligned}$$



$\vec{R}' = \text{Zero}$  (the vectors exactly cancel)

$$\begin{aligned} \vec{R}' &= \vec{R} + \vec{C} \\ &= \vec{A} + \vec{B} + \vec{C} \end{aligned}$$

**TABLE 10.2 Common Cases of Adding Dipole Moments to Determine whether a Molecule Is Polar**

 Linear Nonpolar	 Bent Polar
<p>The dipole moments of two identical polar bonds pointing in opposite directions will cancel. The molecule is nonpolar.</p>	<p>The dipole moments of two polar bonds with an angle of less than 180° between them will not cancel. The resultant dipole moment vector is shown in red. The molecule is polar.</p>
 Trigonal planar Nonpolar	 Tetrahedral Nonpolar
<p>The dipole moments of three identical polar bonds at 120° from each other will cancel. The molecule is nonpolar.</p>	<p>The dipole moments of four identical polar bonds in a tetrahedral arrangement (109.5° from each other) will cancel. The molecule is nonpolar.</p>
 Trigonal pyramidal Polar	
<p>The dipole moments of three polar bonds in a trigonal pyramidal arrangement (109.5° from each other) will not cancel. The resultant dipole moment vector is shown in red. The molecule is polar.</p>	

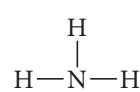
Note: In all cases in which the dipoles of two or more polar bonds cancel, the bonds are assumed to be identical. If one or more of the bonds are different from the other(s), the dipoles will not cancel and the molecule will be polar.

### EXAMPLE 10.5 Determining if a Molecule Is Polar

Determine if NH<sub>3</sub> is polar.

#### SOLUTION

Draw the Lewis structure for the molecule and determine its molecular geometry.



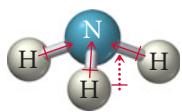
The Lewis structure has three bonding groups and one lone pair about the central atom. Therefore the molecular geometry is trigonal pyramidal.

**Determine if the molecule contains polar bonds.** Sketch the molecule and superimpose a vector for each polar bond. The relative length of each vector should be proportional to the electronegativity difference between the atoms forming each bond. The vector should point in the direction of the more electronegative atom.



The electronegativities of nitrogen and hydrogen are 3.0 and 2.1, respectively. Therefore, the bonds are polar.

**Determine if the polar bonds add together to form a net dipole moment.** Examine the symmetry of the vectors (representing dipole moments) and determine if they cancel each other or sum to a net dipole moment.

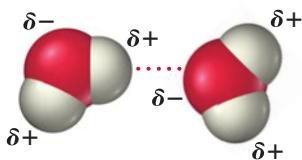


The three dipole moments sum to a net dipole moment. The molecule is polar.

#### FOR PRACTICE 10.5

Determine if CF<sub>4</sub> is polar.

Opposite magnetic poles attract one another.

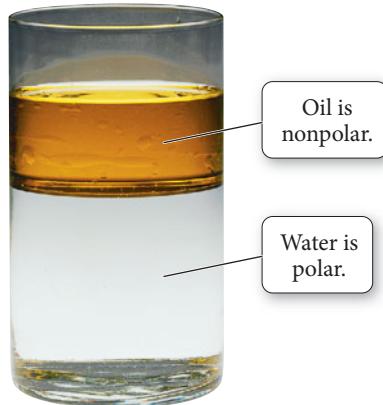


Opposite partial charges on molecules attract one another.

### ▲ FIGURE 10.5 Interaction of Polar Molecules

The north pole of one magnet attracts the south pole of another magnet. In an analogous way, the positively charged end of one molecule attracts the negatively charged end of another (although the forces involved are different). As a result of this electrical attraction, polar molecules interact strongly with one another.

Polar and nonpolar molecules have different properties. Water and oil do not mix, for example, because water molecules are polar and the molecules that compose oil are generally nonpolar. Polar molecules interact strongly with other polar molecules because the positive end of one molecule is attracted to the negative end of another, just as the south pole of a magnet is attracted to the north pole of another magnet (Figure 10.5 ▲). A mixture of polar and nonpolar molecules is similar to a mixture of small magnetic particles and nonmagnetic ones. The magnetic particles (which are like polar molecules) clump together, excluding the nonmagnetic particles (which are like nonpolar molecules) and separating into distinct regions.



▲ Oil and water do not mix, because water molecules are polar and the molecules that compose oil are nonpolar.



▲ A mixture of polar and nonpolar molecules is analogous to a mixture of magnetic marbles (opaque) and nonmagnetic marbles (transparent). As with the magnetic marbles, mutual attraction causes polar molecules to clump together, excluding the nonpolar molecules.



## Chemistry in Your Day

### How Soap Works

Imagine eating a greasy cheeseburger with both hands and without a napkin. By the end of the meal, your hands are coated with grease and oil. If you try to wash them with only water, they remain greasy. However, if you add a little soap, the grease washes away. Why? As we just learned, water molecules are polar and the molecules that compose grease and oil are nonpolar. As a result, water and grease do not mix.

The molecules that compose soap, however, have a special structure that allows them to interact strongly with both water and grease. One end of a soap molecule is polar while the other end is nonpolar.

The nonpolar end is a long hydrocarbon chain. Hydrocarbons are always nonpolar because the electronegativity difference between carbon and hydrogen is small and because the tetrahedral arrangement about each carbon atom tends to cancel any small dipole moments of individual bonds. The polar head of a soap molecule—usually, though not always, ionic—strongly attracts water molecules, while the nonpolar tail interacts more strongly with grease and oil molecules (we will examine the nature of these interactions in Chapter 11). Thus, soap acts as a sort of molecular liaison, one end interacting with water and the other end interacting with grease. Soap allows water and grease to mix, removing the grease from your hands and washing it down the drain.

### Question

Consider the detergent molecule shown here. Which end do you think is polar? Which end is nonpolar?



Polar head  
attracts water.

Nonpolar tail  
interacts with grease.



## 10.6 Valence Bond Theory: Orbital Overlap as a Chemical Bond

In the Lewis model, we use “dots” to represent electrons as they are transferred or shared between bonding atoms. We know from quantum-mechanical theory, however, that such a treatment is an oversimplification. More advanced bonding theories treat electrons in a quantum-mechanical manner. These theories are actually extensions of quantum mechanics, applied to molecules. Although a detailed quantitative treatment of these theories is beyond the scope of this book, we introduce them in a *qualitative* manner in the sections that follow. Keep in mind, however, that modern *quantitative* approaches to chemical bonding using these theories accurately predict many of the properties of molecules—such as bond lengths, bond strengths, molecular geometries, and dipole moments—that we have been discussing in this book.

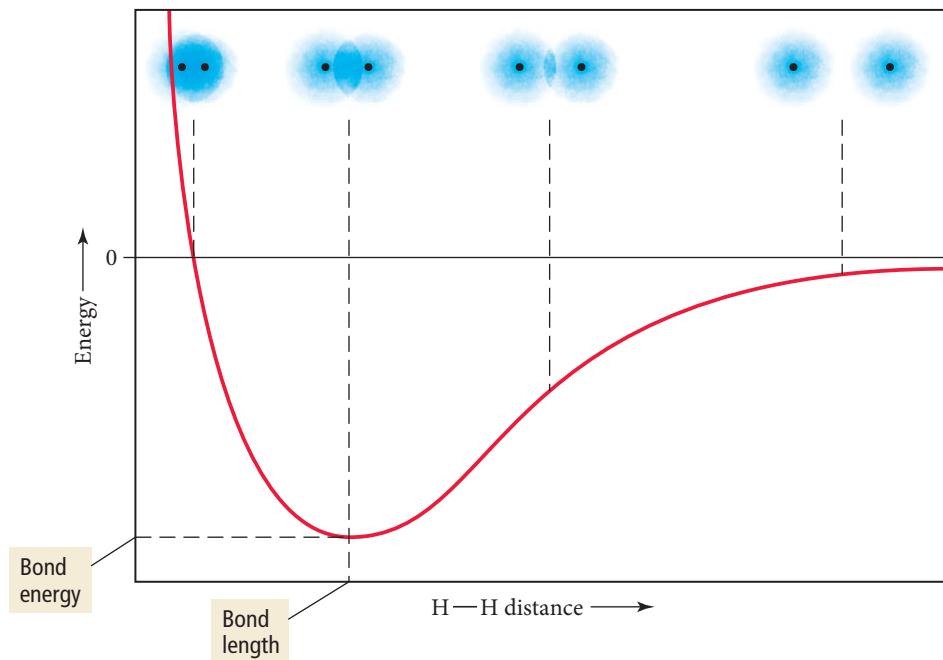
The simpler of the two more advanced bonding theories is called **valence bond theory**. According to valence bond theory, electrons reside in quantum-mechanical orbitals localized on individual atoms. In many cases, these orbitals are simply the standard *s*, *p*, *d*, and *f* atomic orbitals that we learned about in Chapter 7. In other cases, these orbitals are *hybridized atomic orbitals*, a kind of blend or combination of two or more standard atomic orbitals.

When two atoms approach each other, the electrons and nucleus of one atom interact with the electrons and nucleus of the other atom. In valence bond theory, we calculate the effect of these interactions on the energies of the electrons in the atomic orbitals. If the energy of the system is lowered because of the interactions, then a chemical bond forms. If the energy of the system is raised by the interactions, then a chemical bond does not form.

The interaction energy is usually calculated as a function of the internuclear distance between the two bonding atoms. For example, Figure 10.6 ▶ shows the calculated interaction energy between two hydrogen atoms as a function of the distance between them. The *y*-axis of the graph is the potential energy of the interaction between the electron and nucleus of one hydrogen atom and the electron and nucleus of the other. The *x*-axis is the separation (or internuclear distance) between the two atoms. As we can see from the graph, when the atoms are far apart (right side of the graph), the interaction energy is nearly zero because the two atoms do not interact to any significant extent. As the atoms get closer, the interaction energy becomes negative. This is a net stabilization that attracts

Valence bond theory is an application of a general quantum-mechanical approximation method called *perturbation theory*. In perturbation theory, a complex system (such as a molecule) is viewed as a simpler system (such as two atoms) that is slightly altered or perturbed by some additional force or interaction (such as the interaction between the two atoms).

**Interaction Energy of Two Hydrogen Atoms**



◀ FIGURE 10.6 Interaction Energy

**Diagram for H<sub>2</sub>** The potential energy of two hydrogen atoms is lowest when they are separated by a distance that allows their 1s orbitals a substantial degree of overlap without too much repulsion between their nuclei. This distance, at which the system is most stable, is the bond length of the H<sub>2</sub> molecule.

one hydrogen atom to the other. If the atoms get too close, however, the interaction energy begins to rise, primarily because of the mutual repulsion of the two positively charged nuclei. The most stable point on the curve occurs at the minimum of the interaction energy—this is the equilibrium bond length. At this distance, the two atomic 1s orbitals have a significant amount of overlap and the electrons spend time in the internuclear region where they can interact with both nuclei. The value of the interaction energy at the equilibrium bond distance is the bond energy.

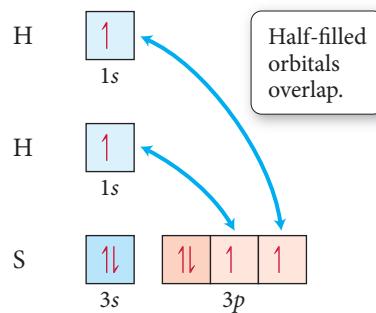
When we apply valence bond theory to a number of atoms and their corresponding molecules, we arrive at the following general observation: *the interaction energy is usually negative (or stabilizing) when the interacting atomic orbitals contain a total of two electrons that can spin-pair (orient with opposing spins)*. Most commonly, the two electrons come from two half-filled orbitals, but in some cases, the two electrons come from one filled orbital overlapping with a completely empty orbital (this is called a coordinate covalent bond and we will cover it in more detail in Chapter 24). In other words, when two atoms with half-filled orbitals approach each other, the half-filled orbitals *overlap*—parts of the orbitals occupy the same space—and the electrons occupying them align with opposite spins. This results in a net energy stabilization that constitutes a covalent chemical bond. The resulting geometry of the molecule emerges from the geometry of the overlapping orbitals.

**When completely filled orbitals overlap, the interaction energy is positive (or destabilizing) and no bond forms.**

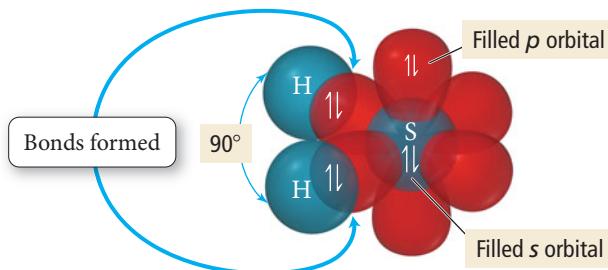
### Summarizing Valence Bond Theory:

- ▶ The valence electrons of the atoms in a molecule reside in quantum-mechanical atomic orbitals. The orbitals can be the standard  $s$ ,  $p$ ,  $d$ , and  $f$  orbitals or they may be hybrid combinations of these.
- ▶ A chemical bond results from the overlap of two half-filled orbitals with spin-pairing of the two valence electrons (or less commonly the overlap of a completely filled orbital with an empty orbital).
- ▶ The geometry of the overlapping orbitals determines the shape of the molecule.

We can apply the general concepts of valence bond theory to explain bonding in hydrogen sulfide,  $\text{H}_2\text{S}$ . The valence electron configurations of the atoms in the molecule are as follows:



The hydrogen atoms each have one half-filled orbital, and the sulfur atom has two half-filled orbitals. The half-filled orbitals on each hydrogen atom overlap with the two half-filled orbitals on the sulfur atom, forming two chemical bonds:



To show the spin-pairing of the electrons in the overlapping orbitals, we superimpose a half-arrow for each electron in each half-filled orbital and show that, within a bond, the electrons are spin-paired (one half-arrow is pointing up and the other is pointing down).

We also superimpose paired half-arrows in the filled sulfur  $s$  and  $p$  orbitals to represent the lone pair electrons in those orbitals. (Since those orbitals are full, they are not involved in bonding.)

A quantitative calculation of  $\text{H}_2\text{S}$  using valence bond theory yields bond energies, bond lengths, and bond angles. In our qualitative treatment, we simply show how orbital overlap leads to bonding and make a rough sketch of the molecule based on the overlapping orbitals. Notice that, because the overlapping orbitals on the central atom (sulfur) are  $p$  orbitals, and because  $p$  orbitals are oriented at  $90^\circ$  to one another, the predicted bond angle is  $90^\circ$ . The actual bond angle in  $\text{H}_2\text{S}$  is  $92^\circ$ . In the case of  $\text{H}_2\text{S}$ , a simple valence bond treatment matches well with the experimentally measured bond angle (in contrast to VSEPR theory, which predicts a bond angle of less than  $109.5^\circ$ ).

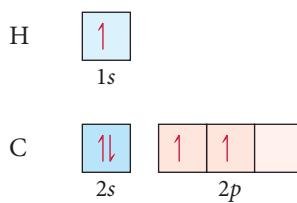
### Conceptual Connection 10.5 What Is a Chemical Bond? Part I

The answer to the question “What is a chemical bond?” depends on the bonding model. Answer these three questions:

- What is a covalent chemical bond according to the Lewis model?
- What is a covalent chemical bond according to valence bond theory?
- Why are the answers different?

## 10.7 Valence Bond Theory: Hybridization of Atomic Orbitals

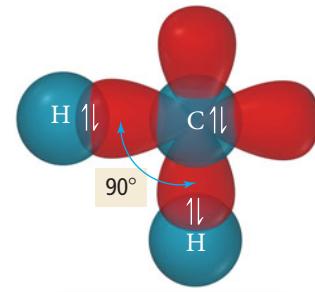
Although the overlap of half-filled *standard* atomic orbitals adequately explains the bonding in  $\text{H}_2\text{S}$ , it cannot adequately explain the bonding in many other molecules. For example, suppose we try to explain the bonding between hydrogen and carbon using the same approach. The valence electron configurations of H and C are as follows:



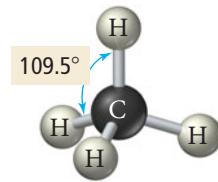
Carbon has only two half-filled orbitals and should therefore form only two bonds with two hydrogen atoms. We would therefore predict that carbon and hydrogen should form a molecule with the formula  $\text{CH}_2$  and with a bond angle of  $90^\circ$  (corresponding to the angle between any two  $p$  orbitals).

However, from experiments, we know that the stable compound formed from carbon and hydrogen is  $\text{CH}_4$  (methane), with bond angles of  $109.5^\circ$ . The experimental reality is different from our simple prediction in two ways. First, carbon forms bonds to four hydrogen atoms, not two. Second, the bond angles are much larger than the angle between two  $p$  orbitals. Valence bond theory accounts for the bonding in  $\text{CH}_4$  and many other polyatomic molecules by incorporating an additional concept called *orbital hybridization*.

So far, we have assumed that the overlapping orbitals that form chemical bonds are simply the standard  $s$ ,  $p$ , or  $d$  atomic orbitals. Valence bond theory treats the electrons in a molecule as if they occupied these standard atomic orbitals, but this is a major oversimplification. The concept of hybridization in valence bond theory is essentially a step toward recognizing that *the orbitals in a molecule are not necessarily the same as the orbitals in an atom*. **Hybridization** is a mathematical procedure in which the standard atomic orbitals are combined to form new atomic orbitals called **hybrid orbitals** that



Theoretical prediction



Observed reality

In Section 10.8, we examine another theory called *molecular orbital theory*, which treats electrons in a molecule as occupying orbitals that belong to the molecule as a whole.

As we saw in Chapter 9, the word *hybrid* comes from breeding. A *hybrid* is an offspring of two animals or plants of different standard races or breeds. Similarly, a hybrid orbital is a product of mixing two or more standard atomic orbitals.

In a more nuanced treatment, hybridization is not an all-or-nothing process—it can occur to varying degrees that are not always easy to predict. We saw earlier, for example, that sulfur does not hybridize very much in forming H<sub>2</sub>S.

correspond more closely to the actual distribution of electrons in chemically bonded atoms. Hybrid orbitals are still localized on individual atoms, but they have different shapes and energies from those of standard atomic orbitals.

Why do we hypothesize that electrons in some molecules occupy hybrid orbitals? In valence bond theory, a chemical bond is the overlap of two orbitals that together contain two electrons. The greater the overlap, the stronger the bond and the lower the energy. In hybrid orbitals, the electron probability density is more concentrated in a single directional lobe, allowing greater overlap with the orbitals of other atoms. Hybrid orbitals *minimize* the energy of the molecule by *maximizing* the orbital overlap in a bond.

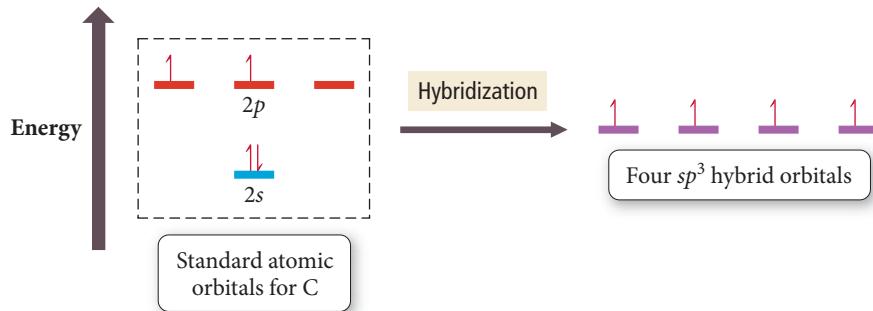
Hybridization, however, is not a free lunch—in most cases it actually costs some energy. So hybridization occurs only to the degree that the energy payback through bond formation is large. In general, therefore, the more bonds that an atom forms, the greater the tendency of its orbitals to hybridize. Central or interior atoms, which form the most bonds, have the greatest tendency to hybridize. Terminal atoms, which form the fewest bonds, have the least tendency to hybridize. *In this book, we focus on the hybridization of interior atoms and assume that all terminal atoms—those bonding to only one other atom—are unhybridized.* Hybridization is particularly important in carbon, which tends to form four bonds in its compounds and therefore always hybridizes.

Although we cannot examine the procedure for obtaining hybrid orbitals in mathematical detail here, we can make the following general statements regarding hybridization:

- ▶ The *number of standard atomic orbitals added together always equals the number of hybrid orbitals formed.* The total number of orbitals is conserved.
- ▶ The *particular combinations of standard atomic orbitals added together determines the shapes and energies of the hybrid orbitals formed.*
- ▶ The *particular type of hybridization that occurs* is the one that yields the *lowest overall energy for the molecule.* Since actual energy calculations are beyond the scope of this book, we use electron geometries as determined by VSEPR theory to predict the type of hybridization.

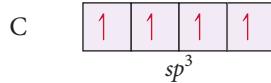
## sp<sup>3</sup> Hybridization

We can account for the tetrahedral geometry in CH<sub>4</sub> by the hybridization of the one 2s orbital and the three 2p orbitals on the carbon atom. The four new orbitals that result, called sp<sup>3</sup> hybrids, are shown in the following energy diagram:

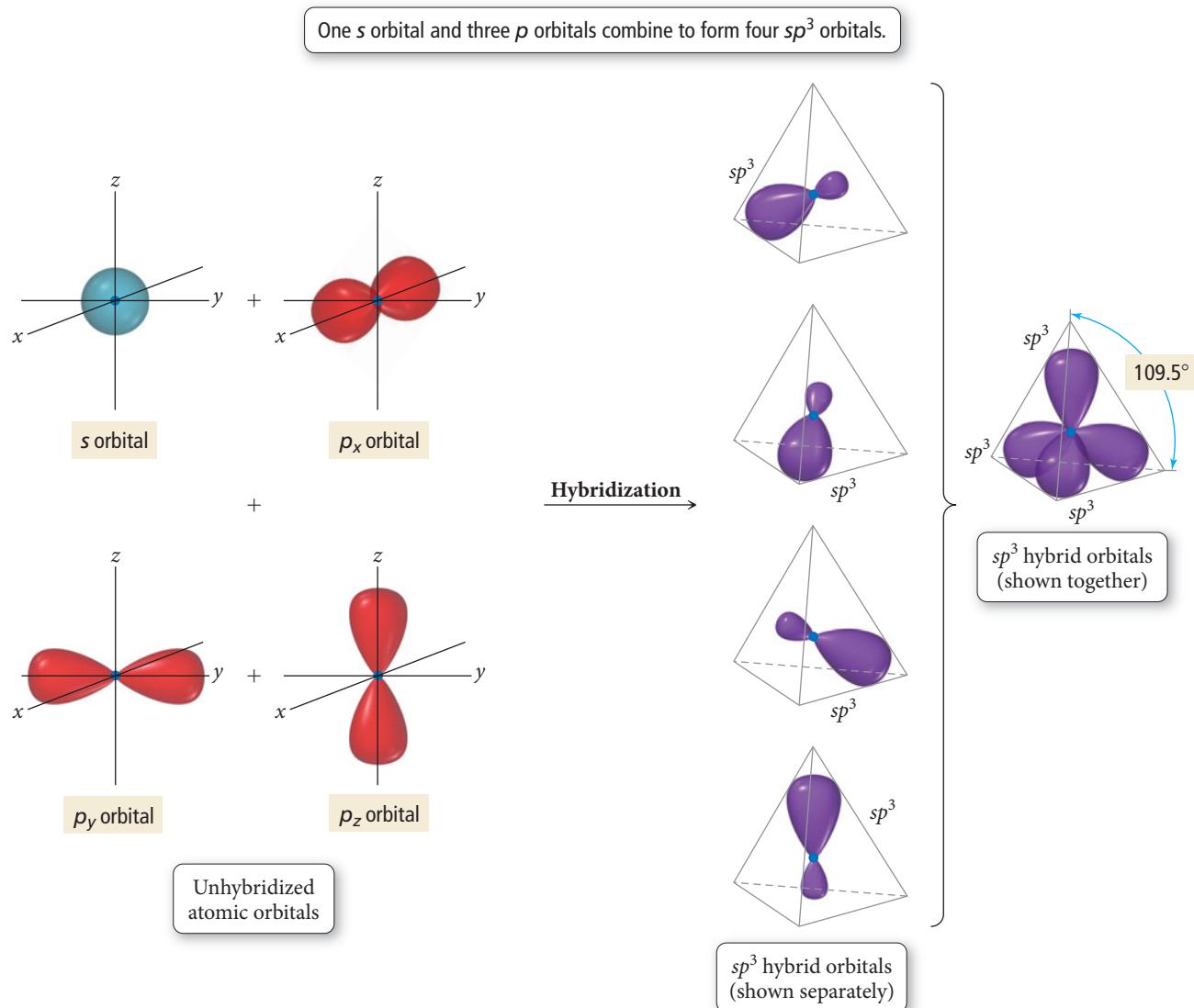


The notation “sp<sup>3</sup>” indicates that the hybrid orbitals are mixtures of one s orbital and three p orbitals. Notice that the hybrid orbitals all have the same energy—they are degenerate. The shapes of the sp<sup>3</sup> hybrid orbitals are shown in Figure 10.7 ▶. The four hybrid orbitals are arranged in a tetrahedral geometry with 109.5° angles between them.

We can write an orbital diagram for carbon using these hybrid orbitals:

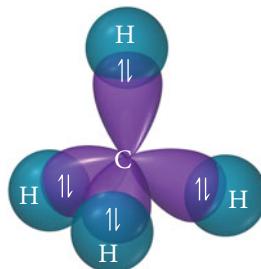


### Formation of $sp^3$ Hybrid Orbitals



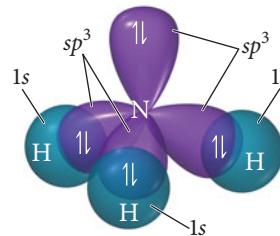
**▲ FIGURE 10.7**  $sp^3$  Hybridization One  $s$  orbital and three  $p$  orbitals combine to form four  $sp^3$  hybrid orbitals.

Carbon's four valence electrons occupy the orbitals singly with parallel spins as dictated by Hund's rule. With this electron configuration, carbon has four half-filled orbitals and can form four bonds with four hydrogen atoms:



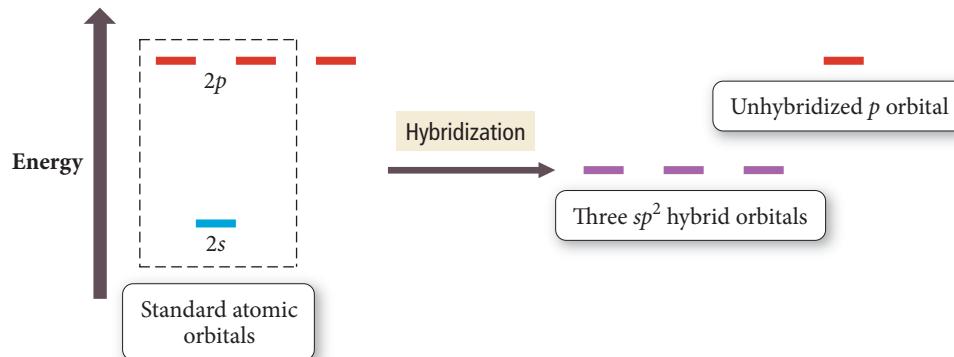
The geometry of the *overlapping orbitals* (the hybrids) is tetrahedral, with angles of  $109.5^\circ$  between the orbitals, so the *resulting geometry of the molecule* is tetrahedral, with  $109.5^\circ$  bond angles, in agreement with the experimentally measured geometry of  $\text{CH}_4$  and with the predicted VSEPR geometry.

Hybridized orbitals readily form chemical bonds because they tend to maximize overlap with other orbitals. However, if the central atom of a molecule contains lone pairs, hybrid orbitals can also accommodate them. For example, the nitrogen orbitals in ammonia are  $sp^3$  hybrids. Three of the hybrids are involved in bonding with three hydrogen atoms, but the fourth hybrid contains a lone pair. The presence of the lone pair lowers the tendency of nitrogen's orbitals to hybridize. (Remember that the tendency to hybridize increases with the number of bonds formed.) Therefore the bond angle in  $\text{NH}_3$  is  $107^\circ$ , a bit closer to the unhybridized  $p$  orbital bond angle of  $90^\circ$ .



## $sp^2$ Hybridization and Double Bonds

Hybridization of one  $s$  and two  $p$  orbitals results in three  $sp^2$  hybrids and one leftover unhybridized  $p$  orbital.

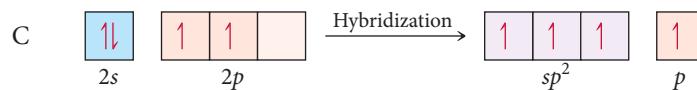


The notation “ $sp^2$ ” indicates that the hybrids are mixtures of one  $s$  orbital and two  $p$  orbitals. The shapes of the  $sp^2$  hybrid orbitals are shown in Figure 10.8 ►. Notice that the three hybrid orbitals have a trigonal planar geometry with  $120^\circ$  angles between them. The unhybridized  $p$  orbital is oriented perpendicular to the three hybridized orbitals.

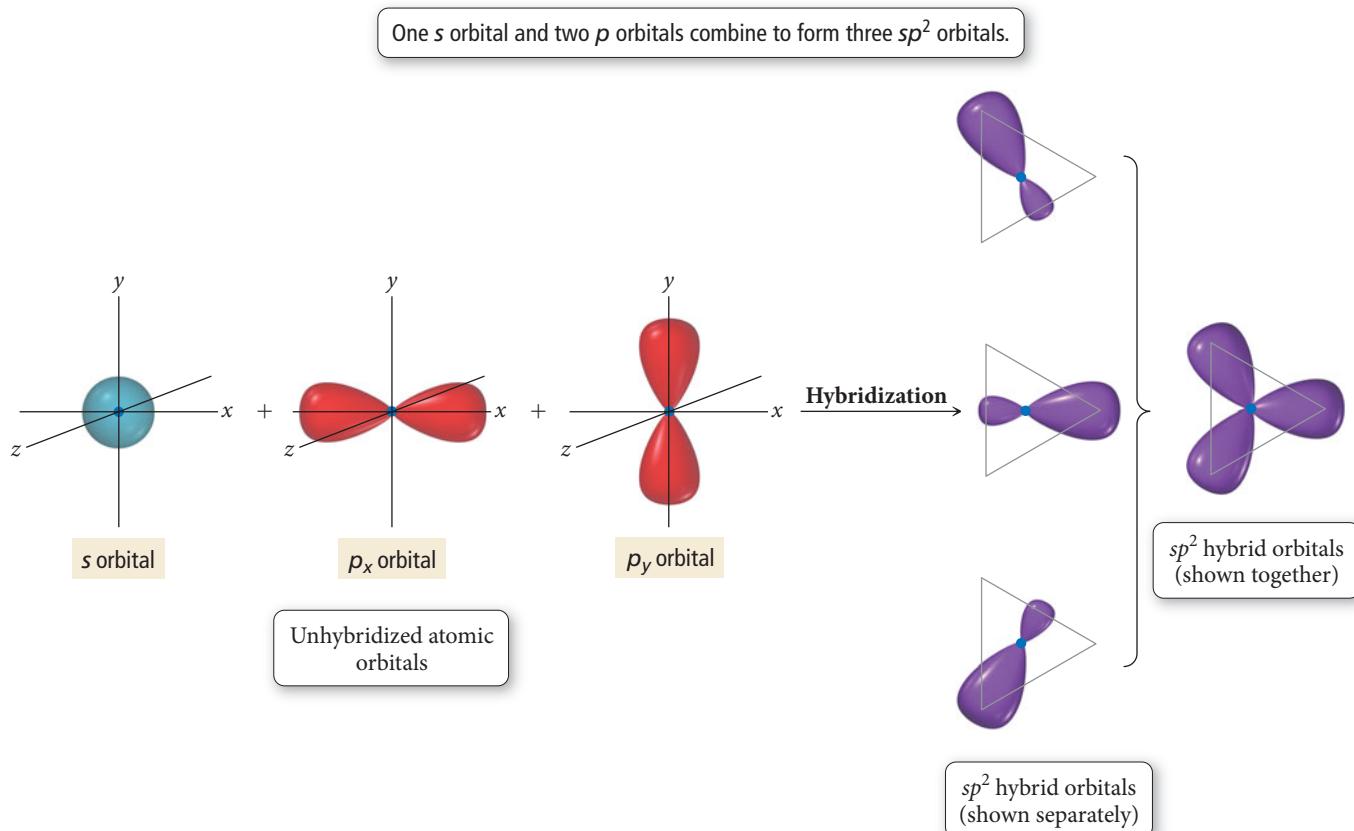
As an example of a molecule with  $sp^2$  hybrid orbitals, consider  $\text{H}_2\text{CO}$ . The unhybridized valence electron configurations of each of the atoms are as follows:

H	1		
	1s		
O	1 1	1 1	1 1
	2s	2p	
C	1 1	1 1	
	2s	2p	

Carbon is the central atom and the hybridization of its orbitals is  $sp^2$ :

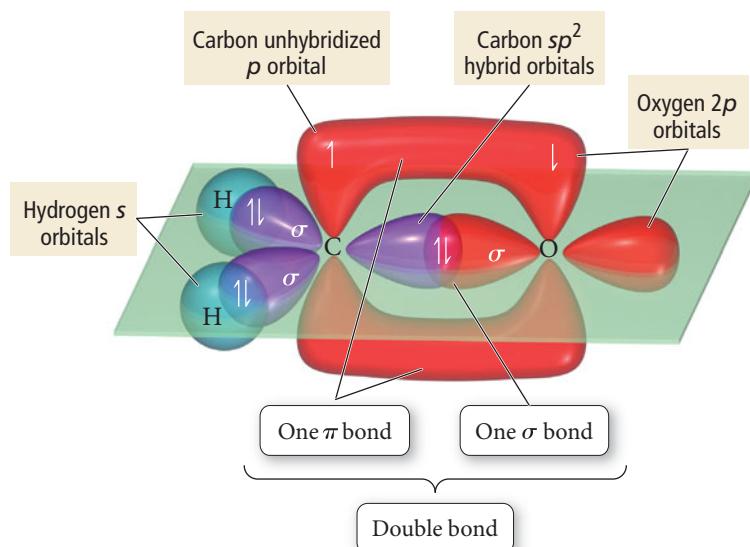


### Formation of $sp^2$ Hybrid Orbitals



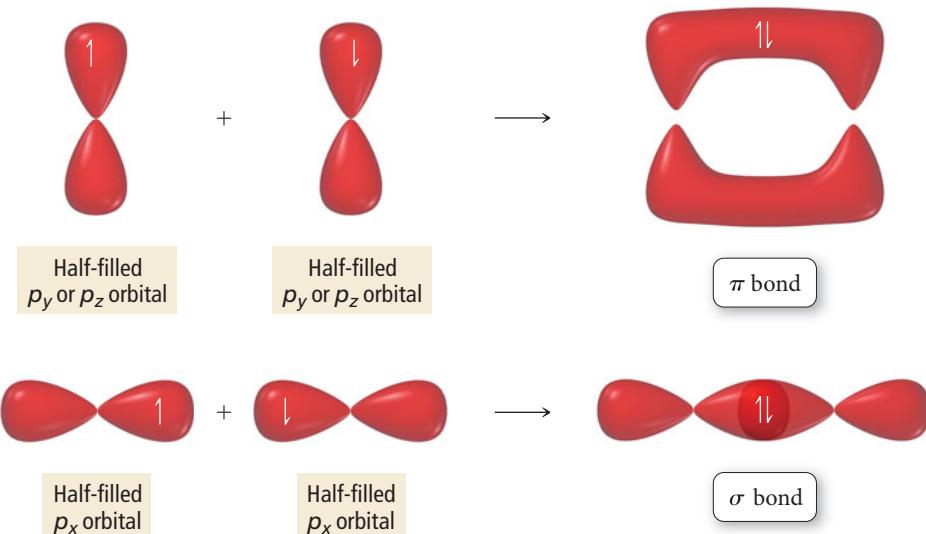
**▲ FIGURE 10.8**  $sp^2$  Hybridization One  $s$  orbital and two  $p$  orbitals combine to form three  $sp^2$  hybrid orbitals. One  $p$  orbital (not shown) remains unhybridized.

Each of the  $sp^2$  orbitals is half filled. The remaining electron occupies the leftover  $p$  orbital, even though it is slightly higher in energy. We can now see that the carbon atom has four half-filled orbitals and can therefore form four bonds: two with two hydrogen atoms and two (a double bond) with the oxygen atom. We draw the molecule and the overlapping orbitals as follows:

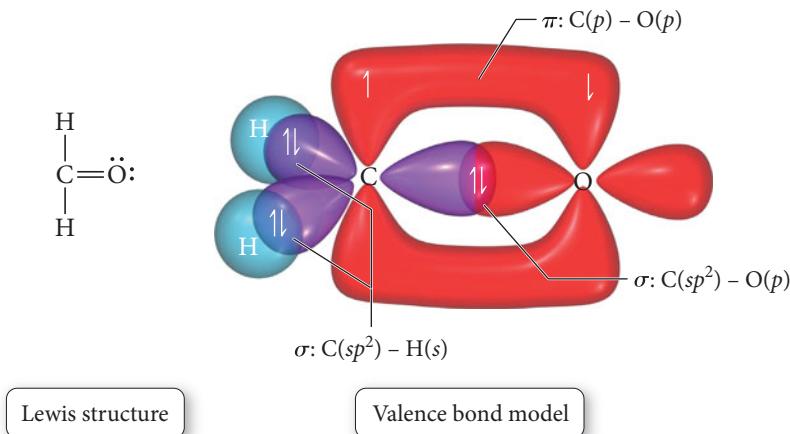


► **FIGURE 10.9 Sigma and Pi Bonding**

**Pi Bonding** When orbitals overlap side-by-side, the result is a pi ( $\pi$ ) bond. When orbitals overlap end-to-end, they form a sigma ( $\sigma$ ) bond. Two atoms can form only one sigma bond. A single bond is a sigma bond, a double bond consists of a sigma bond and a pi bond, a triple bond consists of a sigma bond and two pi bonds.



Notice the overlap between the half-filled  $p$  orbitals on the carbon and oxygen atoms. When  $p$  orbitals overlap this way (side by side) the resulting bond is a **pi ( $\pi$ ) bond**, and the electron density is above and below the internuclear axis. When orbitals overlap end-to-end, as in all of the rest of the bonds in the molecule, the resulting bond is a **sigma ( $\sigma$ ) bond** (Figure 10.9 ▲). Even though we represent the two electrons in a  $\pi$  bond as two half arrows in the upper lobe, they are actually spread out over both the upper and lower lobes (this is one of the limitations we encounter when we try to represent electrons with arrows). We can label all the bonds in the molecule using a notation that specifies the type of bond ( $\sigma$  or  $\pi$ ) as well as the type of overlapping orbitals. We have included this notation, as well as the Lewis structure of  $\text{H}_2\text{CO}$  for comparison, in the bonding diagram for  $\text{H}_2\text{CO}$ :

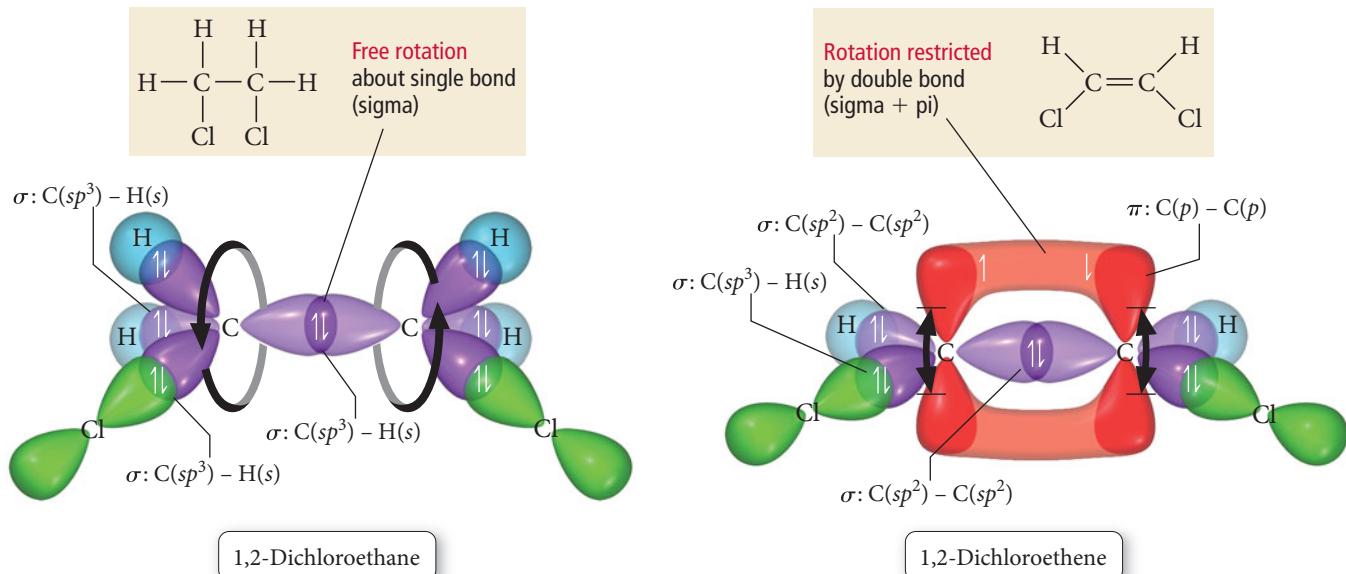


Notice the correspondence between valence bond theory and the Lewis model. In both models, the central carbon atom is forming four bonds: two single bonds and one double bond. However, valence bond theory gives us more insight into the bonds. The double bond between carbon and oxygen according to valence bond theory consists of two different kinds of bonds—one  $\sigma$  and one  $\pi$ —while in the Lewis model the two bonds within the double bond appear identical. *A double bond in the Lewis model always corresponds to one  $\sigma$  and one  $\pi$  bond in valence bond theory.* In general,  $\pi$  bonds are weaker than  $\sigma$  bonds because the side-to-side orbital overlap tends to be less efficient than the end-to-end orbital overlap. Consequently, the  $\pi$  bond in a double bond is generally easier to break than the  $\sigma$  bond. Valence bond theory, as you can see, gives us more insight into the nature of a double bond than the Lewis model.

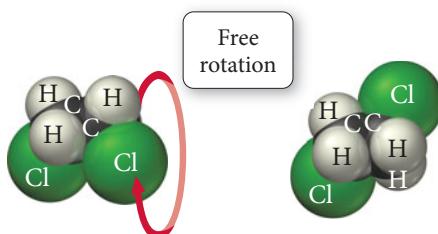
One—and only one— $\sigma$  bond forms between any two atoms. Additional bonds must be  $\pi$  bonds.

Valence bond theory allows us to see why the rotation about a double bond is severely restricted. Because of the side-by-side overlap of the  $p$  orbitals, the  $\pi$  bond must essentially break for rotation to occur (see Chemistry in Your Day: *The Chemistry of Vision*). Valence bond theory shows us the types of orbitals involved in the bonding and their shapes. In  $\text{H}_2\text{CO}$ , the  $sp^2$  hybrid orbitals on the central atom are trigonal planar with  $120^\circ$  angles between them, so the resulting predicted geometry of the molecule is trigonal planar with  $120^\circ$  bond angles. The experimentally measured bond angles in  $\text{H}_2\text{CO}$ , as discussed previously, are  $121.9^\circ$  for the HCO bond and  $116.2^\circ$  for the HCH bond angle, close to the predicted values.

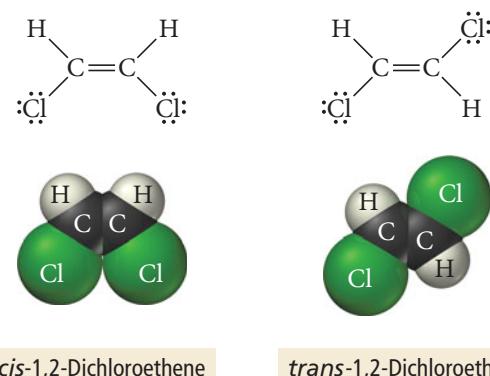
Although rotation about a double bond is highly restricted, rotation about a single bond is relatively unrestricted. Consider, for example, the structures of two chlorinated hydrocarbons, 1,2-dichloroethane and 1,2-dichloroethene.



The hybridization of the carbon atoms in 1,2-dichloroethane is  $sp^3$ , resulting in relatively free rotation about the sigma single bond. Consequently, there is no difference between the following two structures at room temperature, because they quickly interconvert:



In contrast, rotation about the double bond (sigma + pi) in 1,2-dichloroethene is restricted, so that, at room temperature, 1,2-dichloroethene exists in two forms:

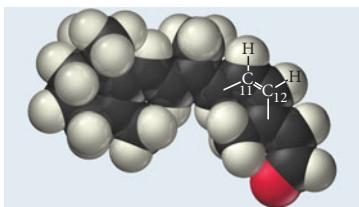




## Chemistry in Your Day

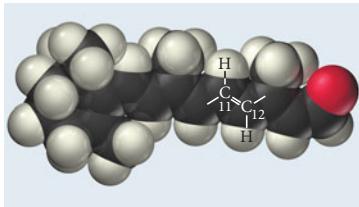
### The Chemistry of Vision

In the human eye, light is detected by a chemical switch involving the breaking and re-forming of a  $\pi$  bond. The back portion of the eye, the retina, is coated with millions of light-sensitive cells called rods and cones. Each of these cells contains proteins that bind a compound called 11-*cis*-retinal, which has the following structure:



11-*cis*-Retinal

When a photon of sufficient energy strikes a rod or cone, it causes the isomerization of 11-*cis*-retinal to all-*trans*-retinal:

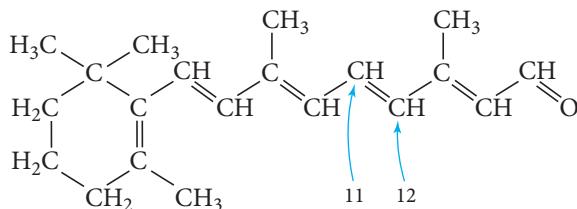


all-*trans*-Retinal

The isomerization occurs because visible light contains enough energy to break the  $\pi$  bond between the eleventh and twelfth carbon atom in 11-*cis*-retinal. The  $\sigma$  bond, which is stronger, does not break, allowing the molecule to freely rotate about that bond. The  $\pi$  bond then re-forms with the molecule in the *trans* conformation. The different shape of the resultant all-*trans*-retinal causes conformational changes in the protein to which it is bound. These changes cause an electrical signal to be transmitted to the brain.

### Question

What is the hybridization of the eleventh and twelfth carbon atoms in retinal?



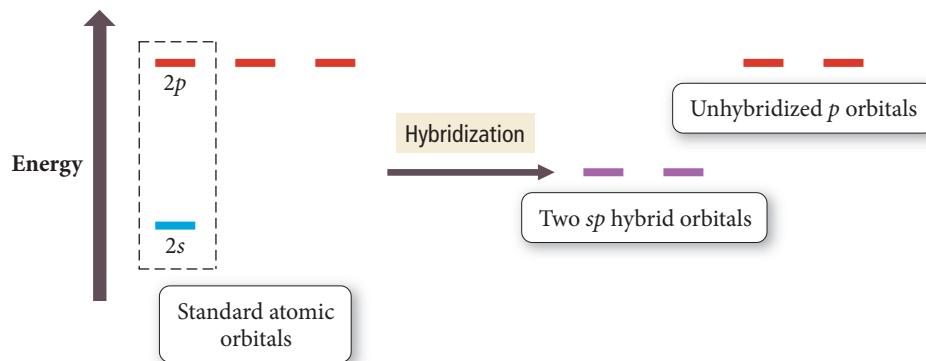
These two forms of 1,2-dichloroethene are indeed different compounds with different properties. We distinguish between them with the designations *cis* (meaning “same side”) and *trans* (meaning “opposite sides”). Compounds such as these, with the same molecular formula but different structures or different spatial arrangement of atoms, are called *isomers*. Nature can—and does—make different compounds out of the same atoms by arranging the atoms in different ways. Isomerism is common throughout chemistry and especially important in organic chemistry, as we will discuss in Chapter 20.

### Conceptual Connection 10.6 Single and Double Bonds

In Section 9.10 we learned that double bonds are stronger and shorter than single bonds. For example, a C—C single bond has an average bond energy of 347 kJ/mole while a C=C double bond has an average bond energy of 611 kJ/mole. Use valence bond theory to explain why a double bond is *not* simply twice as strong as a single bond.

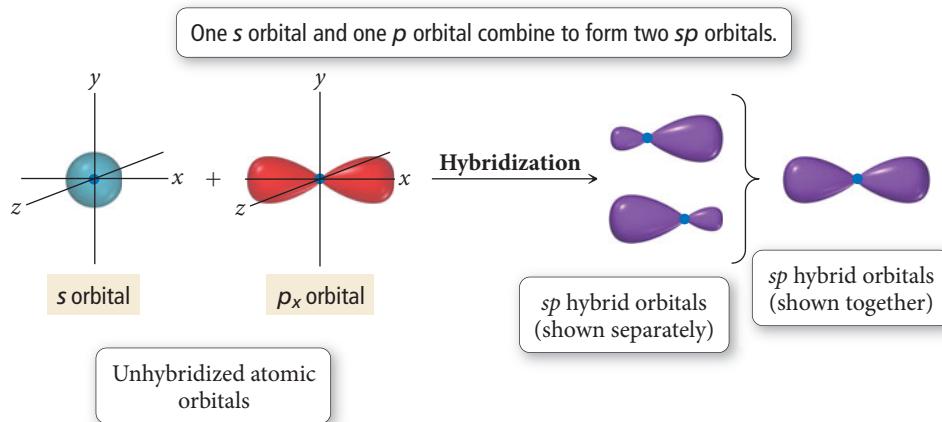
### *sp* Hybridization and Triple Bonds

Hybridization of one *s* and one *p* orbital results in two *sp* hybrid orbitals and two leftover unhybridized *p* orbitals.



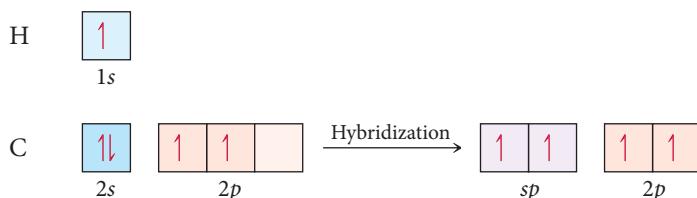
The shapes of the *sp* hybrid orbitals are shown in Figure 10.10 ▼. Notice that the two *sp* hybrid orbitals are arranged in a linear geometry with a 180° angle between them. The unhybridized *p* orbitals are oriented in the plane that is perpendicular to the hybridized *sp* orbitals.

### Formation of *sp* Hybrid Orbitals

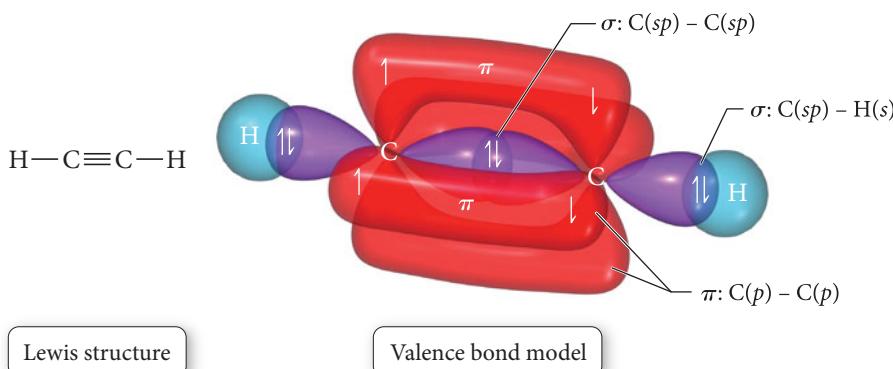


◀ FIGURE 10.10 *sp* Hybridization One *s* orbital and one *p* orbital combine to form two *sp* hybrid orbitals. Two *p* orbitals (not shown) remain unhybridized.

The acetylene molecule,  $\text{HC}\equiv\text{CH}$ , has *sp* hybrid orbitals. The four valence electrons of carbon can distribute themselves among the two *sp* hybrid orbitals and the two *p* orbitals:



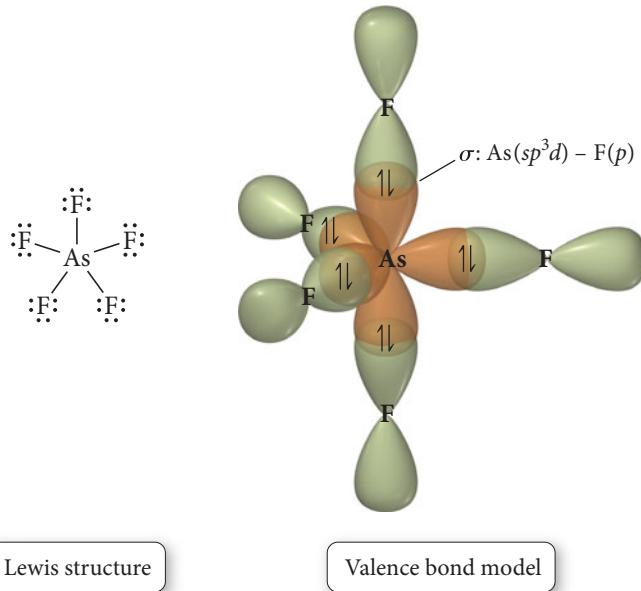
Each carbon atom then has four half-filled orbitals and can form four bonds: one with a hydrogen atom and three (a triple bond) with the other carbon atom. We draw the molecule and the overlapping orbitals as follows:



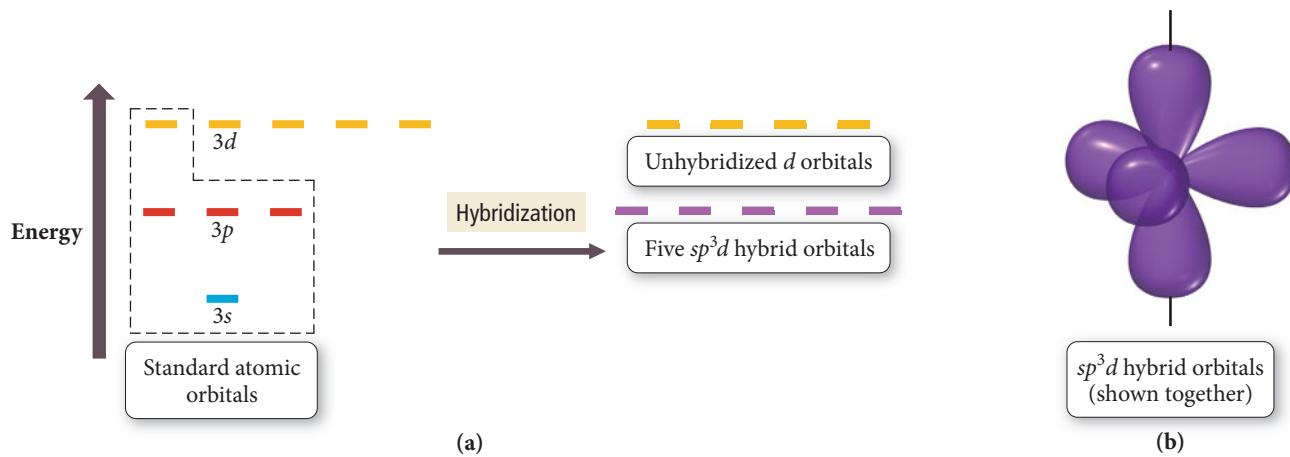
Notice that the triple bond between the two carbon atoms consists of two  $\pi$  bonds (overlapping  $p$  orbitals) and one  $\sigma$  bond (overlapping  $sp$  orbitals). The  $sp$  orbitals on the carbon atoms are linear with  $180^\circ$  between them, so the resulting geometry of the molecule is linear with  $180^\circ$  bond angles, in agreement with the experimentally measured geometry of  $\text{HC}\equiv\text{CH}$ , and also in agreement with the prediction of VSEPR theory.

### $sp^3d$ and $sp^3d^2$ Hybridization

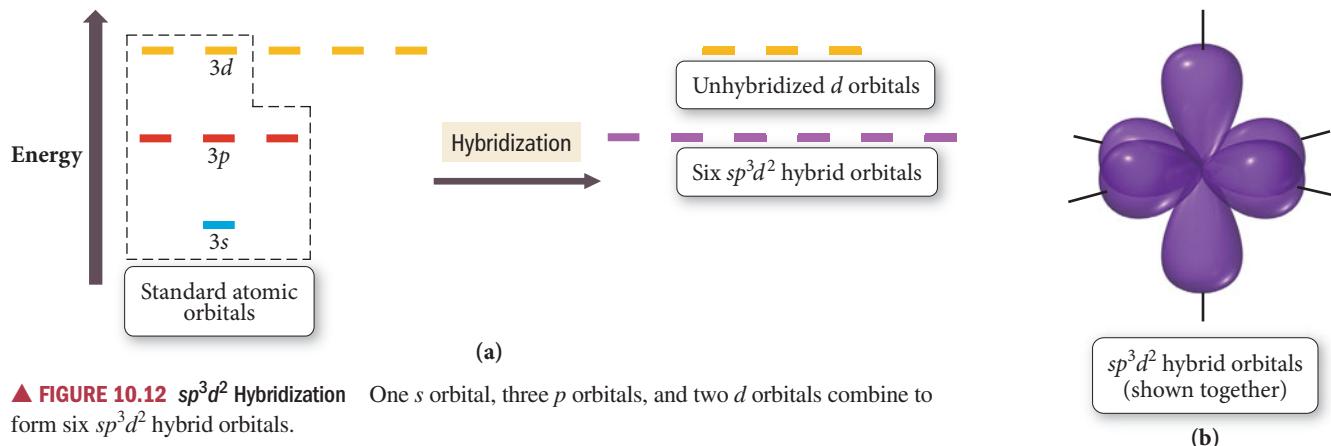
Recall that, according to the Lewis model, elements occurring in the third row of the periodic table (or below) can exhibit expanded octets (see Section 9.9). The equivalent concept in valence bond theory is hybridization involving the  $d$  orbitals. For third-period elements, the  $3d$  orbitals are involved in hybridization because their energies are close to the energies of the  $3s$  and  $3p$  orbitals. The hybridization of one  $s$  orbital, three  $p$  orbitals, and one  $d$  orbital results in  $sp^3d$  hybrid orbitals, as shown in Figure 10.11a ▶. The five  $sp^3d$  hybrid orbitals have a trigonal bipyramidal arrangement, as shown in Figure 10.11b ▶. As an example of  $sp^3d$  hybridization, consider arsenic pentafluoride,  $\text{AsF}_5$ . The arsenic atom bonds to five fluorine atoms by overlap between the  $sp^3d$  hybrid orbitals on arsenic and  $p$  orbitals on the fluorine atoms, as shown here:



The  $sp^3d$  orbitals on the arsenic atom are trigonal bipyramidal, so the molecular geometry is trigonal bipyramidal.

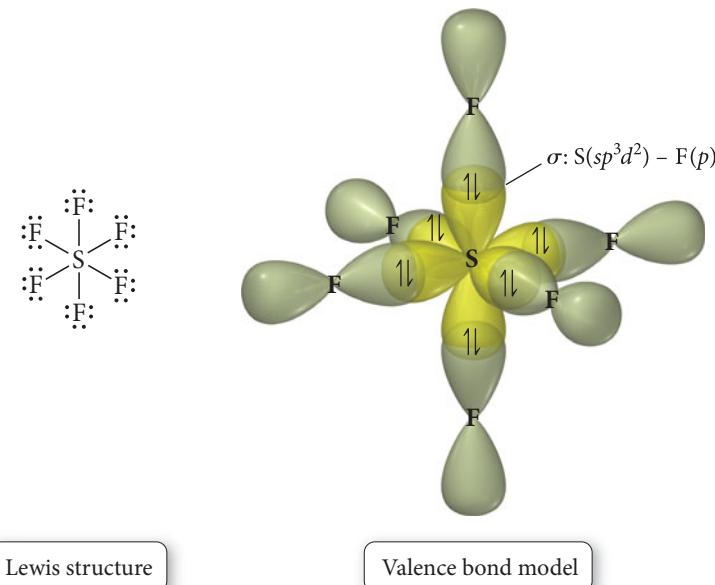


▲ FIGURE 10.11  $sp^3d$  Hybridization One  $s$  orbital, three  $p$  orbitals, and one  $d$  orbital combine to form five  $sp^3d$  hybrid orbitals.



**▲ FIGURE 10.12**  $sp^3d^2$  Hybridization One  $s$  orbital, three  $p$  orbitals, and two  $d$  orbitals combine to form six  $sp^3d^2$  hybrid orbitals.

The hybridization of one  $s$  orbital, three  $p$  orbitals, and *two*  $d$  orbitals results in  $sp^3d^2$  hybrid orbitals, as shown in Figure 10.12a ▲. The six  $sp^3d^2$  hybrid orbitals have an octahedral geometry, shown in Figure 10.12b ▲. As an example of  $sp^3d^2$  hybridization, consider sulfur hexafluoride,  $SF_6$ . The sulfur atom bonds to six fluorine atoms by overlap between the  $sp^3d^2$  hybrid orbitals on sulfur and  $p$  orbitals on the fluorine atoms:



The  $sp^3d^2$  orbitals on the sulfur atom are octahedral, so the molecular geometry is octahedral, again in agreement with VSEPR theory and with the experimentally observed geometry.

## Writing Hybridization and Bonding Schemes

We have now studied examples of the five main types of atomic orbital hybridization. *But how do we know which hybridization scheme best describes the orbitals of a specific atom in a specific molecule?* In computational valence bond theory, the energy of the molecule is calculated using a computer; the degree of hybridization as well as the type of hybridization are varied to find the combination that gives the molecule the lowest overall energy. For our purposes, we can assign a hybridization scheme from the electron geometry—determined using VSEPR theory—of the central atom (or interior atoms) of the molecule. The five VSEPR electron geometries and the corresponding hybridization

**TABLE 10.3 Hybridization Scheme from Electron Geometry**

Number of Electron Groups	Electron Geometry (from VSEPR Theory)	Hybridization Scheme
2	Linear	$sp$
3	Trigonal planar	$sp^2$
4	Tetrahedral	$sp^3$
5	Trigonal bipyramidal	$sp^3d$
6	Octahedral	$sp^3d^2$

schemes are shown in Table 10.3. For example, if the electron geometry of the central atom is tetrahedral, then the hybridization is  $sp^3$ , and if the electron geometry is octahedral, then the hybridization is  $sp^3d^2$ , and so on. Although this method of determining the hybridization scheme is not 100% accurate (for example, it predicts that  $H_2S$  should be  $sp^3$  when in fact  $H_2S$  is largely unhybridized) it is the best we can do without more complex computer-based calculations.

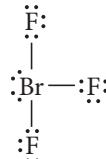
We are now ready to put the Lewis model and valence bond theory together to describe bonding in molecules. In the procedure and examples that follow, you will learn how to write a *hybridization and bonding scheme* for a molecule. This involves drawing the Lewis structure for the molecule, determining its geometry using VSEPR theory, determining the hybridization of the interior atoms, drawing the molecule with its overlapping orbitals, and labeling each bond with the  $\sigma$  and  $\pi$  notation followed by the type of overlapping orbitals. As you can see, this procedure involves virtually everything you have learned about bonding in this chapter and Chapter 9. The procedure for writing a hybridization and bonding scheme is shown in the left column, with two examples of how to apply the procedure in the columns to the right.

**PROCEDURE FOR...****Hybridization and Bonding Scheme****1. Write the Lewis structure for the molecule.****EXAMPLE 10.6****Hybridization and Bonding Scheme**

Write a hybridization and bonding scheme for bromine trifluoride,  $\text{BrF}_3$ .

**SOLUTION**

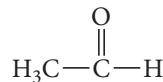
$\text{BrF}_3$  has 28 valence electrons and the following Lewis structure:

**2. Use VSEPR theory to predict the electron geometry about the central atom (or interior atoms).**

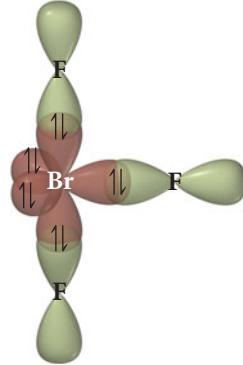
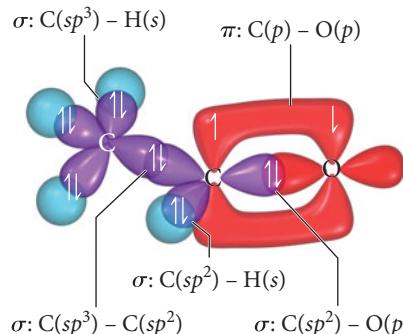
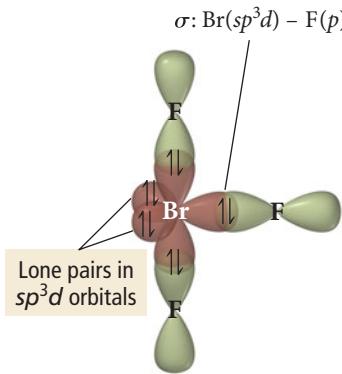
The bromine atom has five electron groups and therefore has a trigonal bipyramidal electron geometry.

**EXAMPLE 10.7****Hybridization and Bonding Scheme**

Write a hybridization and bonding scheme for acetaldehyde,

**3. Select the correct hybridization for the central atom (or interior atoms) based on the electron geometry (see Table 10.3).**

A trigonal bipyramidal electron geometry corresponds to  $sp^3d$  hybridization.

**4. Sketch the molecule, beginning with the central atom and its orbitals. Show overlap with the appropriate orbitals on the terminal atoms.****5. Label all bonds using the  $\sigma$  or  $\pi$  notation followed by the type of overlapping orbitals.****FOR PRACTICE 10.6**

Write a hybridization and bonding scheme for  $\text{XeF}_4$ .

**FOR PRACTICE 10.7**

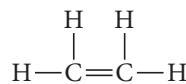
Write a hybridization and bonding scheme for HCN.

**EXAMPLE 10.8** Hybridization and Bonding Scheme


Use valence bond theory to write a hybridization and bonding scheme for ethene,  
 $\text{H}_2\text{C}=\text{CH}_2$

**SOLUTION**

1. Write the Lewis structure for the molecule.



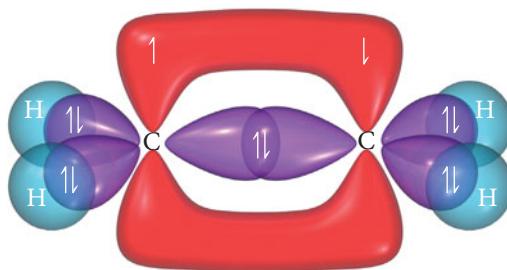
2. Apply VSEPR theory to predict the electron geometry about the central atom (or interior atoms).

The molecule has two interior atoms. Since each atom has three electron groups (one double bond and two single bonds), the electron geometry about each atom is trigonal planar.

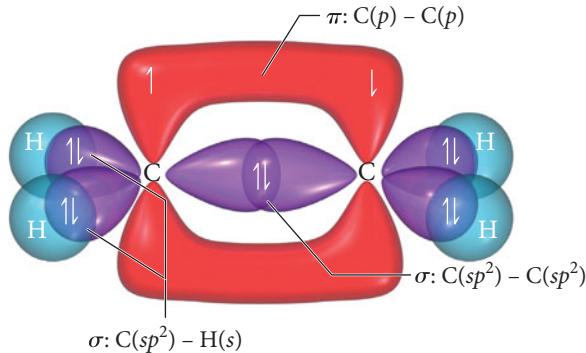
3. Select the correct hybridization for the central atom (or interior atoms) based on the electron geometry (see Table 10.3).

A trigonal planar geometry corresponds to  $sp^2$  hybridization.

4. Sketch the molecule, beginning with the central atom and its orbitals. Show overlap with the appropriate orbitals on the terminal atoms.



5. Label all bonds using the  $\sigma$  or  $\pi$  notation followed by the type of overlapping orbitals.


**FOR PRACTICE 10.8**

Use valence bond theory to write a hybridization and bonding scheme for  $\text{CO}_2$ .

**FOR MORE PRACTICE 10.8**

What is the hybridization of the central iodine atom in  $\text{I}_3^-$ ?

## 10.8 Molecular Orbital Theory: Electron Delocalization

Valence bond theory can explain many aspects of chemical bonding—such as the rigidity of a double bond—but it also has limitations. In valence bond theory, we treat electrons as if they reside in the quantum-mechanical orbitals that we calculated for atoms. This is a significant oversimplification that we partially compensate for by hybridization. Nevertheless, we can do better.

In Chapter 7, we learned that the mathematical derivation of energies and orbitals for electrons *in atoms* comes from solving the Schrödinger equation for the atom of interest. For a molecule, we can theoretically do the same thing. The resulting orbitals would be the actual *molecular* orbitals of the molecule as a whole (in contrast to valence bond theory, in which the orbitals are those of individual atoms). As it turns out, however, solving the Schrödinger equation exactly for even the simplest molecules is impossible without making some approximations.

In **molecular orbital (MO) theory**, we do not actually solve the Schrödinger equation for a molecule directly. Instead, we use a trial function, an “educated guess” as to what the solution might be. In other words, rather than mathematically solving the Schrödinger equation, which would give us a mathematical function describing an orbital, we start with a trial mathematical function for the orbital. We then test the trial function to see how well it “works.”

We can understand this process by analogy to solving an algebraic equation. Suppose we want to know  $x$  in the equation  $4x + 5 = 70$  without actually solving the equation. For an easy equation like this one, we might first estimate that  $x = 16$ . We can then determine how well our estimate works by substituting  $x = 16$  into the equation. If the estimate did not work, we could try again until we found the right value of  $x$ . (In this case, we can quickly see that  $x$  must be a little more than 16.)

In molecular orbital theory, the estimating procedure is analogous. However, we need to add one more important concept to get at the heart of molecular orbital theory. In order to determine how well a trial function for an orbital “works” in molecular orbital theory, we calculate its energy. No matter how good our trial function, *we can never do better than nature at minimizing the energy of the orbital*. In other words, we can devise any trial function for an orbital in a molecule and calculate its energy. The energy we calculate for the devised orbital will always be greater than or (at best) equal to the energy of the actual orbital.

How does this help us? The best possible orbital will therefore be the one with the minimum energy. In modern molecular orbital theory, computer programs are designed to try many different variations of a guessed orbital and compare the energies of each one. The variation with the lowest energy is the best approximation for the actual molecular orbital.

Molecular orbital theory is a specific application of a more general quantum-mechanical approximation technique called the variational method. In the variational method, the energy of a trial function within the Schrödinger equation is minimized.

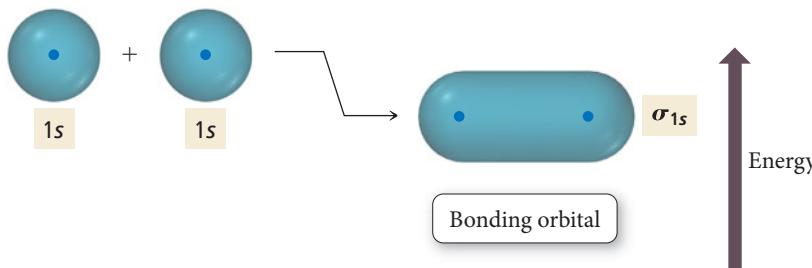
We calculate the energy of an estimated orbital by substituting it into the Schrödinger equation and solving for the energy.

## Linear Combination of Atomic Orbitals (LCAO)

The simplest trial functions that work reasonably well in molecular orbital theory turn out to be linear combinations of atomic orbitals, or LCAOs. An LCAO molecular orbital is a *weighted linear sum—analogous to a weighted average—of the valence atomic orbitals* of the atoms in the molecule. At first glance, this concept might seem very similar to that of hybridization in valence bond theory. However, in valence bond theory, hybrid orbitals are weighted linear sums of the valence atomic orbitals of a *particular atom*, and the hybrid orbitals remain *localized* on that atom. In molecular orbital theory, the molecular orbitals are weighted linear sums of the valence atomic orbitals of *all the atoms* in a molecule, and many of the molecular orbitals are *delocalized* over the entire molecule.

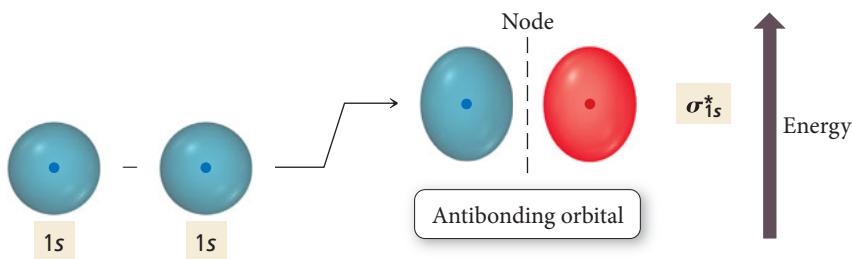
When molecular orbitals are calculated mathematically, it is actually the wave functions corresponding to the orbitals that are combined.

Consider the  $\text{H}_2$  molecule. One of the molecular orbitals for  $\text{H}_2$  is simply an equally weighted sum of the  $1s$  orbital from one atom and the  $1s$  orbital from the other. We can represent this pictorially and energetically as follows:



The name of this molecular orbital is  $\sigma_{1s}$ . The  $\sigma$  comes from the shape of the orbital, which looks like a  $\sigma$  bond in valence bond theory, and the  $1s$  comes from its formation by a linear sum of  $1s$  orbitals. The  $\sigma_{1s}$  orbital is lower in energy than either of the two  $1s$  atomic orbitals from which it was formed. For this reason, this orbital is called a **bonding orbital**. When electrons occupy bonding molecular orbitals, the energy of the electrons is lower than it would be if they were occupying atomic orbitals.

We can think of a molecular orbital in a molecule in much the same way that we think about an atomic orbital in an atom. Electrons will seek the lowest energy molecular orbital available, but just as an atom has more than one atomic orbital (and some may be empty), a molecule has more than one molecular orbital (and some may be empty). The next molecular orbital of  $H_2$  is approximated by summing the  $1s$  orbital on one hydrogen atom with the *negative* (opposite phase) of the  $1s$  orbital on the other hydrogen atom.

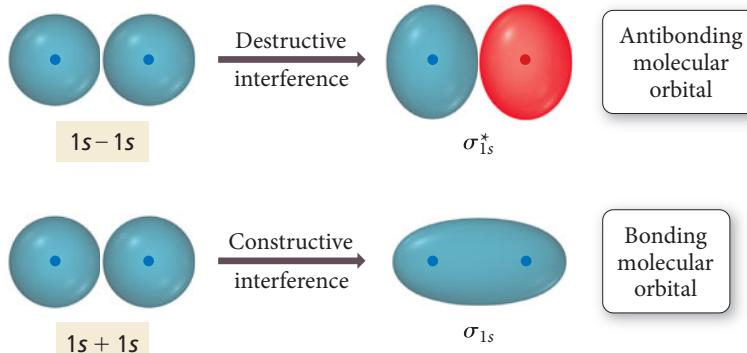


The different phases of the orbitals result in *destructive interference* between them. The resulting molecular orbital therefore has a node between the two atoms. The different colors (red and blue) on either side of the node represent the different phases of the orbital (see Section 7.6). The name of this molecular orbital is  $\sigma_{1s}^*$ . The star indicates that this orbital is an **antibonding orbital**. Electrons in antibonding orbitals have higher energies than they did in their respective atomic orbitals and therefore tend to raise the energy of the system (relative to the unbonded atoms).

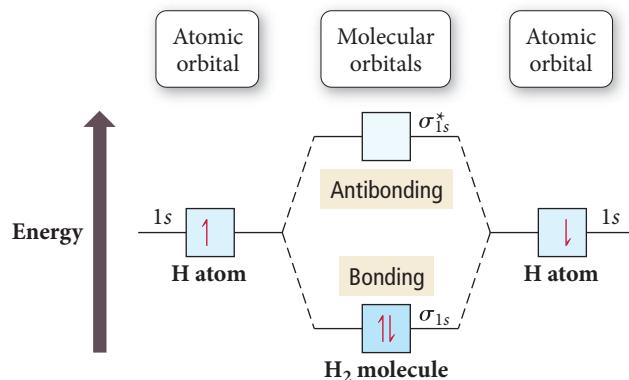
In general, when two atomic orbitals are added together to form molecular orbitals, one of the resultant molecular orbitals will be lower in energy (the bonding orbital) than the atomic orbitals and the other will be higher in energy (the antibonding orbital). Remember that electrons in orbitals behave like waves. The bonding molecular orbital arises out of constructive interference between the overlapping atomic orbitals because both orbitals have the same phase. The antibonding orbital arises out of destructive interference between the overlapping atomic orbitals because *subtracting* one from the other means the two interacting orbitals have opposite phases (Figure 10.13 ▶).

For this reason, the bonding orbital has an increased electron density in the internuclear region while the antibonding orbital has a node in the internuclear region. Bonding orbitals have greater electron density in the internuclear region, thereby lowering their energy compared to the orbitals in nonbonded atoms. Antibonding orbitals have less electron density in the internuclear region, and their energies are generally higher than in the orbitals of nonbonded atoms.

► **FIGURE 10.13** Formation of Bonding and Antibonding Orbitals Constructive interference between two atomic orbitals gives rise to a molecular orbital that is lower in energy than the atomic orbitals. This is the bonding orbital. Destructive interference between two atomic orbitals gives rise to a molecular orbital that is higher in energy than the atomic orbitals. This is the antibonding orbital.



We put all of this together in the molecular orbital energy diagram for H<sub>2</sub>:



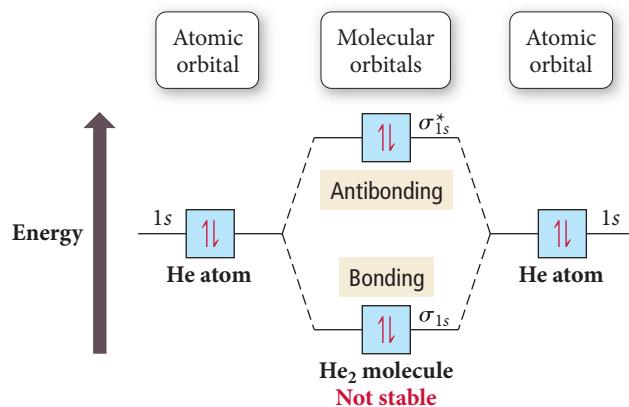
The molecular orbital (MO) diagram shows that two hydrogen atoms can lower their overall energy by forming H<sub>2</sub> because the electrons can move from higher energy atomic orbitals into the lower energy σ<sub>1s</sub> bonding molecular orbital. In molecular orbital theory, we define the **bond order** of a diatomic molecule such as H<sub>2</sub> as follows:

$$\text{Bond order} = \frac{(\text{number of electrons in bonding MOs}) - (\text{number of electrons in antibonding MOs})}{2}$$

For H<sub>2</sub>, the bond order is 1:

$$\text{H}_2 \text{ bond order} = \frac{2 - 0}{2} = 1$$

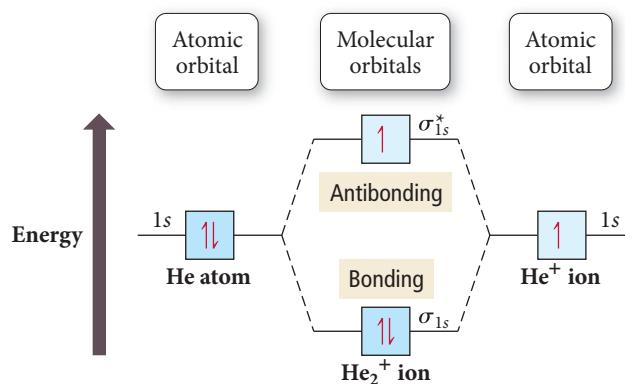
A positive bond order means that there are more electrons in bonding molecular orbitals than in antibonding molecular orbitals. The electrons will therefore have lower energy than they did in the orbitals of the isolated atoms, and a chemical bond will form. In general, the higher the bond order, the stronger the bond. A negative or zero bond order indicates that a bond will *not* form between the atoms. For example, consider the MO diagram for He<sub>2</sub>:



Notice that the two additional electrons must go into the higher energy antibonding orbital. There is no net stabilization by joining two helium atoms to form a helium molecule, as indicated by the bond order:

$$\text{He}_2 \text{ bond order} = \frac{2 - 2}{2} = 0$$

So according to MO theory,  $\text{He}_2$  should not exist as a stable molecule, and indeed it does not. Another interesting case is the helium–helium ion,  $\text{He}_2^+$ , with the following MO diagram:



The bond order is  $\frac{1}{2}$ , indicating that  $\text{He}_2^+$  should exist, and indeed it does.

### Summarizing LCAO–MO Theory:

- ▶ We can approximate molecular orbitals (MOs) as a linear combination of atomic orbitals (AOs). The total number of MOs formed from a particular set of AOs always equals the number of AOs in the set.
- ▶ When two AOs combine to form two MOs, one MO is lower in energy (the bonding MO) and the other is higher in energy (the antibonding MO).
- ▶ When assigning the electrons of a molecule to MOs, fill the lowest energy MOs first with a maximum of two spin-paired electrons per orbital.
- ▶ When assigning electrons to two MOs of the same energy, follow Hund's rule—fill the orbitals singly first, with parallel spins, before pairing.
- ▶ The bond order in a diatomic molecule is the number of electrons in bonding MOs minus the number in antibonding MOs divided by two. Stable bonds require a positive bond order (more electrons in bonding MOs than in antibonding MOs).

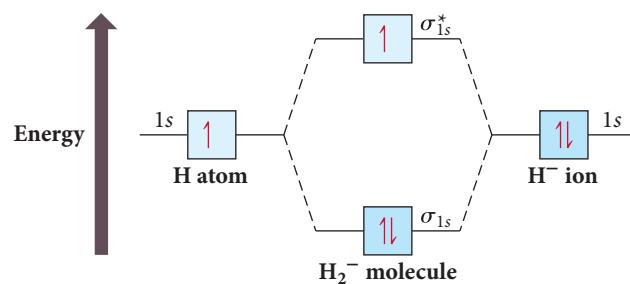
Notice the power of the molecular orbital approach. Every electron that enters a bonding molecular orbital stabilizes the molecule or polyatomic ion, and every electron that enters an antibonding molecular orbital destabilizes it. The emphasis on electron pairs has been removed. One electron in a bonding molecular orbital stabilizes half as much as two, so a bond order of one-half is nothing mysterious.

### EXAMPLE 10.9 Bond Order

Use molecular orbital theory to predict the bond order in  $\text{H}_2^-$ . Is the  $\text{H}_2^-$  bond a stronger or weaker bond than the  $\text{H}_2$  bond?

#### SOLUTION

The  $\text{H}_2^-$  ion has three electrons. Assign the three electrons to the molecular orbitals, filling lower energy orbitals first and proceeding to higher energy orbitals.



Calculate the bond order by subtracting the number of electrons in antibonding orbitals from the number in bonding orbitals and dividing the result by two.

$$\text{H}_2^- \text{ bond order} = \frac{2 - 1}{2} = +\frac{1}{2}$$

Since the bond order is positive,  $\text{H}_2^-$  should be stable. However, the bond order of  $\text{H}_2^-$  is lower than the bond order of  $\text{H}_2$  (which is 1); therefore, the bond in  $\text{H}_2^-$  is weaker than in  $\text{H}_2$ .

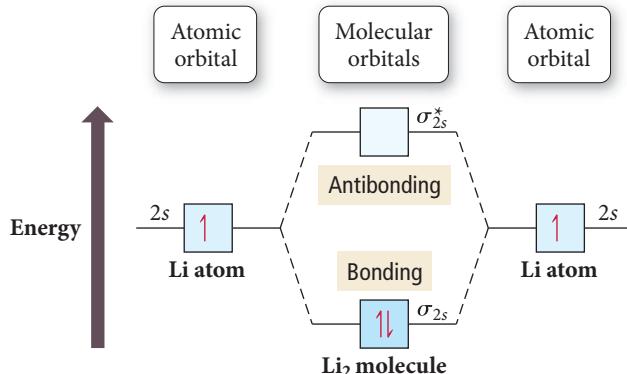
### FOR PRACTICE 10.9

Use molecular orbital theory to predict the bond order in  $\text{H}_2^+$ . Is the  $\text{H}_2^+$  bond a stronger or weaker bond than the  $\text{H}_2$  bond?

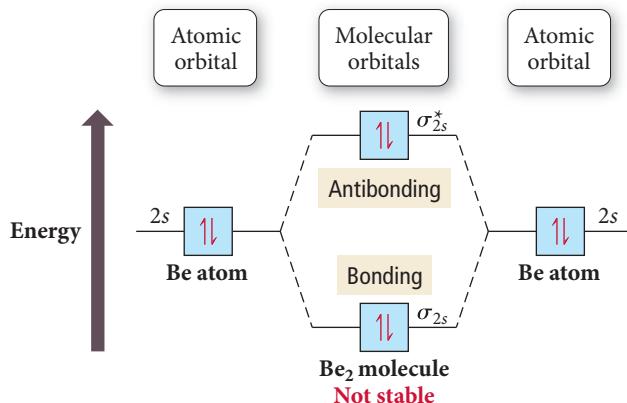
## Period Two Homonuclear Diatomic Molecules

Homonuclear diatomic molecules (molecules made up of two atoms of the same kind) formed from second-period elements have between 2 and 16 valence electrons. To explain bonding in these molecules, we must consider the next set of higher energy molecular orbitals, which can be approximated by linear combinations of the valence atomic orbitals of the period 2 elements.

We begin with  $\text{Li}_2$ . Even though lithium is normally a metal, we can use MO theory to predict whether or not the  $\text{Li}_2$  molecule should exist in the gas phase. We approximate the molecular orbitals in  $\text{Li}_2$  as linear combinations of the  $2s$  atomic orbitals. The resulting molecular orbitals look much like those of the  $\text{H}_2$  molecule. The MO diagram for  $\text{Li}_2$  therefore looks a lot like the MO diagram for  $\text{H}_2$ :



The two valence electrons of  $\text{Li}_2$  occupy a bonding molecular orbital. We would predict that the  $\text{Li}_2$  molecule is stable with a bond order of 1. Experiments confirm this prediction. In contrast, consider the MO diagram for  $\text{Be}_2$ :

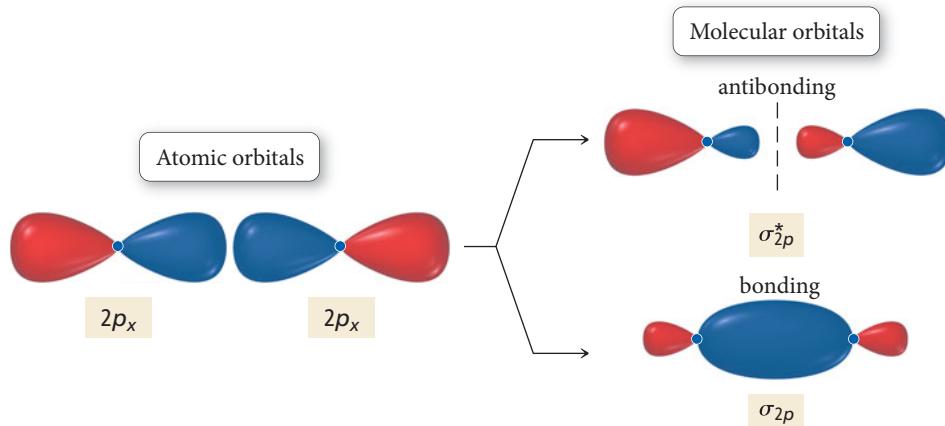


The four valence electrons of  $\text{Be}_2$  occupy one bonding MO and one antibonding MO. The bond order is 0 and we predict that  $\text{Be}_2$  should not be stable, again consistent with experimental findings.

The next homonuclear molecule composed of second row elements is  $\text{B}_2$ , which has six total valence electrons to accommodate. We can approximate the next higher energy molecular orbitals for  $\text{B}_2$  and the rest of the period 2 diatomic molecules as linear

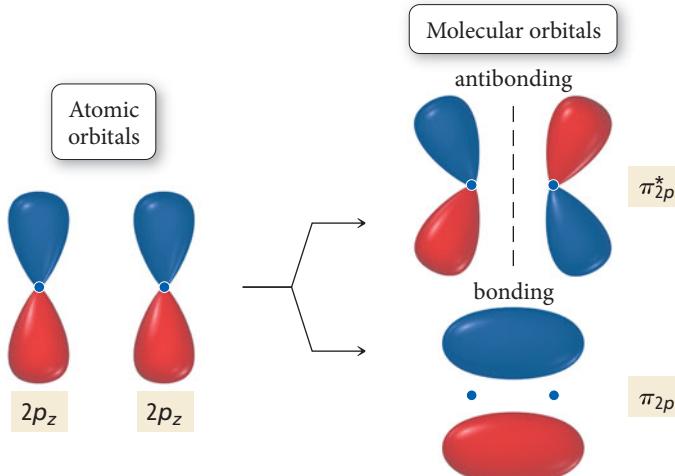
The core electrons can be ignored (as they are in other models for bonding), because these electrons do not contribute significantly to chemical bonding.

combinations of the  $2p$  orbitals taken pairwise. Since the three  $2p$  orbitals orient along three orthogonal axes, we must assign similar axes to the molecule. In this book, we assign the internuclear axis to be the  $x$  direction. Then the LCAO–MOs that result from combining the  $2p_x$  orbitals—the ones that lie along the internuclear axis—from each atom are represented pictorially as follows:



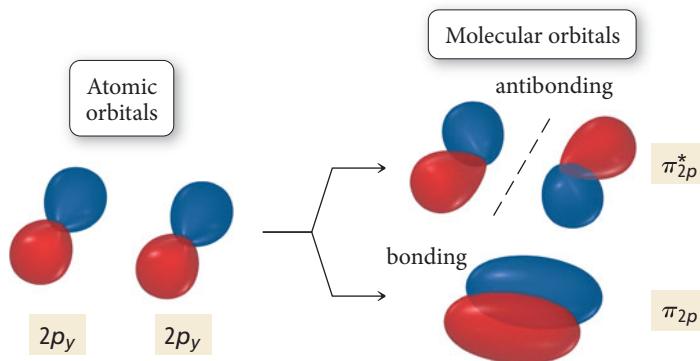
The bonding MO in this pair looks something like candy in a wrapper, with increased electron density in the internuclear region due to constructive interference between the two  $2p$  atomic orbitals. It has the characteristic  $\sigma$  shape (it is cylindrically symmetric about the bond axis) and is therefore called the  $\sigma_{2p}$  bonding orbital. The antibonding orbital, called  $\sigma_{2p}^*$ , has a node between the two nuclei (due to destructive interference between the two  $2p$  orbitals) and is higher in energy than either of the  $2p_x$  orbitals.

The LCAO–MOs that result from combining the  $2p_z$  orbitals from each atom are represented pictorially as follows:



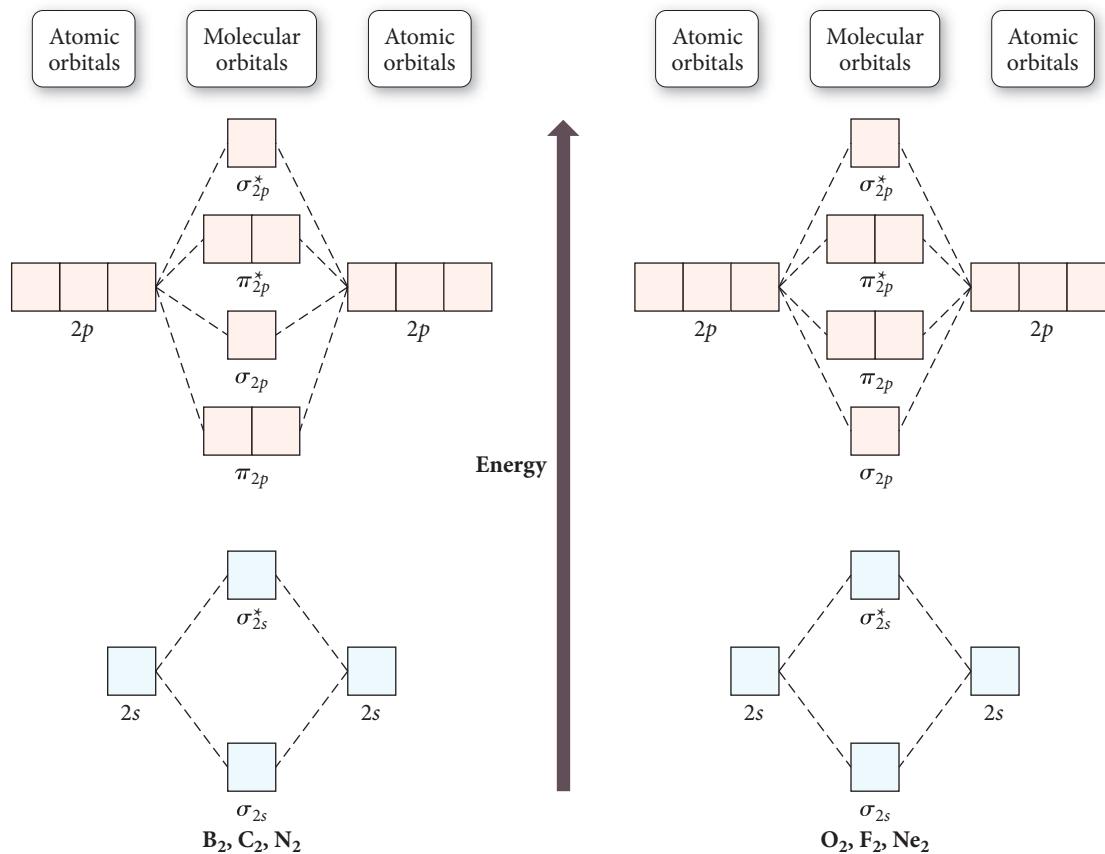
Notice that in this case the  $p$  orbitals are added together in a side-by-side orientation (in contrast to the  $2p_x$  orbitals, which were oriented end to end). The resultant molecular orbitals consequently have a different shape. The electron density in the bonding molecular orbital is above and below the internuclear axis with a nodal plane that includes the internuclear axis. This orbital resembles the electron density distribution of a  $\pi$  bond in valence bond theory. We call this orbital the  $\pi_{2p}$  orbital. The corresponding antibonding orbital has an additional node *between* the nuclei (perpendicular to the internuclear axis) and is called the  $\pi_{2p}^*$  orbital.

The LCAO–MOs that result from combining the  $2p_y$  orbitals from each atom are represented pictorially as follows:



The only difference between the  $2p_y$  and the  $2p_z$  atomic orbitals is a  $90^\circ$  rotation about the internuclear axis. Consequently, the only difference between the resulting MOs is a  $90^\circ$  rotation about the internuclear axis. The energies and the names of the bonding and antibonding MOs obtained from the combination of the  $2p_y$  AOs are identical to those obtained from the combination of the  $2p_z$  AOs.

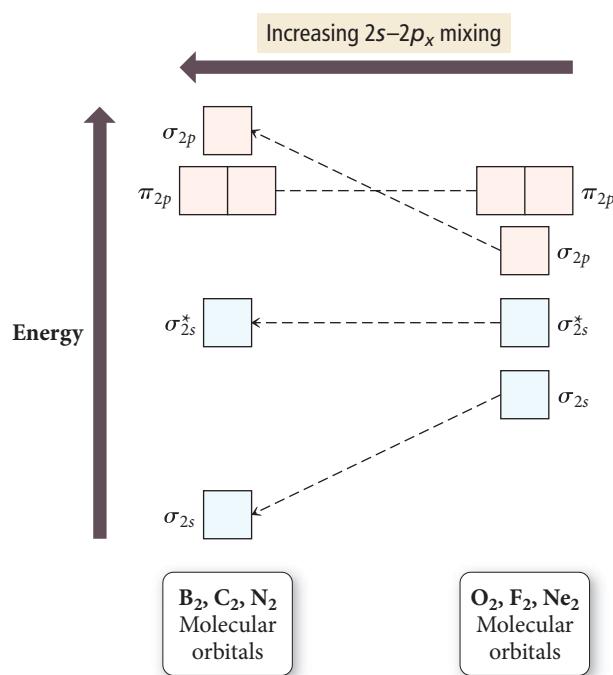
Before we can draw MO diagrams for  $B_2$  and the other second-period diatomic molecules, we must determine the relative energy ordering of the MOs obtained from the  $2p$  AO combinations. This is not a simple task. The relative ordering of MOs obtained from LCAO–MO theory is usually determined computationally. There is no single order that works for all molecules. For second-period diatomic molecules, computations reveal that the energy ordering for  $B_2$ ,  $C_2$ , and  $N_2$  is slightly different than that for  $O_2$ ,  $F_2$ , and  $Ne_2$  as follows:



▲ Molecular orbital energy diagrams for second-period diatomic molecules show that the energy ordering of the  $\pi_{2p}$  and  $\sigma_{2p}$  molecular orbitals can vary.

► FIGURE 10.14 The Effects of 2s–2p Mixing

**Mixing** The degree of mixing between two orbitals decreases with increasing energy difference between them. Mixing of the 2s and 2p<sub>x</sub> orbitals is therefore greater in B<sub>2</sub>, C<sub>2</sub>, and N<sub>2</sub> than in O<sub>2</sub>, F<sub>2</sub>, and Ne<sub>2</sub> because in B, C, and N the energy levels of the atomic orbitals are more closely spaced than in O, F, and Ne. This mixing produces a change in energy ordering for the π<sub>2p</sub> and σ<sub>2p</sub> molecular orbitals.



The reason for the difference in energy ordering can only be explained by going back to our LCAO–MO model. In our simplified treatment, we assumed that the MOs that result from the second-period AOs could be calculated pairwise. In other words, we took the linear combination of a 2s from one atom with the 2s from another, a 2p<sub>x</sub> from one atom with a 2p<sub>x</sub> from the other and so on. However, in a more comprehensive treatment, the MOs are formed from linear combinations that include all of the AOs that are relatively close to each other in energy and of the correct symmetry. Specifically, in a more detailed treatment, the two 2s orbitals and the two 2p<sub>x</sub> orbitals should all be combined to form a total of four molecular orbitals. The extent to which you include this type of mixing affects the energy levels of the corresponding MOs, as shown in Figure 10.14 ▲. The bottom line is that s–p mixing is significant in B<sub>2</sub>, C<sub>2</sub>, and N<sub>2</sub> but not in O<sub>2</sub>, F<sub>2</sub>, and Ne<sub>2</sub>. The result is a different energy ordering, depending on the specific molecule.

The MO energy diagrams for the rest of the second-period homonuclear diatomic molecules, as well as their bond orders, bond energies, and bond lengths, are shown in Figure 10.15 ▼. Notice that as bond order increases, the bond gets stronger (greater

Large 2s–2p <sub>x</sub> interaction			Small 2s–2p <sub>x</sub> interaction		
B <sub>2</sub>	C <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	F <sub>2</sub>	Ne <sub>2</sub>
σ <sub>2p</sub> <sup>*</sup>	↑	↑	σ <sub>2p</sub> <sup>*</sup>	↑	↑↑
π <sub>2p</sub> <sup>*</sup>	↑↑	↑↑	π <sub>2p</sub> <sup>*</sup>	↑↑	↑↑↑↑
σ <sub>2p</sub>	↑	↑	π <sub>2p</sub>	↑↑	↑↑↑↑
π <sub>2p</sub>	↑↑	↑↑	σ <sub>2p</sub>	↑	↑↑
σ <sub>2s</sub> <sup>*</sup>	↑↓	↑↓	σ <sub>2s</sub> <sup>*</sup>	↑	↑↓
σ <sub>2s</sub>	↑↓	↑↓	σ <sub>2s</sub>	↑↓	↑↓
Bond order			2	1	0
Bond energy (kJ/mol)			290	498	—
Bond length (pm)			159	121	143

▲ FIGURE 10.15 Molecular Orbital Energy Diagrams for Second-Row p-block Homonuclear Diatomic Molecules

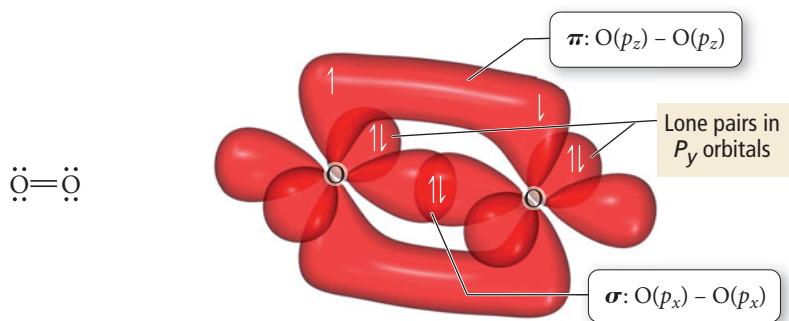
bond energy) and shorter (smaller bond length). For  $\text{B}_2$ , with six electrons, the bond order is 1. For  $\text{C}_2$ , the bond order is 2, and for  $\text{N}_2$ , the bond order reaches a maximum with a value of 3. Recall that the Lewis structure for  $\text{N}_2$  has a triple bond, so both the Lewis model and molecular orbital theory predict a strong bond for  $\text{N}_2$ , which is experimentally observed.

In  $\text{O}_2$ , the two additional electrons occupy antibonding orbitals and the bond order is 2. These two electrons are unpaired—they occupy the  $\pi_{2p}^*$  orbitals *singly with parallel spins*, as indicated by Hund's rule. The presence of unpaired electrons in the molecular orbital diagram of oxygen is significant because oxygen is known from experiment to be *paramagnetic* (see Section 8.7)—it is attracted to a magnetic field. The paramagnetism of oxygen can be demonstrated by suspending liquid oxygen between the poles of a magnet. This magnetic property is the direct result of *unpaired electrons*, whose spin and movement around the nucleus (more accurately known as orbital angular momentum) generate tiny magnetic fields. When a paramagnetic substance is placed in an external magnetic field, the magnetic fields of each atom or molecule align with the external field, creating the attraction (much as two magnets attract each other when properly oriented). In contrast, when the electrons in an atom or molecule are all *paired*, the magnetic fields caused by electron spin and orbital angular momentum tend to cancel each other, resulting in diamagnetism. A **diamagnetic** substance is not attracted to a magnetic field (and is, in fact, slightly repelled).



▲ Liquid oxygen can be suspended between the poles of a magnet because it is paramagnetic. It contains unpaired electrons (depicted here in the inset) that generate tiny magnetic fields, which align with and interact with the external field.

In the Lewis structure of  $\text{O}_2$ , as well as in the valence bond model of  $\text{O}_2$ , all of the electrons seem to be paired:



The  $s$  orbital on each  $\text{O}$  atom contains two electrons, but for clarity neither the  $s$  orbitals nor the electrons that occupy them are shown.

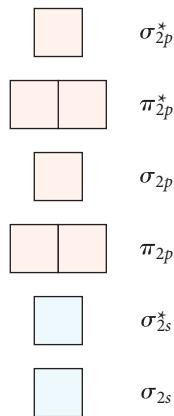
In the MO diagram for  $\text{O}_2$ , however, we can see the unpaired electrons. Molecular orbital theory is the more powerful theory in that it can account for the paramagnetism of  $\text{O}_2$ —it gives us a picture of bonding that more closely corresponds to what we see in experiments. Continuing along the second-row homonuclear diatomic molecules we see that  $\text{F}_2$  has a bond order of 1 and  $\text{Ne}_2$  has a bond order of 0, again consistent with experiment since  $\text{F}_2$  exists and  $\text{Ne}_2$  does not.

### EXAMPLE 10.10 Molecular Orbital Theory

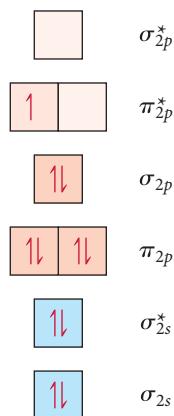
Draw an MO energy diagram and determine the bond order for the  $\text{N}_2^-$  ion. Do you expect the bond to be stronger or weaker than in the  $\text{N}_2$  molecule? Is  $\text{N}_2^-$  diamagnetic or paramagnetic?

#### SOLUTION

Write an energy level diagram for the molecular orbitals in  $\text{N}_2^-$ . Use the energy ordering for  $\text{N}_2$ .



The  $\text{N}_2^-$  ion has 11 valence electrons (5 for each nitrogen atom plus 1 for the negative charge). Assign the electrons to the molecular orbitals beginning with the lowest energy orbitals and following Hund's rule.



Calculate the bond order by subtracting the number of electrons in antibonding orbitals from the number in bonding orbitals and dividing the result by two.

$$\text{N}_2^- \text{ bond order} = \frac{8 - 3}{2} = +2.5$$

The bond order is 2.5, which is a lower bond order than in the  $\text{N}_2$  molecule (bond order = 3); therefore, the bond is weaker. The MO diagram shows that the  $\text{N}_2^-$  ion has one unpaired electron and is therefore paramagnetic.

#### FOR PRACTICE 10.10

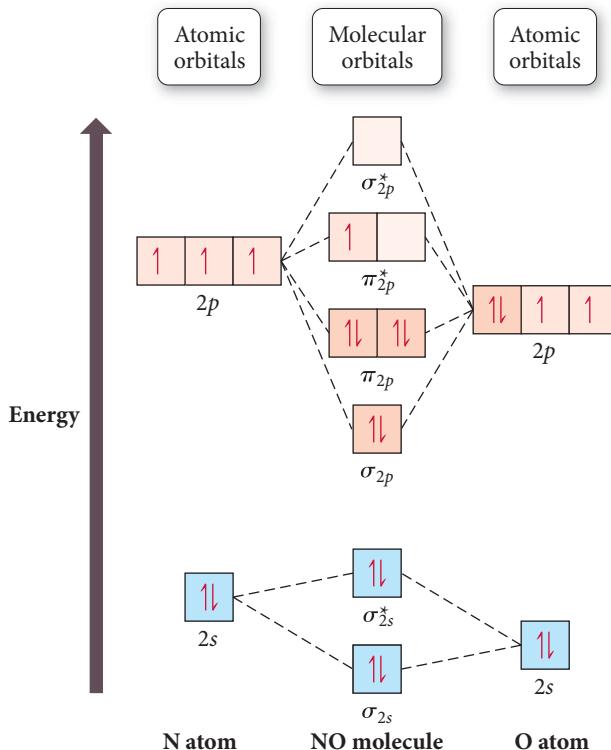
Draw an MO energy diagram and determine the bond order for the  $\text{N}_2^+$  ion. Do you expect the bond to be stronger or weaker than in the  $\text{N}_2$  molecule? Is  $\text{N}_2^+$  diamagnetic or paramagnetic?

#### FOR MORE PRACTICE 10.10

Use molecular orbital theory to determine the bond order of  $\text{Ne}_2$ .

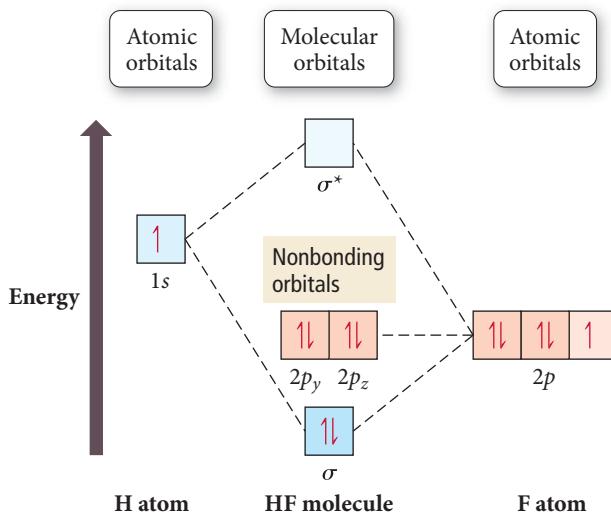
## Second-Period Heteronuclear Diatomic Molecules

We can also apply molecular orbital theory to heteronuclear diatomic molecules (two different atoms). For example, we can draw an MO diagram for NO as follows:

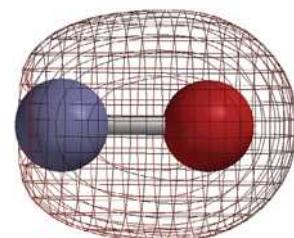


Oxygen is more electronegative than nitrogen, so its atomic orbitals are lower in energy than nitrogen's atomic orbitals. When two atomic orbitals are identical and of equal energy, the weighting of each orbital in forming a molecular orbital is identical. However, when two atomic orbitals are different, the weighting of each orbital in forming a molecular orbital may be different. More specifically, when a molecular orbital is approximated as a linear combination of atomic orbitals of different energies, the lower energy atomic orbital makes a greater contribution to the bonding molecular orbital and the higher energy atomic orbital makes a greater contribution to the antibonding molecular orbital. For example, notice that the  $\sigma_{2s}$  bonding orbital is closer in energy to the oxygen 2s orbital than to the nitrogen 2s orbital. We can also see this unequal weighting in the shape of the resultant molecular orbital, in which the electron density is concentrated on the oxygen atom, as shown in Figure 10.16 ►.

As another example of a heteronuclear diatomic molecule, consider the MO diagram for HF:



A given orbital will have lower energy in a more electronegative atom. For this reason, electronegative atoms have the ability to attract electrons to themselves.



**▲ FIGURE 10.16** Shape of  $\sigma_{2s}$  bonding orbital in NO The molecular orbital shows more electron density at the oxygen end of the molecule because the atomic orbitals of oxygen, the more electronegative element, are lower in energy than those of nitrogen. They therefore contribute more to the bonding molecular orbital.

Fluorine is so electronegative that all of its atomic orbitals are lower in energy than hydrogen's atomic orbitals. In fact, fluorine's  $2s$  orbital is so low in energy compared to hydrogen's  $1s$  orbital that it does not contribute appreciably to the molecular orbitals. The molecular orbitals in HF are approximated by the linear combination of the fluorine  $2p_x$  orbital and the hydrogen  $1s$  orbital. The other  $2p$  orbitals remain localized on the fluorine and appear in the energy diagram as **nonbonding orbitals**. The electrons in the nonbonding orbitals remain localized on the fluorine atom.

### EXAMPLE 10.11 Molecular Orbital Theory for Heteronuclear Diatomic Molecules and Ions

Use molecular orbital theory to determine the bond order of the  $\text{CN}^-$  ion. Is the ion paramagnetic or diamagnetic?

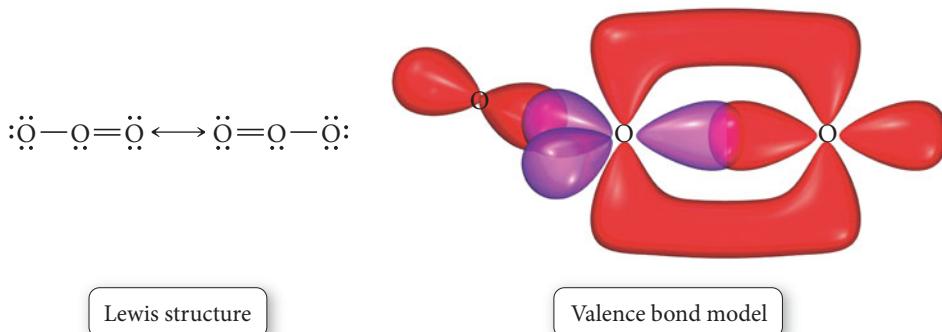
#### SOLUTION

Determine the number of valence electrons in the molecule or ion.	Number of valence electrons = 4 (from C) + 5 (from N) + 1 (from negative charge) = 10
Write an energy level diagram using Figure 10.15 as a guide. Fill the orbitals beginning with the lowest energy orbital and progressing upward until all electrons have been assigned to an orbital. Remember to allow no more than two electrons (with paired spins) per orbital and to fill degenerate orbitals with single electrons (with parallel spins) before pairing.	
Calculate the bond order using the appropriate formula: $\frac{\text{Bond order} = (\text{number of } e^- \text{ in bonding MOs}) - (\text{number of } e^- \text{ in antibonding MOs})}{2}$	$\text{CN}^- \text{ bond order} = \frac{8 - 2}{2} = +3$
If the MO diagram has unpaired electrons, the molecule or ion is paramagnetic. If the electrons are all paired, the molecule or ion is diamagnetic.	Since the MO diagram has no unpaired electrons, the ion is diamagnetic.

**FOR PRACTICE 10.11**  
Use molecular orbital theory to determine the bond order of NO. (Use the energy ordering of  $\text{O}_2$ .) Is the molecule paramagnetic or diamagnetic?

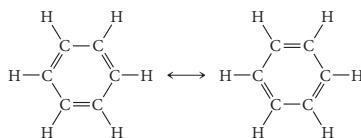
### Polyatomic Molecules

With the aid of computers, molecular orbital theory can be applied to polyatomic molecules and ions, yielding results that correlate very well with experimental measurements. These applications are beyond the scope of this text. However, the delocalization of electrons over an entire molecule is an important contribution of molecular orbital theory to our basic understanding of chemical bonding. For example, consider the Lewis structure and valence bond diagram of ozone:



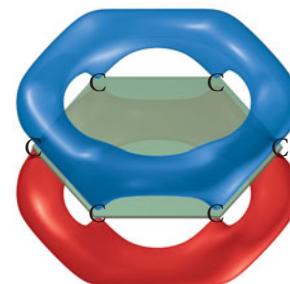
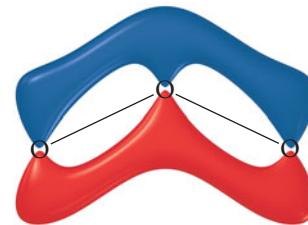
In the Lewis model, we use resonance forms to represent the two equivalent bonds. In valence bond theory, it appears that the two oxygen–oxygen bonds should be different. In molecular orbital theory, however, the  $\pi$  molecular orbitals in ozone are formed from a linear combination of the three oxygen  $2p$  orbitals and are delocalized over the entire molecule. The lowest energy  $\pi$  bonding molecular orbital is shown here.

When we examine ozone in nature, we indeed find two equivalent bonds. A similar situation occurs with benzene ( $C_6H_6$ ). In the Lewis model, we represent the structure with two resonance forms:



In molecular orbital theory, the  $\pi$  molecular orbitals in benzene are formed from a linear combination of the six carbon  $2p$  orbitals and are delocalized over the entire molecule. The lowest energy  $\pi$  bonding molecular orbital is shown here.

Benzene is in fact a highly symmetric molecule with six identical carbon–carbon bonds. The best picture of the  $\pi$  electrons in benzene is one in which the electrons occupy roughly circular-shaped orbitals above and below the plane of the molecule, as depicted in the molecular orbital theory approach.



### Conceptual Connection 10.7 What Is a Chemical Bond? Part II

We have learned that the Lewis model portrays a chemical bond as the transfer or sharing of electrons represented as dots. Valence bond theory portrays a chemical bond as the overlap of two half-filled atomic orbitals. What is a chemical bond according to molecular orbital theory?

## CHAPTER IN REVIEW

### Self Assessment Quiz

- Q1.** Determine the molecular geometry of  $CBr_4$ .
- linear
  - trigonal planar
  - tetrahedral
  - trigonal pyramidal
- Q2.** Determine the molecular geometry of  $SeF_4$ .
- tetrahedral
  - trigonal bipyramidal
  - T-shaped
  - seesaw
- Q3.** Predict the relative bond angles in  $BF_3$  and  $SO_2$ .
- $BF_3$  bond angles >  $SO_2$  bond angle
  - $SO_2$  bond angle >  $BF_3$  bond angles
  - $BF_3$  bond angles =  $SO_2$  bond angle
  - Relative bond angles cannot be predicted.
- Q4.** Predict the molecular geometry about N in the molecule  $CH_3NHCH_3$ .
- linear
  - trigonal planar
  - trigonal pyramidal
  - bent
- Q5.** Which molecule is polar?
- $SF_2$
  - $BH_3$
  - $PF_5$
  - $CS_2$
- Q6.** Determine the hybridization about O in  $CH_3OH$ .
- $sp$
  - $sp^2$
  - $sp^3$
  - $sp^3d$
- Q7.** Determine the hybridization about C in  $H_2CO$ .
- $sp$
  - $sp^2$
  - $sp^3$
  - $sp^3d$

- Q8.** According to valence bond theory, which kind of orbitals overlap to form the P—Cl bonds in  $\text{PCl}_5$ ?
- $\text{P}(sp^3) - \text{Cl}(p)$
  - $\text{P}(sp^3d) - \text{Cl}(s)$
  - $\text{P}(sp^3) - \text{Cl}(s)$
  - $\text{P}(sp^3d) - \text{Cl}(p)$
- Q9.** Use molecular orbital theory to determine the bond order in  $\text{C}_2$ .
- 0
  - 1
  - 2
  - 3
- Q10.** Use molecular orbital theory to predict which species has the strongest bond.
- $\text{N}_2$
  - $\text{N}_2^-$
  - $\text{N}_2^+$
  - All bonds are equivalent according to molecular orbital theory.
- Q11.** Use molecular orbital theory to determine which molecule is diamagnetic.
- $\text{CO}$
  - $\text{B}_2$
  - $\text{O}_2$
  - None of the above (all are paramagnetic)
- Q12.** Which hybridization scheme occurs about nitrogen when nitrogen forms a double bond?
- $\text{sp}$
  - $\text{sp}^2$
  - $\text{sp}^3$
  - $\text{sp}^3\text{d}$
- Q13.** Which molecule geometry results when a central atom has five total electron groups, with three of those being bonding groups and two being lone pairs?
- trigonal bipyramidal
  - seesaw
  - T-shaped
  - bent
- Q14.** Determine the correct molecular geometry (from left to right) about each interior atom in  $\text{CH}_3\text{CH}_2\text{OH}$ .
- 1st C tetrahedral; 2nd C trigonal planar; O linear
  - 1st C trigonal planar; 2nd C bent; O linear
  - 1st C trigonal planar; 2nd C trigonal pyramidal; O bent
  - 1st C tetrahedral; 2nd C tetrahedral; O bent
- Q15.** The central atom in a molecule has a bent molecular geometry. Determine the hybridization of the orbitals in the atom.
- $\text{sp}$
  - $\text{sp}^2$
  - $\text{sp}^3$
  - Hybridization cannot be determined from information given.

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

## Key Terms

### Section 10.2

valence shell electron pair repulsion (VSEPR) theory (426)  
electron groups (426)  
linear geometry (427)  
trigonal planar geometry (427)  
tetrahedral geometry (428)  
trigonal bipyramidal geometry (429)

### octahedral geometry (429)

### Section 10.3

electron geometry (430)  
molecular geometry (430)  
trigonal pyramidal geometry (430)  
bent geometry (431)  
seesaw geometry (432)

### T-shaped geometry (432)

square pyramidal geometry (433)  
square planar geometry (433)

### Section 10.6

valence bond theory (443)

### Section 10.7

hybridization (445)  
hybrid orbitals (445)

### pi ( $\pi$ ) bond (450)

sigma ( $\sigma$ ) bond (450)

### Section 10.8

molecular orbital theory (459)  
bonding orbital (460)  
antibonding orbital (460)  
bond order (461)  
diamagnetic (467)  
nonbonding orbitals (470)

## Key Concepts

### Molecular Shape and VSEPR Theory (10.1–10.4)

- The properties of molecules are directly related to their shapes. In VSEPR theory, molecular geometries are determined by the repulsions between electron groups on the central atom. An electron group can be a single bond, double bond, triple bond, lone pair, or even a single electron.
- The five basic molecular shapes are linear (two electron groups), trigonal planar (three electron groups), tetrahedral (four electron groups), trigonal bipyramidal (five electron groups), and octahedral (six electron groups).

- When lone pairs are present on the central atom, the *electron* geometry is still one of the five basic shapes, but one or more positions are occupied by lone pairs. The *molecular* geometry is therefore different from the electron geometry. Lone pairs are positioned so as to minimize repulsions with other lone pairs and with bonding pairs.

### Polarity (10.5)

- The polarity of a polyatomic molecule containing polar bonds depends on its geometry. If the dipole moments of the polar

- bonds are aligned in such a way that they cancel one another, the molecule will not be polar. If they are aligned in such a way as to sum together, the molecule will be polar.
- Highly symmetric molecules tend to be nonpolar, while asymmetric molecules containing polar bonds tend to be polar. The polarity of a molecule dramatically affects its properties.

### Valence Bond Theory (10.6–10.7)

- In contrast to the Lewis model, in which a covalent chemical bond is the sharing of electrons represented by dots, in valence bond theory a chemical bond is the overlap of half-filled atomic orbitals (or in some cases the overlap between a completely filled orbital and an empty one).
- The overlapping orbitals may be the standard atomic orbitals, such as  $1s$  or  $2p$  or they may be hybridized atomic orbitals, which are mathematical combinations of the standard orbitals on a single atom. The basic hybridized orbitals are  $sp$ ,  $sp^2$ ,  $sp^3$ ,  $sp^3d$ , and  $sp^3d^2$ .
- The geometry of the molecule is determined by the geometry of the overlapping orbitals.
- In our treatment of valence bond theory, we use the molecular geometry determined by VSEPR theory to determine the correct hybridization scheme.

- In valence bond theory, we distinguish between two types of bonds,  $\sigma$  (sigma) and  $\pi$  (pi). In a  $\sigma$  bond, the orbital overlap occurs in the region that lies directly between the two bonding atoms. In a  $\pi$  bond, formed from the side-by-side overlap of  $p$  orbitals, the overlap occurs above and below the region that lies directly between the two bonding atoms.
- Rotation about a  $\sigma$  bond is relatively free, while rotation about a  $\pi$  bond is restricted.

### Molecular Orbital Theory (10.8)

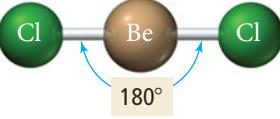
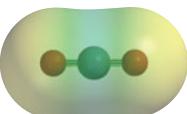
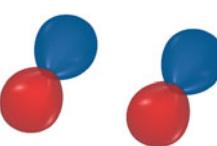
- The simplest molecular orbitals are linear combinations of atomic orbitals (LCAOs), weighted averages of the atomic orbitals of the different atoms in the molecule.
- When two atomic orbitals combine to form molecular orbitals, they will form one molecular orbital of lower energy (the bonding orbital) and one of higher energy (the antibonding orbital).
- A set of molecular orbitals are filled in much the same way as atomic orbitals.
- The stability of the molecule and the strength of the bond depend on the number of electrons in bonding orbitals compared to the number in antibonding orbitals.

## Key Equations and Relationships

### Bond Order of a Diatomic Molecule (10.8)

$$\text{Bond order} = \frac{(\text{number of electron in bonding MOs}) - (\text{number of electrons in antibonding MOs})}{2}$$

## Key Learning Outcomes

Chapter Objectives	Assessment
Using VSEPR Theory to Predict the Basic Shapes of Molecules (10.2) 	Example 10.1 For Practice 10.1 Exercises 31–32
Predicting Molecular Geometries Using VSEPR Theory and the Effects of Lone Pairs (10.4)	Examples 10.2–10.3 For Practice 10.2–10.3 Exercises 35–36
Predicting the Shapes of Larger Molecules (10.4)	Example 10.4 For Practice 10.4 Exercises 41–42, 45–46
Using Molecular Shape to Determine Polarity of a Molecule (10.5) 	Example 10.5 For Practice 10.5 Exercises 49–52
Writing Hybridization and Bonding Schemes Using Valence Bond Theory (10.7)	Examples 10.6–10.8 For Practice 10.6–10.8 For More Practice 10.8 Exercises 61–66
Drawing Molecular Orbital Diagrams to Predict Bond Order and Magnetism of a Diatomic Molecule (10.8) 	Examples 10.9–10.11 For Practice 10.9–10.11 For More Practice 10.10 Exercises 71–72, 75–78, 81–82

## EXERCISES

### Review Questions

1. Why is molecular geometry important? Cite some examples.
2. According to VSEPR theory, what determines the geometry of a molecule?
3. Name and sketch the five basic electron geometries, and state the number of electron groups corresponding to each. What constitutes an *electron group*?
4. Explain the difference between electron geometry and molecular geometry. Under what circumstances are they not the same?
5. Give the correct electron and molecular geometries that correspond to each set of electron groups around the central atom of a molecule.
  - a. four electron groups overall; three bonding groups and one lone pair
  - b. four electron groups overall; two bonding groups and two lone pairs
  - c. five electron groups overall; four bonding groups and one lone pair
  - d. five electron groups overall; three bonding groups and two lone pairs
  - e. five electron groups overall; two bonding groups and three lone pairs
  - f. six electron groups overall; five bonding groups and one lone pair
  - g. six electron groups overall; four bonding groups and two lone pairs
6. How do you apply VSEPR theory to predict the shape of a molecule with more than one interior atom?
7. How do you determine if a molecule is polar? Why is polarity important?
8. What is a chemical bond according to valence bond theory?
9. In valence bond theory, what determines the geometry of a molecule?
10. In valence bond theory, the interaction energy between the electrons and nucleus of one atom with the electrons and nucleus of another atom is usually negative (stabilizing) when \_\_\_\_\_.
11. What is hybridization? Why is hybridization necessary in valence bond theory?
12. How does hybridization of the atomic orbitals in the central atom of a molecule help lower the overall energy of the molecule?
13. How is the *number* of hybrid orbitals related to the number of standard atomic orbitals that are hybridized?
14. Sketch each hybrid orbital:
 

a. $sp$	b. $sp^2$
c. $sp^3$	d. $sp^3d$
e. $sp^3d^2$	
15. In the Lewis model, the two bonds in a double bond look identical. However, valence bond theory shows that they are not. Describe a double bond according to valence bond theory. Explain why rotation is restricted about a double bond, but not about a single bond.
16. Name the hybridization scheme that corresponds to each electron geometry:
 

a. linear	b. trigonal planar
c. tetrahedral	d. trigonal bipyramidal
e. octahedral	
17. What is a chemical bond according to molecular orbital theory?
18. Explain the difference between hybrid atomic orbitals in valence bond theory and LCAO molecular orbitals in molecular orbital theory.
19. What is a bonding molecular orbital?
20. What is an antibonding molecular orbital?
21. What is the role of wave interference in determining whether a molecular orbital is bonding or antibonding?
22. In molecular orbital theory, what is bond order? Why is it important?
23. How is the number of molecular orbitals approximated by a linear combination of atomic orbitals related to the number of atomic orbitals used in the approximation?
24. Sketch each molecular orbital.
 

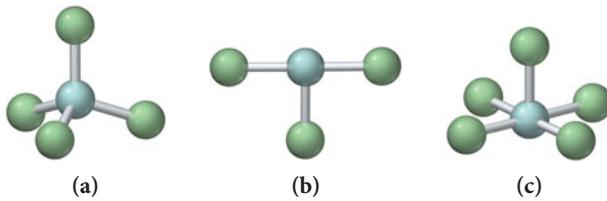
a. $\sigma_{2s}$	b. $\sigma_{2s}^*$
c. $\sigma_{2p}$	d. $\sigma_{2p}^*$
e. $\pi_{2p}$	f. $\pi_{2p}^*$
25. Draw an energy diagram for the molecular orbitals of period 2 diatomic molecules. Show the difference in ordering for  $B_2$ ,  $C_2$ , and  $N_2$  compared to  $O_2$ ,  $F_2$ , and  $Ne_2$ .
26. Why does the energy ordering of the molecular orbitals of the period 2 diatomic molecules change in going from  $N_2$  to  $O_2$ ?
27. Explain the difference between a paramagnetic species and a diamagnetic one.
28. When applying molecular orbital theory to heteronuclear diatomic molecules, the atomic orbitals used may be of different energies. If two atomic orbitals of different energies make two molecular orbitals, how are the energies of the molecular orbitals related to the energies of the atomic orbitals? How is the shape of the resultant molecular orbitals related to the shapes of the atomic orbitals?
29. In molecular orbital theory, what is a nonbonding orbital?
30. Write a short paragraph describing chemical bonding according to the Lewis model, valence bond theory, and molecular orbital theory. Indicate how the theories differ in their description of a chemical bond and indicate the strengths and weaknesses of each theory. Which theory is correct?

### Problems by Topic

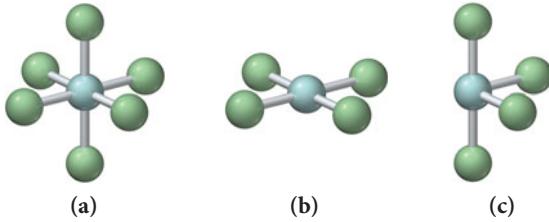
#### VSEPR Theory and Molecular Geometry

31. A molecule with the formula  $AB_3$  has a trigonal pyramidal geometry. How many electron groups are on the central atom (A)?
32. A molecule with the formula  $AB_3$  has a trigonal planar geometry. How many electron groups are on the central atom?

33. For each molecular geometry, list the number of total electron groups, the number of bonding groups, and the number of lone pairs on the central atom.



34. For each molecular geometry, list the number of total electron groups, the number of bonding groups, and the number of lone pairs on the central atom.



35. Determine the electron geometry, molecular geometry, and idealized bond angles for each molecule. In which cases do you expect deviations from the idealized bond angle?

- a.  $\text{PF}_3$   
b.  $\text{SBr}_2$   
c.  $\text{CHCl}_3$   
d.  $\text{CS}_2$

36. Determine the electron geometry, molecular geometry, and idealized bond angles for each molecule. In which cases do you expect deviations from the idealized bond angle?

- a.  $\text{CF}_4$   
b.  $\text{NF}_3$   
c.  $\text{OF}_2$   
d.  $\text{H}_2\text{S}$

37. Which species has the smaller bond angle,  $\text{H}_3\text{O}^+$  or  $\text{H}_2\text{O}$ ? Explain.

38. Which species has the smaller bond angle,  $\text{ClO}_4^-$  or  $\text{ClO}_3^-$ ? Explain.

39. Determine the molecular geometry and sketch each molecule or ion using the bond conventions shown in the "Representing Molecular Geometries on Paper" box in Section 10.4.

- a.  $\text{SF}_4$   
b.  $\text{ClF}_3$   
c.  $\text{IF}_2^-$   
d.  $\text{IBr}_4^-$

40. Determine the molecular geometry and sketch each molecule or ion, using the bond conventions shown in the "Representing Molecular Geometries on Paper" Box in Section 10.4.

- a.  $\text{BrF}_5$   
b.  $\text{SCl}_6$   
c.  $\text{PF}_5$   
d.  $\text{IF}_4^+$

41. Determine the molecular geometry about each interior atom and sketch each molecule.

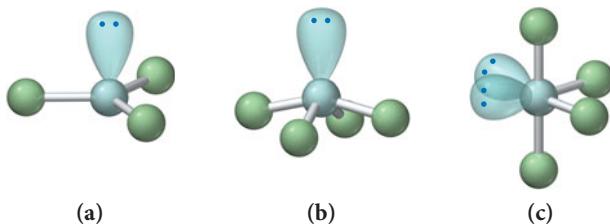
- a.  $\text{C}_2\text{H}_2$  (skeletal structure  $\text{HCCH}$ )  
b.  $\text{C}_2\text{H}_4$  (skeletal structure  $\text{H}_2\text{CCH}_2$ )  
c.  $\text{C}_2\text{H}_6$  (skeletal structure  $\text{H}_3\text{CCH}_3$ )

42. Determine the molecular geometry about each interior atom and sketch each molecule.

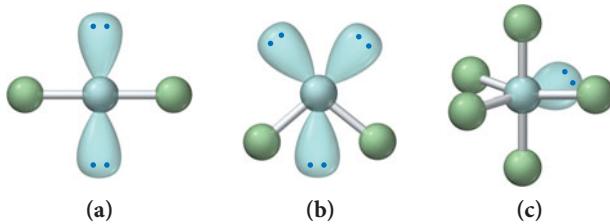
- a.  $\text{N}_2$   
b.  $\text{N}_2\text{H}_2$  (skeletal structure  $\text{HNNH}$ )  
c.  $\text{N}_2\text{H}_4$  (skeletal structure  $\text{H}_2\text{NNH}_2$ )

43. Each ball-and-stick model shows the electron and molecular geometry of a generic molecule. Explain what is wrong with each molecular geometry and provide the correct molecular

geometry, given the number of lone pairs and bonding groups on the central atom.



44. Each ball-and-stick model shows the electron and molecular geometry of a generic molecule. Explain what is wrong with each molecular geometry and provide the correct molecular geometry, given the number of lone pairs and bonding groups on the central atom.



45. Determine the geometry about each interior atom in each molecule and sketch the molecule. (Skeletal structure is indicated in parentheses.)

- a.  $\text{CH}_3\text{OH}$  ( $\text{H}_3\text{COH}$ )  
b.  $\text{CH}_3\text{OCH}_3$  ( $\text{H}_3\text{COCH}_3$ )  
c.  $\text{H}_2\text{O}_2$  ( $\text{HOOH}$ )

46. Determine the geometry about each interior atom in each molecule and sketch the molecule. (Skeletal structure is indicated in parentheses.)

- a.  $\text{CH}_3\text{NH}_2$  ( $\text{H}_3\text{CNH}_2$ )  
b.  $\text{CH}_3\text{CO}_2\text{CH}_3$  ( $\text{H}_3\text{CCOOCH}_3$  both O atoms attached to second C)  
c.  $\text{NH}_2\text{CO}_2\text{H}$  ( $\text{H}_2\text{NCOOH}$  both O atoms attached to C)

### Molecular Shape and Polarity

47. Explain why  $\text{CO}_2$  and  $\text{CCl}_4$  are both nonpolar even though they contain polar bonds.

48.  $\text{CH}_3\text{F}$  is a polar molecule, even though the tetrahedral geometry often leads to nonpolar molecules. Explain.

49. Determine whether each molecule in Exercise 35 is polar or nonpolar.

50. Determine whether each molecule in Exercise 36 is polar or nonpolar.

51. Determine whether each molecule is polar or nonpolar.  
a.  $\text{ClO}_3^-$       b.  $\text{SCl}_2$       c.  $\text{SCl}_4$       d.  $\text{BrCl}_5$

52. Determine whether each molecule is polar or nonpolar.

- a.  $\text{SiCl}_4$       b.  $\text{CF}_2\text{Cl}_2$       c.  $\text{SeF}_6$       d.  $\text{IF}_5$

### Valence Bond Theory

53. The valence electron configurations of several atoms are shown next. How many bonds can each atom make without hybridization?  
a.  $\text{Be}$   $2s^2$   
b.  $\text{P}$   $3s^23p^3$   
c.  $\text{F}$   $2s^22p^5$

54. The valence electron configurations of several atoms are shown next. How many bonds can each atom make without hybridization?  
a.  $\text{B}$   $2s^22p^1$   
b.  $\text{N}$   $2s^22p^3$   
c.  $\text{O}$   $2s^22p^4$

**55.** Write orbital diagrams (boxes with arrows in them) to represent the electron configurations—without hybridization—for all the atoms in  $\text{PH}_3$ . Circle the electrons involved in bonding. Draw a three-dimensional sketch of the molecule and show orbital overlap. What bond angle do you expect from the unhybridized orbitals? How well does valence bond theory agree with the experimentally measured bond angle of  $93.3^\circ$ ?

**56.** Write orbital diagrams (boxes with arrows in them) to represent the electron configurations—without hybridization—for all the atoms in  $\text{SF}_2$ . Circle the electrons involved in bonding. Draw a three-dimensional sketch of the molecule and show orbital overlap. What bond angle do you expect from the unhybridized orbitals? How well does valence bond theory agree with the experimentally measured bond angle of  $98.2^\circ$ ?

**57.** Write orbital diagrams (boxes with arrows in them) to represent the electron configuration of carbon before and after  $sp^3$  hybridization.

**58.** Write orbital diagrams (boxes with arrows in them) to represent the electron configurations of carbon before and after  $sp$  hybridization.

**59.** Which hybridization scheme allows the formation of at least one  $\pi$  bond?

$$sp^3, sp^2, sp^3d^2$$

**60.** Which hybridization scheme allows the central atom to form more than four bonds?

$$sp^3, sp^3d, sp^2$$

**61.** Write a hybridization and bonding scheme for each molecule. Sketch the molecule, including overlapping orbitals, and label all bonds using the notation shown in Examples 10.6 and 10.7.

- |                   |                  |
|-------------------|------------------|
| a. $\text{CCl}_4$ | b. $\text{NH}_3$ |
| c. $\text{OF}_2$  | d. $\text{CO}_2$ |

**62.** Write a hybridization and bonding scheme for each molecule. Sketch the molecule, including overlapping orbitals, and label all bonds using the notation shown in Examples 10.6 and 10.7.

- |                             |                  |
|-----------------------------|------------------|
| a. $\text{CH}_2\text{Br}_2$ | b. $\text{SO}_2$ |
| c. $\text{NF}_3$            | d. $\text{BF}_3$ |

**63.** Write a hybridization and bonding scheme for each molecule or ion. Sketch the structure, including overlapping orbitals, and label all bonds using the notation shown in Examples 10.6 and 10.7.

- |   |
|---|
| a. $\text{COCl}_2$ (carbon is the central atom) |
| b. $\text{BrF}_5$                               |
| c. $\text{XeF}_2$                               |
| d. $\text{I}_3^-$ .                             |

**64.** Write a hybridization and bonding scheme for each molecule or ion. Sketch the structure, including overlapping orbitals, and label all bonds using the notation shown in Examples 10.6 and 10.7.

- |                       |                    |                   |                 |
|-----------------------|--------------------|-------------------|-----------------|
| a. $\text{SO}_3^{2-}$ | b. $\text{PF}_6^-$ | c. $\text{BrF}_3$ | d. $\text{HCN}$ |
|-----------------------|--------------------|-------------------|-----------------|

**65.** Write a hybridization and bonding scheme for each molecule that contains more than one interior atom. Indicate the hybridization about each interior atom. Sketch the structure, including overlapping orbitals, and label all bonds using the notation shown in Examples 10.6 and 10.7.

- |  |
|--|
| a. $\text{N}_2\text{H}_2$ (skeletal structure $\text{HNNH}$ )              |
| b. $\text{N}_2\text{H}_4$ (skeletal structure $\text{H}_2\text{NNH}_2$ )   |
| c. $\text{CH}_3\text{NH}_2$ (skeletal structure $\text{H}_3\text{CNH}_2$ ) |

**66.** Write a hybridization and bonding scheme for each molecule that contains more than one interior atom. Indicate the hybridization about each interior atom. Sketch the structure, including

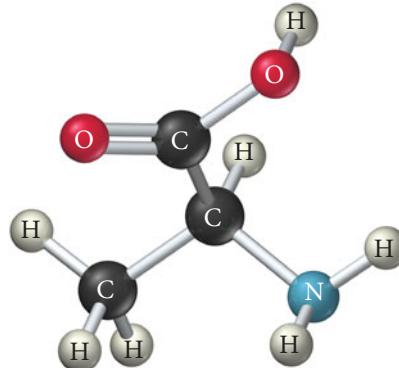
overlapping orbitals, and label all bonds using the notation shown in Examples 10.6 and 10.7.

- a.  $\text{C}_2\text{H}_2$  (skeletal structure  $\text{HCCH}$ )

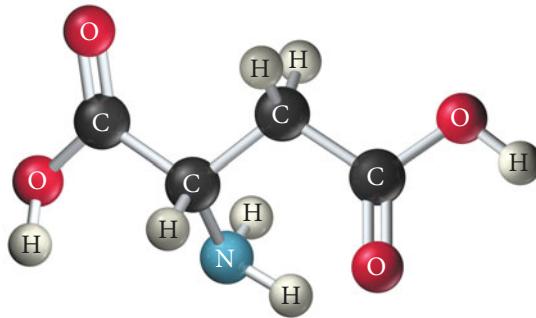
- b.  $\text{C}_2\text{H}_4$  (skeletal structure  $\text{H}_2\text{CCH}_2$ )

- c.  $\text{C}_2\text{H}_6$  (skeletal structure  $\text{H}_3\text{CCH}_3$ )

**67.** Consider the structure of the amino acid alanine. Indicate the hybridization about each interior atom.



**68.** Consider the structure of the amino acid aspartic acid. Indicate the hybridization about each interior atom.



### Molecular Orbital Theory

**69.** Sketch the bonding molecular orbital that results from the linear combination of two  $1s$  orbitals. Indicate the region where interference occurs and state the kind of interference (constructive or destructive).

**70.** Sketch the antibonding molecular orbital that results from the linear combination of two  $1s$  orbitals. Indicate the region where interference occurs and state the kind of interference (constructive or destructive).

**71.** Draw an MO energy diagram and predict the bond order of  $\text{Be}_2^+$  and  $\text{Be}_2^-$ . Do you expect these molecules to exist in the gas phase?

**72.** Draw an MO energy diagram and predict the bond order of  $\text{Li}_2^+$  and  $\text{Li}_2^-$ . Do you expect these molecules to exist in the gas phase?

**73.** Sketch the bonding and antibonding molecular orbitals that result from linear combinations of the  $2p_x$  atomic orbitals in a homonuclear diatomic molecule. (The  $2p_x$  orbitals are those whose lobes are oriented along the bonding axis.)

**74.** Sketch the bonding and antibonding molecular orbitals that result from linear combinations of the  $2p_z$  atomic orbitals in a homonuclear diatomic molecule. (The  $2p_z$  orbitals are those whose lobes are oriented perpendicular to the bonding axis.) How do these molecular orbitals differ from those obtained from linear combinations of the  $2p_y$  atomic orbitals? (The  $2p_y$  orbitals are also oriented perpendicular to the bonding axis, but also perpendicular to the  $2p_z$  orbitals.)

75. Using the molecular orbital energy ordering for second-row homonuclear diatomic molecules in which the  $\pi_{2p}$  orbitals lie at *lower* energy than the  $\sigma_{2p}$ , draw MO energy diagrams and predict the bond order in a molecule or ion with each number of total valence electrons. Will the molecule or ion be diamagnetic or paramagnetic?

- a. 4      b. 6      c. 8      d. 9

76. Using the molecular orbital energy ordering for second-row homonuclear diatomic molecules in which the  $\pi_{2p}$  orbitals lie at *higher* energy than the  $\sigma_{2p}$ , draw MO energy diagrams and predict the bond order in a molecule or ion with each number of total valence electrons. Will the molecule or ion be diamagnetic or paramagnetic?

- a. 10      b. 12      c. 13      d. 14

77. Use molecular orbital theory to predict if each molecule or ion exists in a relatively stable form.

- a.  $\text{H}_2^{2-}$       b.  $\text{Ne}_2$       c.  $\text{He}_2^{2+}$       d.  $\text{F}_2^{2-}$

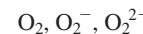
78. Use molecular orbital theory to predict if each molecule or ion exists in a relatively stable form.

- a.  $\text{C}_2^{2+}$       b.  $\text{Li}_2$       c.  $\text{Be}_2^{2+}$       d.  $\text{Li}_2^{2-}$

79. According to MO theory, which molecule or ion has the highest bond order? Highest bond energy? Shortest bond length?



80. According to MO theory, which molecule or ion has the highest bond order? Highest bond energy? Shortest bond length?



81. Draw an MO energy diagram for CO. (Use the energy ordering of  $\text{O}_2$ .) Predict the bond order and make a sketch of the lowest energy bonding molecular orbital.

82. Draw an energy diagram for HCl. Predict the bond order and make a sketch of the lowest energy bonding molecular orbital.

## Cumulative Problems

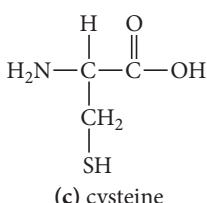
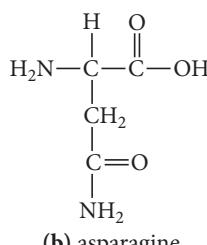
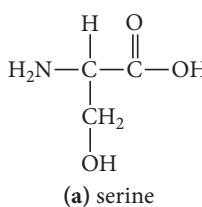
83. For each compound, draw the Lewis structure, determine the geometry using VSEPR theory, determine whether the molecule is polar, identify the hybridization of all interior atoms, and make a sketch of the molecule, according to valence bond theory, showing orbital overlap.

- a.  $\text{COF}_2$  (carbon is the central atom)  
b.  $\text{S}_2\text{Cl}_2$  ( $\text{Cl}-\text{S}-\text{Cl}$ )  
c.  $\text{SF}_4$

84. For each compound, draw the Lewis structure, determine the geometry using VSEPR theory, determine whether the molecule is polar, identify the hybridization of all interior atoms, and make a sketch of the molecule, according to valence bond theory, showing orbital overlap.

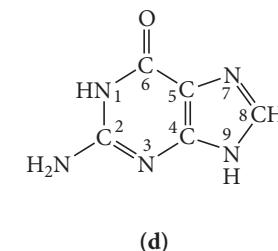
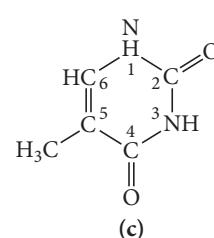
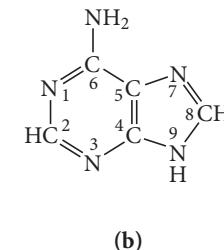
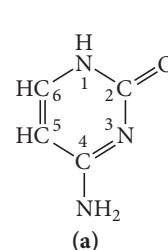
- a.  $\text{IF}_5$       b.  $\text{CH}_2\text{CHCH}_3$       c.  $\text{CH}_3\text{SH}$

85. Amino acids are biological compounds that link together to form proteins, the workhorse molecules in living organisms. The skeletal structures of several simple amino acids are shown here. For each skeletal structure, complete the Lewis structure, determine the geometry and hybridization about each interior atom, and make a sketch of the molecule, using the bond conventions of Section 10.4.

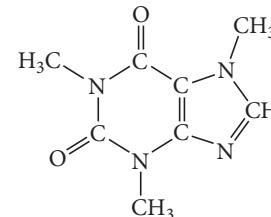


86. The genetic code is based on four different bases with the structures shown here. Assign a geometry and hybridization to each interior atom in these four bases.

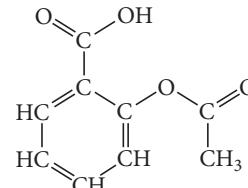
- a. cytosine      b. adenine      c. thymine      d. guanine



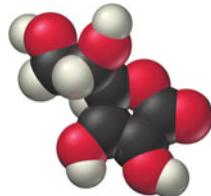
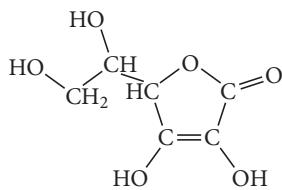
87. The structure of caffeine, present in coffee and many soft drinks, is shown here. How many pi bonds are present in caffeine? How many sigma bonds? Insert the lone pairs in the molecule. What kinds of orbitals do the lone pairs occupy?



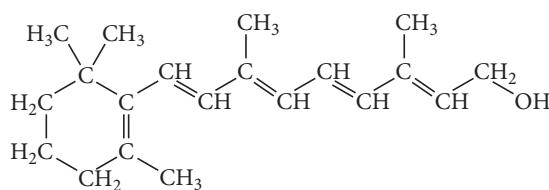
88. The structure of acetylsalicylic acid (aspirin) is shown here. How many pi bonds are present in acetylsalicylic acid? How many sigma bonds? What parts of the molecule are free to rotate? What parts are rigid?



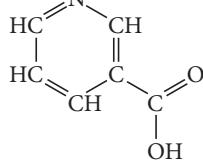
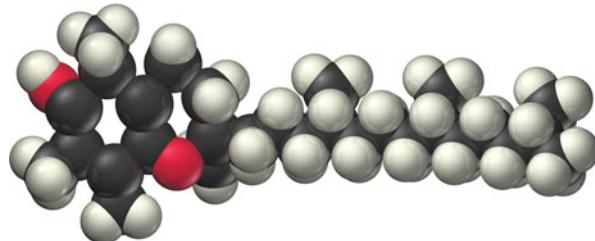
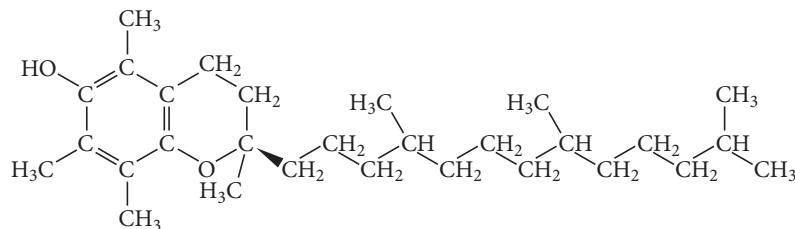
89. Most vitamins can be classified either as fat soluble, which results in their tendency to accumulate in the body (so that taking too much can be harmful), or water soluble, which results in their tendency to be quickly eliminated from the body in urine. Examine the structural formulas and space-filling models of these vitamins and determine whether each one is fat soluble (mostly nonpolar) or water soluble (mostly polar).



(a) vitamin C

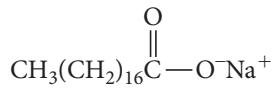


(b) vitamin A

(c) niacin (vitamin B<sub>3</sub>)

(d) vitamin E

90. Water does not easily remove grease from dishes or hands, because grease is nonpolar and water is polar. The addition of soap to water, however, allows the grease to dissolve. Study the structure of sodium stearate (a soap) and describe how it works.



91. Draw a molecular orbital energy diagram for ClF. (Assume that the  $\sigma_p$  orbitals are lower in energy than the  $\pi$  orbitals.) What is the bond order in ClF?
92. Draw Lewis structures and MO diagrams for  $\text{CN}^+$ ,  $\text{CN}$ , and  $\text{CN}^-$ . According to the Lewis model, which species is most stable? According to MO theory, which species is most stable? Do the two theories agree?

93. Bromine can form compounds or ions with any number of fluorine atoms from one to five. Write the formulas of all five of these species, assign a hybridization, and describe their electron and molecular geometry.

94. The compound  $\text{C}_3\text{H}_4$  has two double bonds. Describe its bonding and geometry, using a valence bond approach.

95. Draw the structure of a molecule with the formula  $\text{C}_4\text{H}_6\text{Cl}_2$  that has a dipole moment of 0.

96. Draw the structures of two compounds that have the composition  $\text{CH}_3\text{NO}_2$  and have all three H atoms bonded to the C. Predict which compound has the larger ONO bond angle.

97. How many hybrid orbitals do we use to describe each molecule?

- a.  $\text{N}_2\text{O}_5$
- b.  $\text{C}_2\text{H}_5\text{NO}$  (four C — H bonds and one O — H bond)
- c.  $\text{BrCN}$  (no formal charges)

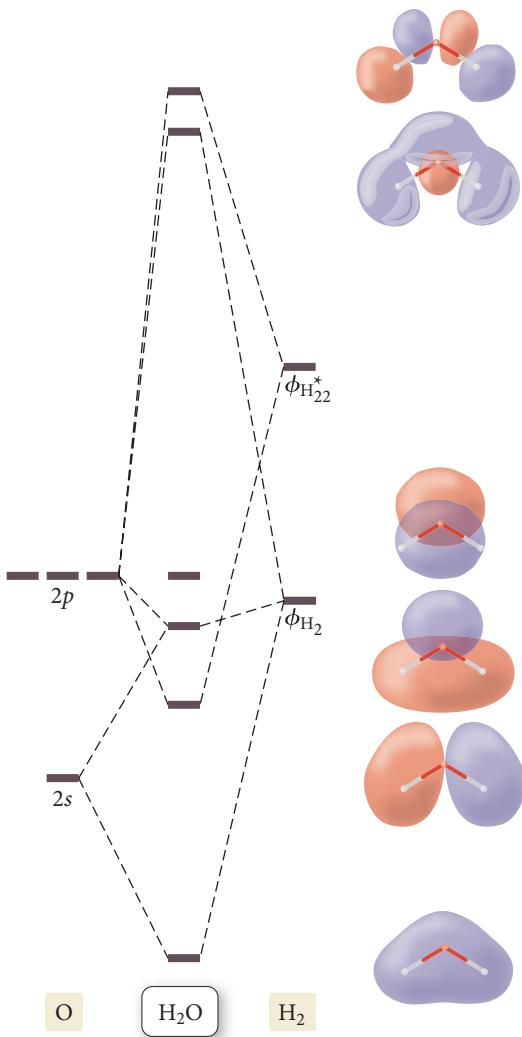
98. Indicate which orbitals overlap to form the  $\sigma$  bonds in the following.

- a.  $\text{BeBr}_2$
- b.  $\text{HgCl}_2$
- c.  $\text{ICN}$

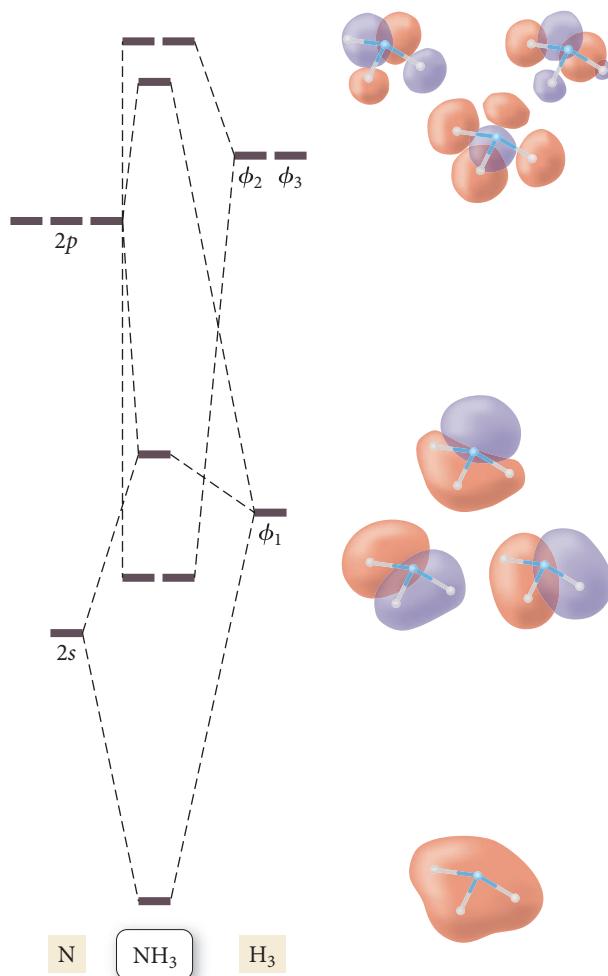
## Challenge Problems

**99.** In VSEPR theory, which uses the Lewis model to determine molecular geometry, the trend of decreasing bond angle in CH<sub>4</sub>, NH<sub>3</sub>, and H<sub>2</sub>O is accounted for by the greater repulsion of lone pair electrons compared to bonding pair electrons. How would this trend be accounted for in valence bond theory?

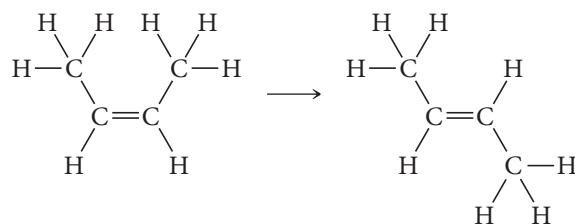
**100.** The results of a molecular orbital calculation for H<sub>2</sub>O are shown here. Examine each of the orbitals and classify them as bonding, antibonding, or nonbonding. Assign the correct number of electrons to the energy diagram. According to this energy diagram, is H<sub>2</sub>O stable? Explain.



**101.** The results of a molecular orbital calculation for NH<sub>3</sub> are shown here. Examine each of the orbitals and classify them as bonding, antibonding, or nonbonding. Assign the correct number of electrons to the energy diagram. According to this energy diagram, is NH<sub>3</sub> stable? Explain.



**102.** *cis*-2-Butene isomerizes to *trans*-2-butene via the reaction



- If isomerization requires breaking the  $\pi$  bond, what minimum energy is required for isomerization in J/mol? In J/molecule?
- If the energy for isomerization came from light, what minimum frequency of light would be required? In what portion of the electromagnetic spectrum does this frequency lie?

- 103.** The species  $\text{NO}_2$ ,  $\text{NO}_2^+$ , and  $\text{NO}_2^-$  in which N is the central atom, have very different bond angles. Predict what these bond angles might be with respect to the ideal angles and justify your prediction.
- 104.** The bond angles increase steadily in the series  $\text{PF}_3$ ,  $\text{PCl}_3$ ,  $\text{PBr}_3$ , and  $\text{PI}_3$ . After consulting the data on atomic radii in Chapter 8, provide an explanation for this observation.
- 105.** The ion  $\text{CH}_5^+$  can form under very special high-energy conditions in the vapor phase in a mass spectrometer. Propose a hybridization for the carbon atom and predict the geometry.
- 106.** Neither the VSEPR model nor the hybridization model is able to account for the experimental observation that the F—Ba—F bond angle in gaseous  $\text{BaF}_2$  is  $108^\circ$  rather than the predicted  $180^\circ$ . Suggest some possible explanations for this observation.
- 107.** Draw the Lewis structure for acetamide ( $\text{CH}_3\text{CONH}_2$ ), an organic compound, and determine the geometry about each interior atom. Experiments show that the geometry about the nitrogen atom in acetamide is nearly planar. What resonance structure can account for the planar geometry about the nitrogen atom?
- 108.** Use VSEPR to predict the geometry (including bond angles) about each interior atom of methyl azide ( $\text{CH}_3\text{N}_3$ ), and make a sketch of the molecule. Would you expect the bond angle between the two interior nitrogen atoms to be the same or different? Would you expect the two nitrogen–nitrogen bond lengths to be the same or different?

## Conceptual Problems

- 109.** Which statement best captures the fundamental idea behind VSEPR theory? Explain what is wrong with each of the other statements.
- The angle between two or more bonds is determined primarily by the repulsions between the electrons within those bonds and other (lone pair) electrons on the central atom of a molecule. Each of these electron groups (bonding electrons or lone pair electrons) will lower its potential energy by maximizing its separation from other electron groups, thus determining the geometry of the molecule.
  - The angle between two or more bonds is determined primarily by the repulsions between the electrons within those bonds. Each of these bonding electrons will lower its potential energy by maximizing its separation from other electron groups, thus determining the geometry of the molecule.
  - The geometry of a molecule is determined by the shapes of the overlapping orbitals that form the chemical bonds. Therefore, to determine the geometry of a molecule, you must determine the shapes of the orbitals involved in bonding.
- 110.** Suppose that a molecule has four bonding groups and one lone pair on the central atom. Suppose further that the molecule is confined to two dimensions (this is a purely hypothetical assumption for the sake of understanding the principles behind VSEPR theory). Make a sketch of the molecule and estimate the bond angles.
- 111.** How does each of the three major bonding theories (the Lewis model, valence bond theory, and molecular orbital theory) define a single chemical bond? A double bond? A triple bond? How are these definitions similar? How are they different?
- 112.** The most stable forms of the nonmetals in groups 4A, 5A, and 6A of the first period are molecules with multiple bonds. Beginning with the second period, the most stable forms of the nonmetals of these groups are molecules without multiple bonds. Propose an explanation for this observation based on valence bond theory.

## Answers to Conceptual Connections

### Electron Groups and Molecular Geometry

**10.1** The geometry of a molecule is determined by how the terminal atoms are arranged around the central atom, which is in turn determined by how the electron groups are arranged around the *central* atom. The electron groups on the terminal atoms do not affect this arrangement.

### Molecular Geometry

**10.2** Linear. HCN has two electron groups (the single bond and the triple bond) resulting in a linear geometry.

### Lone Pair Electrons and Molecular Geometry

**10.3** (c) Positions 1 and 4 would put the greatest distance between the lone pairs and minimize lone pair–lone pair repulsions.

### Molecular Geometry and Electron Group Repulsions

**10.4** (d) All electron groups on the central atom (or interior atoms, if there is more than one) determine the shape of a molecule according to VSEPR theory.

### What Is a Chemical Bond? Part I

**10.5** (a) In the Lewis model, a covalent chemical bond is the sharing of electrons (represented by dots). (b) In valence bond theory, a covalent chemical bond is the overlap of half-filled atomic orbitals. (c) The answers are different because the Lewis model and valence bond theory are different models for chemical bonding. They both make useful and often similar predictions, but the assumptions of each model are different, and so are their respective descriptions of a chemical bond.

### Single and Double Bonds

**10.6** Applying valence bond theory, we see that a double bond is actually composed of two different kinds of bonds, one  $\sigma$  and one  $\pi$ . The orbital overlap in the  $\pi$  bond is side-to-side between two  $p$  orbitals and consequently different than the end-to-end overlap in a  $\sigma$  bond. Since the bonds are different types, the bond energy of the double bond is not just twice the bond energy of the single bond.

### What Is a Chemical Bond? Part II

**10.7** In MO theory, atoms will join together (or bond) when the electrons in the atoms can lower their energy by occupying the molecular orbitals of the resultant molecule. Unlike the Lewis model or valence bond theory, the chemical “bonds” in MO theory are not localized between atoms, but spread throughout the entire molecule.

# 11

# Liquids, Solids, and Intermolecular Forces

*It's a wild dance floor there at the molecular level.*

—Roald Hoffmann (1937–)

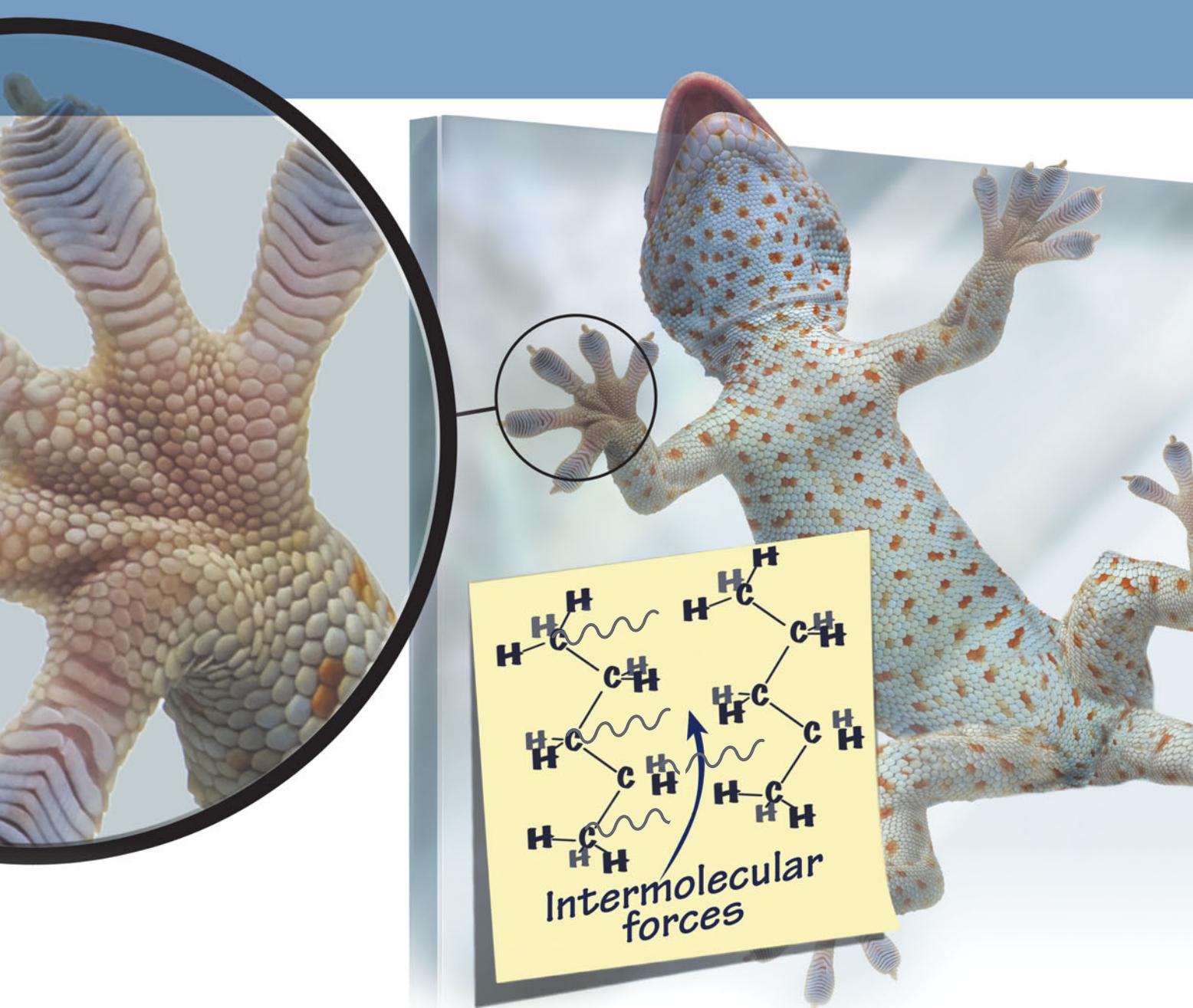
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**R**ECALL FROM CHAPTER 1 that matter exists primarily in three states (or phases): solid, liquid, and gas. In Chapter 5, we examined the gas state. In this chapter we turn to the solid and liquid states, known collectively as the *condensed* states. The solid and liquid states are more similar to each other than they are to the gas state. In the gas state, constituent particles—atoms or molecules—are separated by large distances and do not interact with each other very much. In the condensed states, constituent particles are close together and exert moderate to strong attractive forces on one another. Whether a substance is a solid, liquid, or gas depends on the structure of the particles that compose the substance. Remember the theme we have emphasized since Chapter 1 of this book: the properties of matter are determined by the properties of molecules and atoms. In this chapter, we will see how the structure of a particular atom or molecule determine the state in which it will exist at a given temperature.

## 11.1 Climbing Geckos and Intermolecular Forces

The gecko shown here can run up a polished glass window in seconds or even walk across a ceiling. It can support its entire weight by a single toe in contact with a surface. How? Research by several scientists points to *intermolecular forces*—attractive forces that exist between all





molecules and atoms—as the reason that the gecko can perform its gravity-defying feats. Intermolecular forces are the forces that hold many liquids and solids—such as water and ice, for example—together.

The key to the gecko's sticky feet lies in the millions of microhairs, called *setae*, that line its toes. Each seta is between 30 and 130  $\mu\text{m}$  long and branches out to end in several hundred flattened tips called *spatulae*, as you can see in the photo at right. This unique structure allows the gecko's toes to have unusually close contact with the surfaces it climbs. The close contact allows intermolecular forces—which are significant only at short distances—to hold the gecko to the wall.

All living organisms depend on intermolecular forces, not for adhesion to walls, but for many physiological processes. For example, in Chapter 21 we will examine how intermolecular forces help determine the shapes of protein molecules (the workhorse molecules in living organisms). Later in this chapter, we discuss how intermolecular forces are central to the structure of DNA, the inheritable molecule that carries the blueprints for life. (See the *Chemistry and Medicine* box in Section 11.3.)

More generally, intermolecular forces are responsible for the very existence of condensed states. The state of a sample of matter—solid, liquid, or gas—depends on the magnitude of intermolecular forces between the constituent particles relative to the amount

*Research suggest that the gecko's remarkable ability to climb walls and adhere to surfaces depends on intermolecular forces.*



▲ Each of the millions of microhairs on a gecko's feet branches out to end in flattened tips called *spatulae*.

of thermal energy in the sample. Recall from Chapter 6 that the molecules and atoms composing matter are in constant random motion that increases with increasing temperature. The energy associated with this motion is *thermal energy*. When thermal energy is high relative to intermolecular forces, matter tends to be gaseous. When thermal energy is low relative to intermolecular forces, matter tends to be liquid or solid.

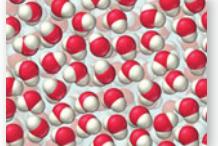
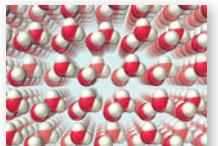
## 11.2 Solids, Liquids, and Gases: A Molecular Comparison

We are all familiar with solids and liquids. Water, gasoline, rubbing alcohol, and nail polish remover are common liquids that you have probably encountered. Ice, dry ice, and diamond are familiar solids. To begin to understand the differences between the three common states of matter, examine Table 11.1, which shows the density and molar volume of water in its three different states, along with molecular representations of each state. Notice that the densities of the solid and liquid states are much greater than the density of the gas state. Notice also that the solid and liquid states are more similar in density and molar volume to one another than they are to the gas state. The molecular representations show the reason for these differences. The molecules in liquid water and ice are in close contact with one another—essentially touching—while those in gaseous water are separated by large distances. The molecular representation of gaseous water in Table 11.1 is actually out of proportion—the water molecules in the figure should be much farther apart for their size. (Only a fraction of a molecule could be included in the figure if it were drawn to scale.) From the molar volumes, we know that 18.0 mL of liquid water (slightly more than a tablespoon) occupies 30.5 L when converted to gas at 100 °C (at atmospheric pressure). The low density of gaseous water is a direct result of this large separation between molecules.

Notice also that, for water, the solid is slightly less dense than the liquid. This is *atypical* behavior. Most solids are slightly denser than their corresponding liquids because the molecules move closer together upon freezing. As we will discuss in Section 11.9, ice is less dense than liquid water because the unique crystal structure of ice results in water molecules moving slightly farther apart upon freezing.

A major difference between liquids and solids is the freedom of movement of the constituent molecules or atoms. Even though the atoms or molecules in a liquid are in close contact, thermal energy partially overcomes the attractions between them, allowing them to move around one another. This is not the case in solids; the atoms or molecules

**TABLE 11.1 The Three States of Water**

Phase	Temperature (°C)	Density (g/cm <sup>3</sup> , at 1 atm)	Molar Volume	Molecular View
Gas (steam)	100	$5.90 \times 10^{-4}$	30.5 L	
Liquid (water)	20	0.998	18.0 mL	
Solid (ice)	0	0.917	19.6 mL	

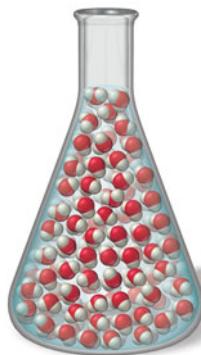
**TABLE 11.2 Properties of the States of Matter**

State	Density	Shape	Volume	Strength of Intermolecular Forces (Relative to Thermal Energy)
Gas	Low	Indefinite	Indefinite	Weak
Liquid	High	Indefinite	Definite	Moderate
Solid	High	Definite	Definite	Strong

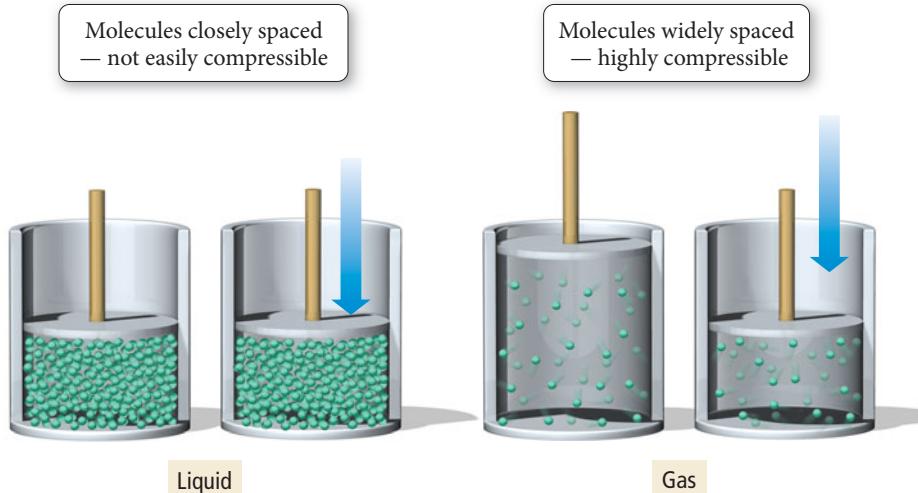
in a solid are virtually locked in their positions, only vibrating back and forth about a fixed point. Table 11.2 summarizes the properties of liquids and solids, as well as the properties of gases for comparison.

Liquids assume the shape of their containers because the atoms or molecules that compose liquids are free to flow (or move around one another). When we pour water into a beaker, the water flows and assumes the shape of the beaker (Figure 11.1 ▶). Liquids are not easily compressed because the molecules or atoms that compose them are already in close contact—they cannot be pushed much closer together. The molecules in a gas, by contrast, have a great deal of space between them and are easily forced into a smaller volume by an increase in external pressure (Figure 11.2 ▼).

Solids have a definite shape because, in contrast to liquids and gases, the molecules or atoms that compose solids are fixed in place—each molecule or atom merely vibrates about a fixed point. Like liquids, solids have a definite volume and generally cannot be compressed because the molecules or atoms composing them are already in close contact.



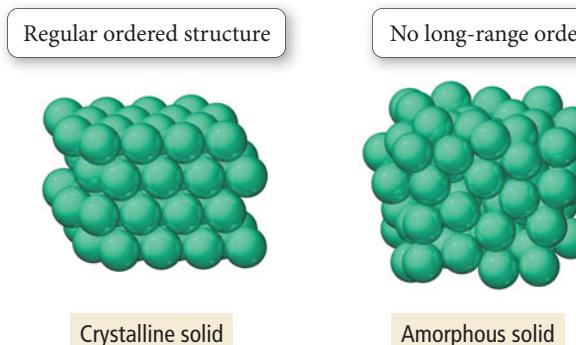
▲ **FIGURE 11.1** Liquids Assume the Shapes of Their Containers When we pour water into a flask, it assumes the shape of the flask because water molecules are free to flow.



▲ **FIGURE 11.2** Gases Are Compressible Molecules in a liquid are closely spaced and are not easily compressed. Molecules in a gas have a great deal of space between them, making gases compressible.

Solids may be **crystalline**, in which case the atoms or molecules that compose them are arranged in a well-ordered three-dimensional array, or they may be **amorphous**, in which case the atoms or molecules that compose them have no long-range order (Figure 11.3 ▼).

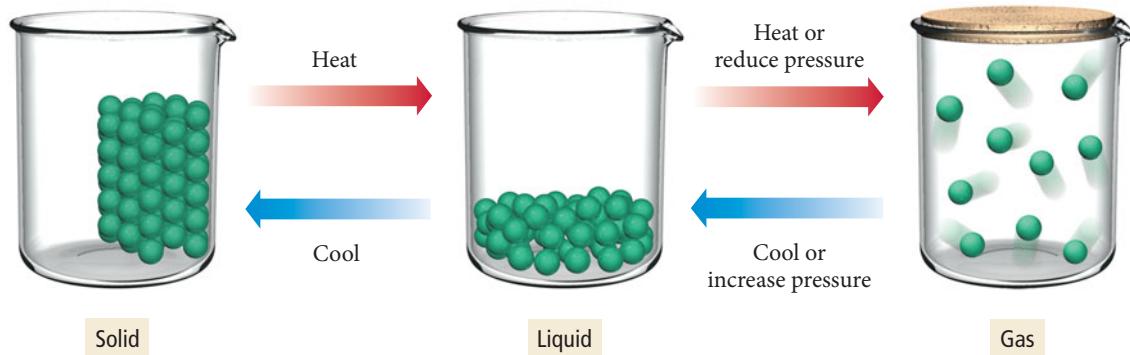
According to some definitions, an **amorphous solid** is considered a unique state, different from the normal solid state because it lacks any long-range order.



◀ **FIGURE 11.3** Crystalline and Amorphous Solids In a crystalline solid, the arrangement of the particles displays long-range order. In an amorphous solid, the arrangement of the particles has no long-range order.

## Changes between States

We can transform one state of matter to another by changing the temperature, pressure, or both. For example, we can convert solid ice to liquid water by heating, and liquid water to solid ice by cooling. The following diagram shows the three states of matter and the changes in conditions that commonly induce transitions between the states.

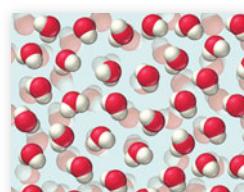


▲ The propane in an LP gas tank is in the liquid state. When you open the tank, some propane vaporizes and escapes as a gas.

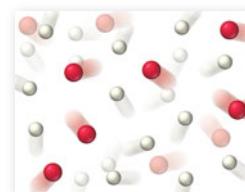
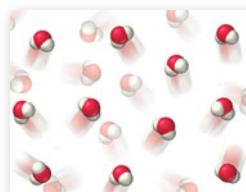
We can induce a transition between the liquid and gas state, not only by heating and cooling, but also through changing the pressure. In general, increases in pressure favor the denser state, so increasing the pressure of a gas sample results in a transition to the liquid state. The most familiar example of this phenomenon occurs in the LP (liquefied petroleum) gas used as a fuel for outdoor grills and lanterns. LP gas is composed primarily of propane, a gas at room temperature and atmospheric pressure. However, it liquefies at pressures exceeding about 2.7 atm. The propane you buy in a tank is under pressure and therefore in the liquid form. When you open the tank, some of the propane escapes as a gas, lowering the pressure in the tank for a brief moment. Immediately, however, some of the liquid propane evaporates, replacing the gas that escaped. Storing gases like propane as liquids is efficient because, in their liquid form, they occupy much less space.

### Conceptual Connection 11.1 State Changes

This molecular diagram shows a sample of liquid water.



Which of the diagrams below best depicts the vapor emitted from a pot of boiling water?



(a)

(b)

(c)

## 11.3 Intermolecular Forces: The Forces That Hold Condensed States Together

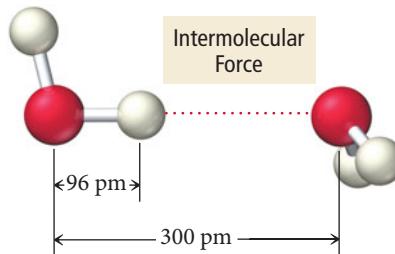
The structure of the particles that compose a substance determine the strength of the intermolecular forces that hold the substance together, which in turn determine whether the substance is a solid, liquid, or gas at a given temperature. At room temperature, moderate to strong intermolecular forces tend to result in liquids and solids (high melting and boiling points) and weak intermolecular forces tend to result in gases (low melting and boiling points).

Intermolecular forces originate from the interactions between charges, partial charges, and temporary charges on molecules (or atoms and ions), much as bonding forces originate from interactions between charged particles in atoms. Recall from Section 8.3 that according to Coulomb's law, the potential energy ( $E$ ) of two oppositely charged particles (with charges  $q_1$  and  $q_2$ ) decreases (becomes more negative) with increasing magnitude of charge and with decreasing separation ( $r$ ):

$$E = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r} \quad (\text{When } q_1 \text{ and } q_2 \text{ are opposite in sign, } E \text{ is negative.})$$

Therefore, as we have seen, protons and electrons are attracted to each other because their potential energy decreases as they get closer together. Similarly, molecules with partial or temporary charges are attracted to each other because *their* potential energy decreases as they get closer together. However, intermolecular forces, even the strongest ones, are generally *much weaker* than bonding forces.

The reason for the relative weakness of intermolecular forces compared to bonding forces is also related to Coulomb's law. Bonding forces are the result of large charges (the charges on protons and electrons) interacting at very close distances. Intermolecular forces are the result of smaller charges (as we shall see in the following discussion) interacting at greater distances. For example, consider the interaction between two water molecules in liquid water:



The length of an O—H bond in liquid water is 96 pm; however, the average distance between water molecules in liquid water is about 300 pm. The larger distances between molecules, as well as the smaller charges involved (the partial charges on the hydrogen and oxygen atoms), result in weaker forces. To break the O—H bonds in water, we have to heat the water to thousands of degrees Celsius. However, to completely overcome the intermolecular forces *between* water molecules, we have to heat water only to its boiling point, 100 °C (at sea level).

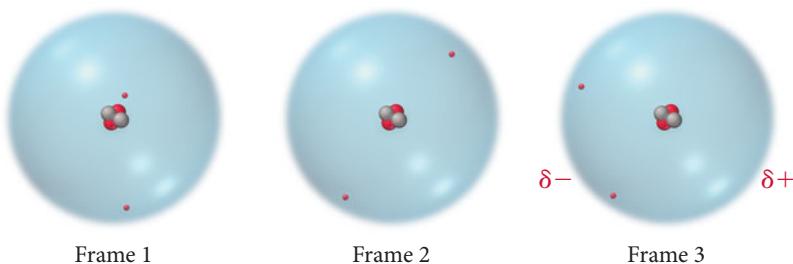
In this section we examine several different types of intermolecular forces, including dispersion forces, dipole–dipole forces, hydrogen bonding, and ion–dipole forces. The first three of these can potentially occur in all substances; the last one occurs only in mixtures.

### Dispersion Force

The one intermolecular force present in all molecules and atoms is the **dispersion force** (also called the London force). Dispersion forces are the result of fluctuations in the electron distribution within molecules or atoms. Since all atoms and molecules have electrons, they all exhibit dispersion forces. The electrons in an atom or molecule may,

The nature of dispersion forces was first recognized by Fritz W. London (1900–1954), a German-American physicist.

at any one instant, be unevenly distributed. Imagine a frame-by-frame movie of a helium atom in which each “frame” captures the position of the helium atom’s two electrons.



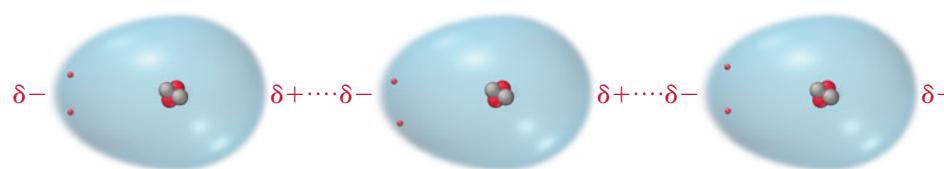
In any one frame, the electrons may not be symmetrically arranged around the nucleus. In frame 3, for example, helium’s two electrons are on the left side of the helium atom. At that instant, the left side will have a slightly negative charge ( $\delta-$ ). The right side of the atom, which temporarily has no electrons, will have a slightly positive charge ( $\delta+$ ) because of the charge of the nucleus. This fleeting charge separation is called an *instantaneous dipole* or a *temporary dipole*. As shown in Figure 11.4 ▼, an instantaneous dipole on one helium atom induces an instantaneous dipole on its neighboring atoms because the positive end of the instantaneous dipole attracts electrons in the neighboring atoms. The neighboring atoms then attract one another—the positive end of one instantaneous dipole attracting the negative end of another. This attraction is the dispersion force.

#### ► FIGURE 11.4 Dispersion Interactions

The temporary dipole in one helium atom induces a temporary dipole in its neighbor. The resulting attraction between the positive and negative charges creates the dispersion force.

#### Dispersion Force

An instantaneous dipole on any one helium atom induces instantaneous dipoles on neighboring atoms, which then attract one another.



To polarize means to form a dipole moment (see Section 9.6).

The *magnitude* of the dispersion force depends on how easily the electrons in the atom or molecule can move or *polarize* in response to an instantaneous dipole, which in turn depends on the size (or volume) of the electron cloud. A larger electron cloud results in a greater dispersion force because the electrons are held less tightly by the nucleus and therefore polarize more easily. If all other variables are constant, the dispersion force increases with increasing molar mass because molecules or atoms of higher molar mass generally have more electrons dispersed over a greater volume. For example, consider the boiling points of the noble gases displayed in Table 11.3 ▲. As the molar masses and electron cloud volumes of the noble gases increase, the greater dispersion forces result in increasing boiling points (because the molecules are more strongly attracted to one another).

Molar mass alone, however, does not determine the magnitude of the dispersion force. Compare the molar masses and boiling points of *n*-pentane and neopentane:

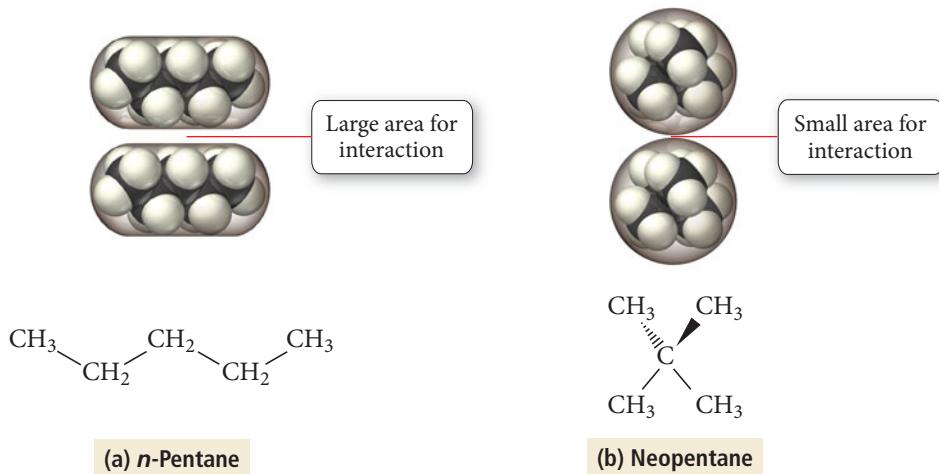


***n*-Pentane**  
molar mass = 72.15 g/mol  
boiling point = 36.1 °C

**Neopentane**  
molar mass = 72.15 g/mol  
boiling point = 9.5 °C

**TABLE 11.3 Boiling Points of the Noble Gases**

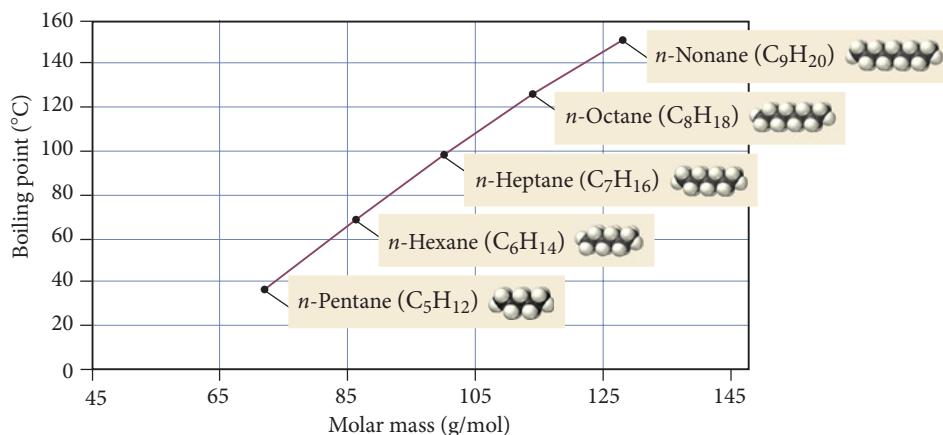
Noble Gas	Molar Mass (g/mol)	Boiling Point (K)
He	4.00	4.2
Ne	20.18	27
Ar	39.95	87
Kr	83.80	120
Xe	131.30	165



▲ **FIGURE 11.5** Dispersion Force and Molecular Shape (a) The straight shape of *n*-pentane molecules allows them to interact with one another along the entire length of the molecules. (b) The nearly spherical shape of neopentane molecules allows for only a small area of interaction. Thus, dispersion forces are weaker in neopentane than in *n*-pentane, resulting in a lower boiling point.

These molecules have identical molar masses, but *n*-pentane has a higher boiling point than neopentane. Why? Because the two molecules have different shapes. The *n*-pentane molecules are long and can interact with one another along their entire length, as shown in Figure 11.5a ▲. In contrast, the bulky, round shape of neopentane molecules results in a smaller area of interaction between neighboring molecules, as shown in Figure 11.5b▲. The result is a lower boiling point for neopentane.

Although molecular shape and other factors must always be considered in determining the magnitude of dispersion forces, molar mass can act as a guide when comparing dispersion forces within a family of similar elements or compounds as shown in Figure 11.6 ▼.



▲ **FIGURE 11.6** Boiling Points of the *n*-Alkanes The boiling points of the *n*-alkanes rise with increasing molar mass and the consequent stronger dispersion forces.

### Conceptual Connection 11.2 Dispersion Forces

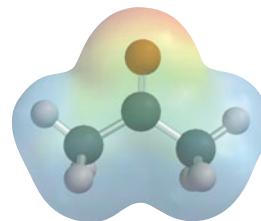
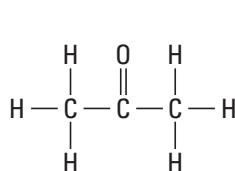
Which halogen has the highest boiling point?

- (a)  $\text{Cl}_2$       (b)  $\text{Br}_2$       (c)  $\text{I}_2$

See Section 9.6 to review how to determine if a molecule is polar.

## Dipole–Dipole Force

The **dipole–dipole force** exists in all molecules that are polar. Polar molecules have electron-rich regions (which have a partial negative charge) and electron deficient regions (which have a partial positive charge). For example, consider acetone:



Structural formula

Space-filling model

Electrostatic potential map

The image on the right is an electrostatic potential map of acetone; these kinds of maps were first introduced in Sections 9.6 and 10.5. Recall that the red areas indicate electron-rich regions in the molecule and that the blue areas indicate electron poor regions. Notice that acetone has an electron-rich region surrounding the oxygen atom (because oxygen is more electronegative than the rest of the molecule) and electron-poorer regions surrounding the carbon and hydrogen atoms. The result is that acetone has a **permanent dipole** that can interact with other acetone molecules as shown in Figure 11.7 ▶. The positive end of one permanent dipole attracts the negative end of another; this attraction is the dipole–dipole force. Polar molecules, therefore, have higher melting and boiling points than nonpolar molecules of similar molar mass. Remember that all molecules (including polar ones) have dispersion forces. Polar molecules have, *in addition*, dipole–dipole forces. This additional attractive force raises their melting and boiling points relative to nonpolar molecules of similar molar mass. For example, consider formaldehyde and ethane:

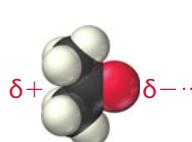
Name	Formula	Molar Mass (amu)	Structure	bp (°C)	mp (°C)
Formaldehyde	CH <sub>2</sub> O	30.03		-19.5	-92
Ethane	C <sub>2</sub> H <sub>6</sub>	30.07		-88	-172

### ► FIGURE 11.7 Dipole–Dipole Interaction

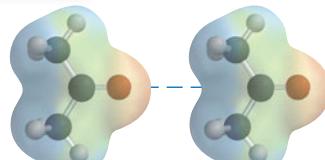
**Interaction** Molecules with permanent dipoles, such as acetone, are attracted to one another via dipole–dipole interactions.

#### Dipole–Dipole Interaction

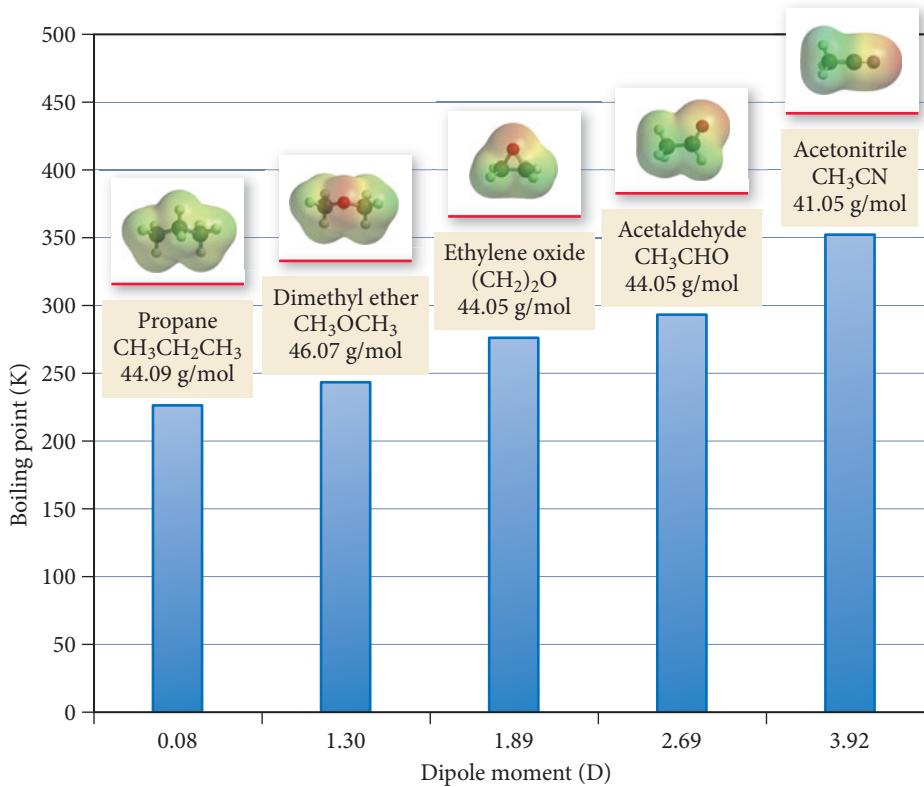
The positive end of a polar molecule is attracted to the negative end of its neighbor.



Space-filling model



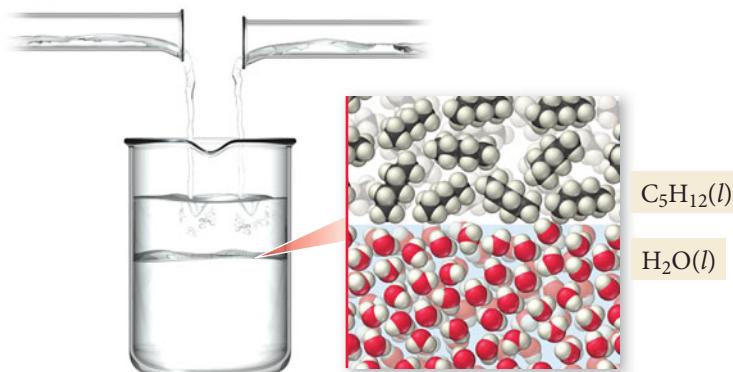
Electrostatic potential map



**▲ FIGURE 11.8 Dipole Moment and Boiling Point** The molecules shown here all have similar molar masses but different dipole moments. The boiling points increase with increasing dipole moment.

Formaldehyde is polar, and has a higher melting point and boiling point than nonpolar ethane, even though the two compounds have the same molar mass. Figure 11.8 ▲ shows the boiling points of a series of molecules with similar molar mass but progressively greater dipole moments. Notice that the boiling points increase with increasing dipole moment.

The polarity of molecules is also important in determining the **miscibility**—the ability to mix without separating into two states—of liquids. In general, polar liquids are miscible with other polar liquids but are not miscible with nonpolar liquids. For example, water, a polar liquid, is not miscible with pentane ( $C_5H_{12}$ ), a nonpolar liquid (Figure 11.9 ▼). Similarly, water and oil (also nonpolar) do not mix. Consequently, oily hands or oily stains on clothes cannot be washed with plain water (see *Chemistry in Your Day: How Soap Works* in Section 10.5).



**▲ FIGURE 11.9 Polar and Nonpolar Compounds** Water and pentane do not mix because water molecules are polar and pentane molecules are nonpolar.

### EXAMPLE 11.1 Dipole–Dipole Forces

Which of these molecules have dipole–dipole forces?

- (a) CO<sub>2</sub>      (b) CH<sub>2</sub>Cl<sub>2</sub>      (c) CH<sub>4</sub>

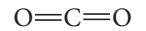
#### SOLUTION

A molecule has dipole–dipole forces if it is polar. To determine if a molecule is polar,

(1) *determine if the molecule contains polar bonds* and (2) *determine if the polar bonds add together to form a net dipole moment* (Section 9.6).

**(a) CO<sub>2</sub>**

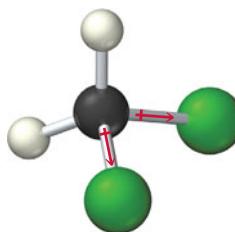
- (1) Since the electronegativity of carbon is 2.5 and that of oxygen is 3.5 (Figure 9.8), CO<sub>2</sub> has polar bonds.
- (2) The geometry of CO<sub>2</sub> is linear. Consequently, the dipoles of the polar bonds cancel, so the molecule is *not polar* and does not have dipole–dipole forces.



No dipole forces present

**(b) CH<sub>2</sub>Cl<sub>2</sub>**

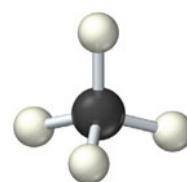
- (1) The electronegativity of C is 2.5, that of H is 2.1, and that of Cl is 3.0. Consequently, CH<sub>2</sub>Cl<sub>2</sub> has two polar bonds (C—Cl) and two bonds that are nearly nonpolar (C—H).
- (2) The geometry of CH<sub>2</sub>Cl<sub>2</sub> is tetrahedral. Since the C—Cl bonds and the C—H bonds are different, their dipoles do not cancel but sum to a net dipole moment. The molecule is polar and has dipole–dipole forces.



Dipole forces present

**(c) CH<sub>4</sub>**

- (1) Since the electronegativity of C is 2.5 and that of hydrogen is 2.1, the C—H bonds are nearly nonpolar.
- (2) In addition, since the geometry of the molecule is tetrahedral, any slight polarities that the bonds might have will cancel. CH<sub>4</sub> is therefore nonpolar and does not have dipole–dipole forces.



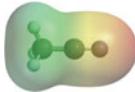
No dipole forces present

#### FOR PRACTICE 11.1

Which molecules have dipole–dipole forces?

- (a) Cl<sub>4</sub>      (b) CH<sub>3</sub>Cl      (c) HCl

### Conceptual Connection 11.3 Dipole–Dipole Interaction



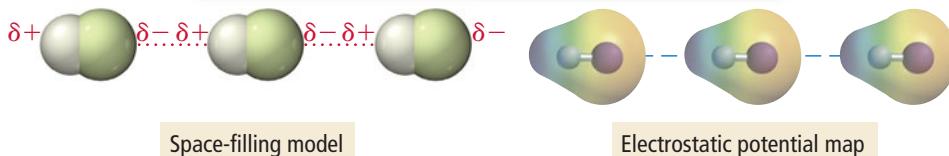
An electrostatic potential map for acetonitrile (CH<sub>3</sub>CN), which is polar, is shown at left. From this map, determine the geometry for how two acetonitrile molecules would interact with each other. Draw structural formulas, using the three-dimensional bond notation introduced in Section 10.4, to illustrate the geometry of the interaction.

### Hydrogen Bonding

Polar molecules containing hydrogen atoms bonded directly to small electronegative atoms—most importantly fluorine, oxygen, or nitrogen—exhibit an intermolecular force called **hydrogen bonding**. HF, NH<sub>3</sub>, and H<sub>2</sub>O, for example, all undergo hydrogen bonding. The hydrogen bond is a sort of *super* dipole–dipole force. The large electronegativity difference

## Hydrogen Bonding

When H bonds directly to F, O, or N, the bonding atoms acquire relatively large partial charges, giving rise to strong dipole–dipole attractions between neighboring molecules.



between hydrogen and any of these electronegative elements causes the hydrogen atom to have a fairly large partial positive charge ( $\delta+$ ) within the bond, while the F, O, or N atom has a fairly large partial negative charge ( $\delta-$ ). In addition, since these atoms are all quite small, the H atom on one molecule can approach the F, O, or N atom on an adjacent molecule very closely. The result is a strong attraction between the H atom on one molecule and the F, O, or N on its neighbor—an attraction called a **hydrogen bond**. For example, in HF, the hydrogen atom in one molecule is strongly attracted to the fluorine atom on a neighboring molecule (Figure 11.10 ▲). The electrostatic potential maps in Figure 11.10 show the large differences in electron density that result in unusually large partial charges.

*Hydrogen bonds should not be confused with chemical bonds.* Chemical bonds occur *between individual atoms within a molecule*, whereas hydrogen bonds—like dispersion forces and dipole–dipole forces—are intermolecular forces that occur *between molecules*. A typical hydrogen bond is only 2–5% as strong as a typical covalent chemical bond. Hydrogen bonds are, however, the strongest of the three *intermolecular* forces we have discussed so far. Substances composed of molecules that form hydrogen bonds have higher melting and boiling points than comparable substances composed of molecules that do not form hydrogen bonds. For example, consider ethanol and dimethyl ether:

Name	Formula	Molar Mass (amu)	Structure	bp (°C)	mp (°C)
Ethanol	C <sub>2</sub> H <sub>6</sub> O	46.07		CH <sub>3</sub> CH <sub>2</sub> OH	78.3    -114.1
Dimethyl Ether	C <sub>2</sub> H <sub>6</sub> O	46.07		CH <sub>3</sub> OCH <sub>3</sub>	-22.0    -138.5

Since ethanol contains hydrogen bonded directly to oxygen, ethanol molecules form hydrogen bonds with each other as shown in Figure 11.11 ▶. The hydrogen that is directly bonded to oxygen in an individual ethanol molecule is also strongly attracted to the oxygen on neighboring molecules. This strong attraction makes the boiling point of ethanol 78.3 °C. Consequently, ethanol is a liquid at room temperature. In contrast, dimethyl ether has an identical molar mass to ethanol but does not exhibit hydrogen bonding because in the dimethyl ether molecule, the oxygen atom is not bonded directly to hydrogen; this results in lower boiling and melting points, and dimethyl ether is a gas at room temperature.

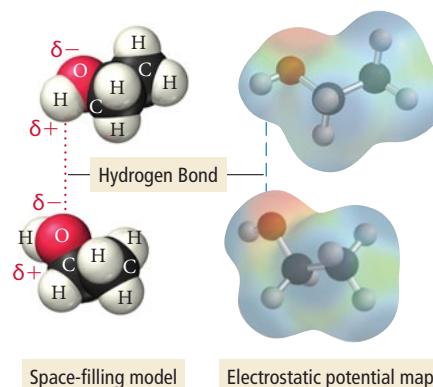
Water is another good example of a molecule with hydrogen bonding (Figure 11.12 ▶). Figure 11.13 ▶ shows the boiling points of the simple hydrogen compounds of the group 4A and group 6A elements. In general, boiling points increase with increasing molar mass, as expected based on increasing dispersion forces. However, because of hydrogen bonding, the boiling point of water (100 °C) is much higher than expected based on its molar mass (18.0 g/mol). Without hydrogen bonding, all the water on our planet would be gaseous.

### ◀ FIGURE 11.10 Hydrogen Bonding

in HF The hydrogen of one HF molecule, with its partial positive charge, is attracted to the fluorine of its neighbor, with its partial negative charge. This dipole–dipole interaction is an example of a hydrogen bond.

## Hydrogen Bonding in Ethanol

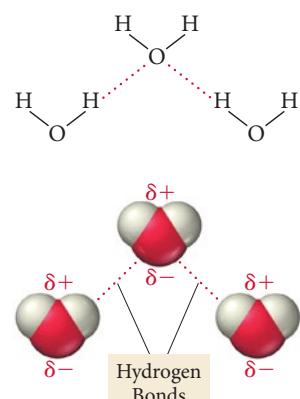
The partially positive charge on H is strongly attracted to the partial negative charge on O.



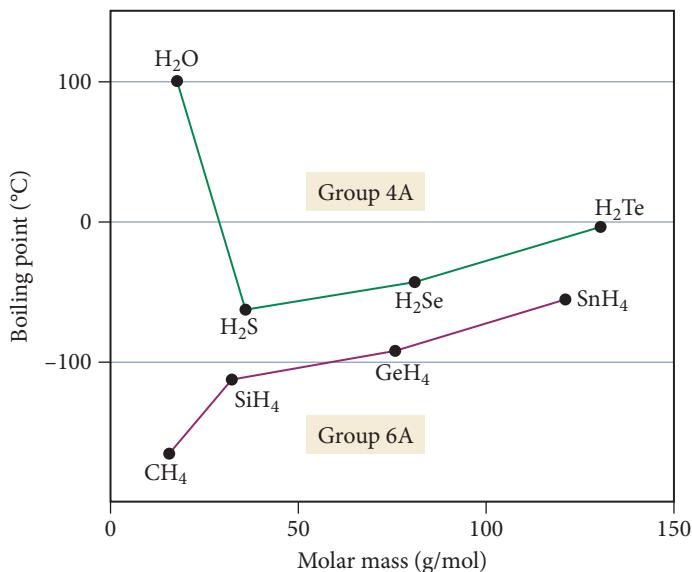
### ◀ FIGURE 11.11 Hydrogen Bonding in Ethanol

The left side shows the space-filling models, and the right side shows the electrostatic potential maps.

## Hydrogen Bonding in Water



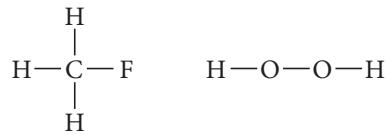
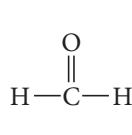
◀ FIGURE 11.12 Hydrogen Bonding in Water



**► FIGURE 11.13** Boiling Points of Group 4A and 6A Compounds Because of hydrogen bonding, the boiling point of water is anomalous compared to the boiling points of other hydrogen-containing compounds.

### EXAMPLE 11.2 Hydrogen Bonding

One of these compounds is a liquid at room temperature. Which one and why?



### SOLUTION

The three compounds have similar molar masses:

Formaldehyde      30.03 g/mol

Fluoromethane      34.03 g/mol

Hydrogen peroxide      34.02 g/mol

So the strengths of their dispersion forces are similar. All three compounds are also polar, so they have dipole–dipole forces. Hydrogen peroxide, however, is the only one of these compounds that also contains H bonded directly to F, O, or N. Therefore, it also has hydrogen bonding and is likely to have the highest boiling point of the three. Since the example stated that only one of the compounds was a liquid, you can safely assume that hydrogen peroxide is the liquid. Note that, although fluoromethane *contains* both H and F, H is not *directly bonded* to F, so fluoromethane does not have hydrogen bonding as an intermolecular force. Similarly, formaldehyde *contains* both H and O, but H is not *directly bonded* to O, so formaldehyde does not have hydrogen bonding either.

### FOR PRACTICE 11.2

Which has the higher boiling point, HF or HCl? Why?

### Ion-Dipole Force

The **ion-dipole force** occurs when an ionic compound is mixed with a polar compound; it is especially important in aqueous solutions of ionic compounds. For example, when sodium chloride is mixed with water, the sodium and chloride ions interact with water

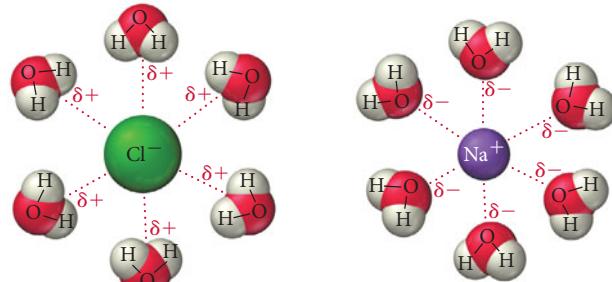
molecules via ion–dipole forces, as shown in Figure 11.14 ►. The positive sodium ions interact with the negative poles of water molecules, while the negative chloride ions interact with the positive poles. Ion–dipole forces are the strongest of the types of intermolecular forces discussed and are responsible for the ability of ionic substances to form solutions with water. We will discuss aqueous solutions more thoroughly in Chapter 12.

### Summarizing Intermolecular Forces (as shown in Table 11.4):

- Dispersion forces are present in all molecules and atoms and increase with increasing molar mass. These forces are always weak in small molecules but can be significant in molecules with high molar masses.
- Dipole–dipole forces are present in polar molecules.
- Hydrogen bonds, the strongest of the intermolecular forces that can occur in pure substances (second only to ion–dipole forces in general), are present in molecules containing hydrogen bonded directly to fluorine, oxygen, or nitrogen.
- Ion–dipole forces are present in mixtures of ionic compounds and polar compounds. These forces are very strong and are especially important in aqueous solutions of ionic compounds.

### Ion–Dipole Forces

The positively charged end of a polar molecule such as  $\text{H}_2\text{O}$  is attracted to negative ions and the negatively charged end of the molecule is attracted to positive ions.



▲ FIGURE 11.14 Ion-Dipole Forces  
Ion–dipole forces exist between  $\text{Na}^+$  and the negative ends of  $\text{H}_2\text{O}$  molecules and between  $\text{Cl}^-$  and the positive ends of  $\text{H}_2\text{O}$  molecules.

**TABLE 11.4 Types of Intermolecular Forces**

Type	Present in	Molecular perspective	Strength
Dispersion	All molecules and atoms		
Dipole-dipole	Polar molecules		
Hydrogen bonding	Molecules containing H bonded to F, O, or N		
Ion-dipole	Mixtures of ionic compounds and polar compounds		

### Conceptual Connection 11.4 Intermolecular Forces and Boiling Point

Which substance has the highest boiling point?

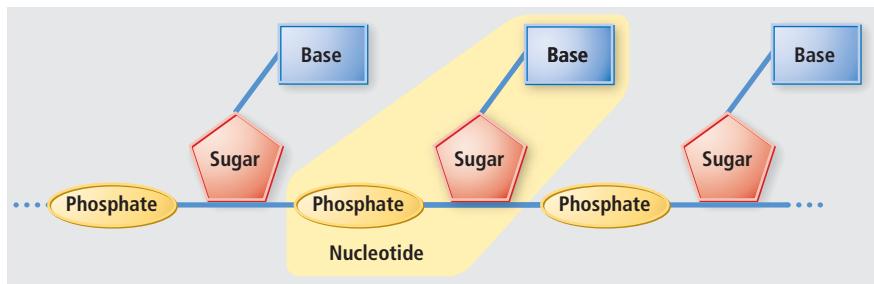
- (a)  $\text{CH}_3\text{OH}$     (b)  $\text{CO}$     (c)  $\text{N}_2$



## Chemistry and Medicine

### Hydrogen Bonding in DNA

**D**NA is a long, chainlike molecule that acts as a blueprint for each living organism. Copies of DNA are passed from parent to offspring, which is how we inherit traits from our parents. A DNA molecule is composed of thousands of repeating units called *nucleotides* (Figure 11.15 ▼). Each nucleotide contains one of four different *organic bases*: adenine, thymine, cytosine, and guanine (abbreviated A, T, C, and G). The sequence of these bases along DNA encodes the information that determines the nature of the proteins that are made in the body (proteins are the molecules that do most of the work in living organisms). Our proteins in turn determine many of our characteristics, including how we look, what diseases we are at risk of developing, and even our behavior.

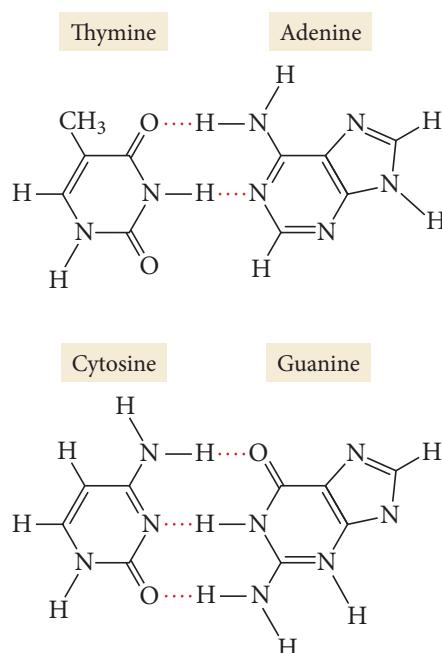


▲ **FIGURE 11.15 Nucleotides** The individual units in a DNA polymer are nucleotides. Each nucleotide contains one of four bases: adenine, thymine, cytosine, and guanine (abbreviated A, T, C, and G).

The replicating mechanism of DNA is related to its structure, which was discovered in 1953 by James Watson and Francis Crick. DNA consists of two *complementary* strands wrapped around each other in the now famous double helix and linked by hydrogen bonds between the bases on each strand. Each base (A, T, C, and G) has a complementary partner with which it forms hydrogen bonds (Figure 11.16 ▲): adenine (A) with thymine (T) and cytosine (C) with guanine (G). The hydrogen

► **FIGURE 11.16**

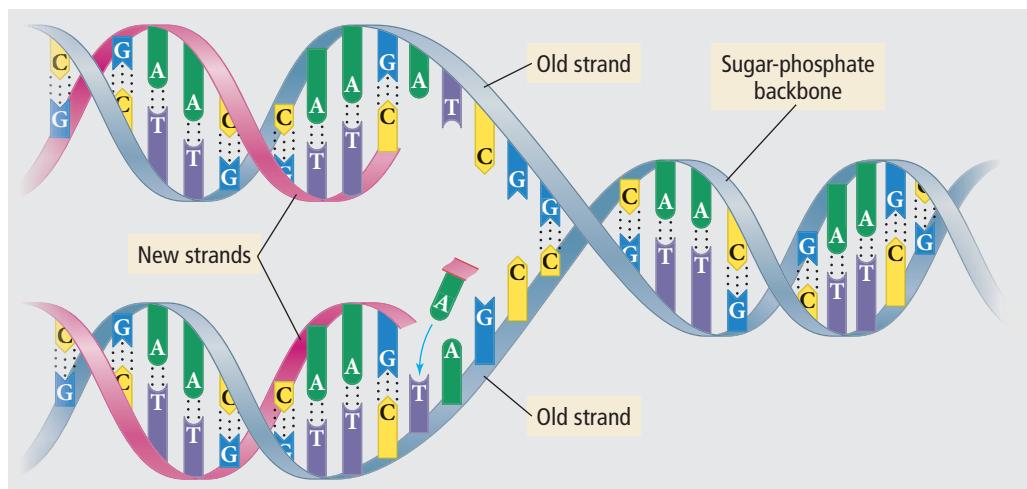
**Complementary Base Pairing via Hydrogen Bonds** The individual bases in DNA interact with one another via specific hydrogen bonds that form between A and T and between C and G.



bonding is so specific that each base will pair only with its complementary partner. When a cell is going to divide, enzymes unzip the DNA molecule across the hydrogen bonds that join its two strands (Figure 11.17 ▼). Then new bases, complementary to the bases in each strand, are added along each of the original strands, forming hydrogen bonds with their complements. The result is two identical copies of the original DNA.

### Question

Why would dispersion forces not work as a way to hold the two strands of DNA together? Why would covalent bonds not work?



◀ **FIGURE 11.17 Copying DNA**

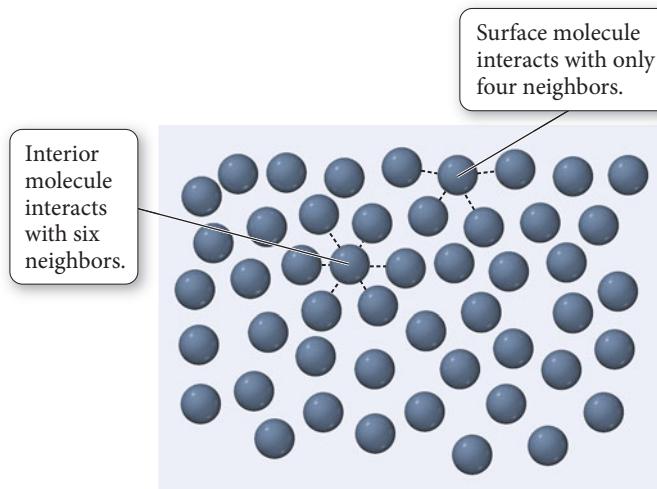
The two strands of the DNA molecule “unzip” by breaking the hydrogen bonds that join the base pairs. New bases complementary to the bases of each strand are assembled and joined together. The result is two molecules, each identical to the original one.

## 11.4 Intermolecular Forces in Action: Surface Tension, Viscosity, and Capillary Action

The most important manifestation of intermolecular forces is the very existence of liquids and solids. In liquids, we also observe several other manifestations of intermolecular forces including surface tension, viscosity, and capillary action.

### Surface Tension

A fly fisherman delicately casts a small fishing fly (a metal hook with a few feathers and strings attached to make it look like an insect) onto the surface of a moving stream. The fly floats on the surface of the water—even though the metal composing the hook is denser than water—and attracts trout. Why? The hook floats because of *surface tension*, the tendency of liquids to minimize their surface area.



▲ A trout fly can float on water because of surface tension.

◀ FIGURE 11.18 The Origin of Surface Tension Molecules at the liquid surface have a higher potential energy than those in the interior. As a result, a liquid tends to minimize its surface area; its surface behaves like a “skin.”

Figure 11.18 ▲ depicts the intermolecular forces experienced by a molecule at the surface of the liquid compared to those experienced by a molecule in the interior. Notice that a molecule at the surface has relatively fewer neighbors with which to interact, and it is therefore inherently less stable—it has higher potential energy—than those in the interior. (Remember that attractive interactions with other molecules lower potential energy.) In order to increase the surface area of the liquid, molecules from the interior have to be moved to the surface, and, because molecules at the surface have a higher potential energy than those in the interior, this movement requires energy. Therefore, liquids tend to minimize their surface area. The **surface tension** of a liquid is the energy required to increase the surface area by a unit amount. For example, at room temperature, water has a surface tension of  $72.8 \text{ mJ/m}^2$ —it takes  $72.8 \text{ mJ}$  to increase the surface area of water by one square meter.

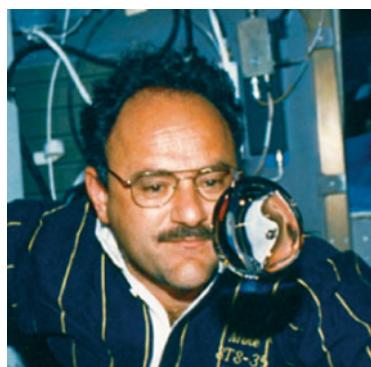
Why does surface tension allow the fly fisherman’s hook to float on water? The tendency for liquids to minimize their surface creates a kind of skin at the surface that resists penetration. For the fisherman’s hook to sink into the water, the water’s surface area must increase slightly—an increase that is resisted by the surface tension. We can observe surface tension by carefully placing a paper clip on the surface of water (Figure 11.19 ▷). The paper clip, even though it is denser than water, floats on the surface of the water. A slight tap on the clip provides the energy necessary to overcome the surface tension and causes the clip to sink.

Surface tension decreases as intermolecular forces decrease. You can’t float a paper clip on benzene, for example, because the dispersion forces among the molecules composing benzene are significantly weaker than the hydrogen bonds among water molecules. The surface tension of benzene is only  $28 \text{ mJ/m}^2$ —just 40% that of water.

Recall from Section 11.3 that the interactions between molecules lower their potential energy in much the same way that the interaction between protons and electrons lowers their potential energy, in accordance with Coulomb’s law.



◀ FIGURE 11.19 Surface Tension in Action A paper clip floats on water because of surface tension.



**▲ FIGURE 11.20** Spherical Water Droplets On the space shuttle in orbit, under weightless conditions, collections of water molecules coalesce into nearly perfect spheres held together by intermolecular forces between molecules.

Surface tension is also the reason that small water droplets (those not large enough to be distorted by gravity) form nearly perfect spheres. On the space shuttle, the complete absence of gravity allows even large samples of water to form nearly perfect spheres (Figure 11.20 ▲). Why? Just as gravity pulls the matter of a planet or star inward to form a sphere, so intermolecular forces among water molecules pull the water into a sphere. A sphere is the geometrical shape with the smallest surface area to volume ratio; the formation of a sphere minimizes the number of molecules at the surface, thus minimizing the potential energy of the system.

## Viscosity

Another manifestation of intermolecular forces is **viscosity**, the resistance of a liquid to flow. Motor oil, for example, is more viscous than gasoline, and maple syrup is more viscous than water. Viscosity is measured in a unit called the poise (P), defined as  $1\text{ g}/\text{cm}\cdot\text{s}$ . The viscosity of water at room temperature is approximately one centipoise (cP). Viscosity is greater in substances with stronger intermolecular forces because if molecules are more strongly attracted to each other, they do not flow around each other as freely. Viscosity also depends on molecular shape, increasing in longer molecules that can interact over a greater area and possibly become entangled. Table 11.5 lists the viscosity of several hydrocarbons. Notice the increase in viscosity with increasing molar mass (and therefore increasing magnitude of dispersion forces) and with increasing length (and therefore increasing potential for molecular entanglement).

Viscosity also depends on temperature because thermal energy partially overcomes the intermolecular forces, allowing molecules to flow past each other more easily. Table 11.6 lists the viscosity of water as a function of temperature. Nearly all liquids become less viscous as temperature increases.

**TABLE 11.6** Viscosity of Liquid Water at Several Temperatures

Temperature (°C)	Viscosity (cP)
20	1.002
40	0.653
60	0.467
80	0.355
100	0.282

**TABLE 11.5** Viscosity of Several Hydrocarbons at 20 °C

Hydrocarbon	Molar Mass (g/mol)	Formula	Viscosity (cP)
n-Pentane	72.15	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	0.240
n-Hexane	86.17	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	0.326
n-Heptane	100.2	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	0.409
n-Octane	114.2	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	0.542
n-Nonane	128.3	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	0.711



## Chemistry in Your Day

### Viscosity and Motor Oil

Viscosity is an important property of the motor oil you put into your car. The oil must be thick enough to adequately coat engine surfaces to lubricate them, but also thin enough to be pumped easily into all the required engine compartments. Motor oil viscosity is usually reported on a scale called the SAE scale (named after the Society of Automotive Engineers). The higher the SAE rating, the more viscous the oil. The thinnest motor oils have SAE ratings of 5 or 10, while the thickest have SAE ratings of up to 50.

Before the 1950s, most automobile owners changed the oil in their engine to accommodate seasonal changes in weather—a higher SAE rating was required in the summer months and a lower rating in the winter. Today, the advent of multigrade oils allows car owners in many climates to keep the same oil all year long. Multigrade oils, such as the 10W-40 oil shown at right, contain polymers (long molecules made up of repeating structural units) that coil at low temperatures but unwind at high temperatures. At low temperatures, the coiled polymers—because of their compact shape—do not contribute very much to the oil's viscosity. As the temperature increases, however, the molecules unwind and their long shape results in intermolecular forces and molecular entanglements that prevent the viscosity from decreasing as much as it would normally. The result is an oil whose viscosity is less temperature-dependent than it would be otherwise, allowing the same oil to be used over a wider range of temperatures. The 10W-40 designation indicates that the oil has an SAE rating of 10 at low temperatures and 40 at high temperatures.



## Capillary Action

Medical technicians take advantage of **capillary action**—the ability of a liquid to flow against gravity up a narrow tube—when taking a blood sample. The technician pokes the patient's finger with a pin, squeezes some blood out of the puncture, and then collects the blood with a thin tube. When the tube's tip comes into contact with the blood, the blood is drawn into the tube by capillary action. The same force helps trees and plants draw water from the soil.

Capillary action results from a combination of two forces: the attraction between molecules in a liquid, called *cohesive forces*, and the attraction between these molecules and the surface of the tube, called *adhesive forces*. The adhesive forces cause the liquid to spread out over the surface of the tube, while the cohesive forces cause the liquid to stay together. If the adhesive forces are greater than the cohesive forces (as is the case for water in a glass tube), the attraction to the surface draws the liquid up the tube and the cohesive forces pull along those molecules not in direct contact with the tube walls (Figure 11.21 ►). The water rises up the tube until the force of gravity balances the capillary action—the thinner the tube, the higher the rise. If the adhesive forces are smaller than the cohesive forces (as is the case for liquid mercury), the liquid does not rise up the tube at all (and in fact will drop to a level below the level of the surrounding liquid).

We can see the result of the differences in the relative magnitudes of cohesive and adhesive forces by comparing the meniscus of water to the meniscus of mercury (Figure 11.22 ►). (The meniscus is the curved shape of a liquid surface within a tube.) The meniscus of water is concave (rounded inward) because the *adhesive forces* are greater than the cohesive forces, causing the edges of the water to creep up the sides of the tube a bit, forming the familiar cupped shape. The meniscus of mercury is convex (rounded outward) because the *cohesive forces*—due to metallic bonding between the atoms—are greater than the adhesive forces. The mercury atoms crowd toward the interior of the liquid to maximize their interactions with each other, resulting in the upward bulge at the center of the surface.



▲ Blood is drawn into a capillary tube by capillary action.



▲ FIGURE 11.21 Capillary Action The attraction of water molecules to the glass surface draws the liquid around the edge of the tube up the walls. The water in the rest of the column is pulled along by the attraction of water molecules to one another. As can be seen in this figure, the narrower the tube, the higher the liquid will rise.

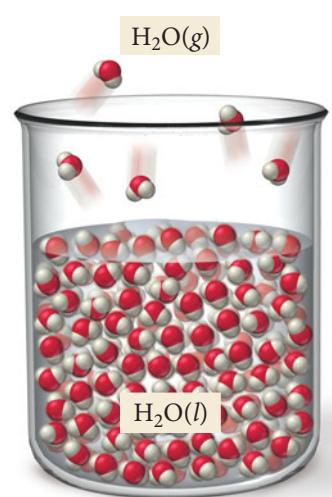
## 11.5 Vaporization and Vapor Pressure

We now turn our attention to vaporization, the process by which thermal energy can overcome intermolecular forces and produce a state change from liquid to gas. We first discuss the process of vaporization itself, then the energetics of vaporization, and finally the concepts of vapor pressure, dynamic equilibrium, and critical point. Vaporization is a common occurrence that we experience every day and even depend on to maintain proper body temperature.

### The Process of Vaporization

Imagine water molecules in a beaker at room temperature and open to the atmosphere (Figure 11.23 ►). The molecules are in constant motion due to thermal energy. If we could actually see the molecules at the surface, we would witness what Roald Hoffmann described as a “wild dance floor” (see the chapter-opening quote) because of all the vibrating, jostling, and molecular movement. *The higher the temperature, the greater the average energy of the collection of molecules.* However, at any one time, some molecules have more thermal energy than the average and some have less.

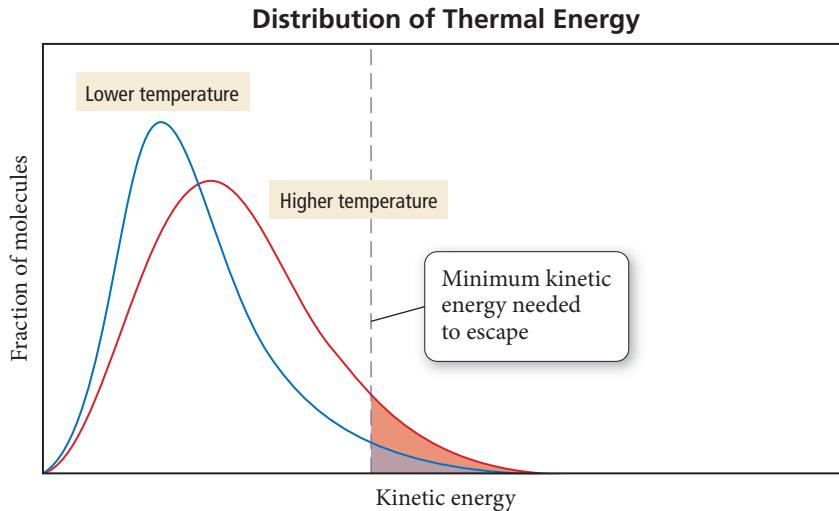
The distributions of thermal energies for the molecules in a sample of water at two different temperatures



▲ FIGURE 11.22 Meniscuses of Water and Mercury The meniscus of water is concave because water molecules are more strongly attracted to the glass wall than to one another. The meniscus of mercury is convex because mercury atoms are more strongly attracted to one another than to the glass walls.

◀ FIGURE 11.23 Vaporization of Water Some molecules in an open beaker have enough kinetic energy to vaporize from the surface of the liquid.

**► FIGURE 11.24** Distribution of Thermal Energy The thermal energies of the molecules in a liquid are distributed over a range. The peak energy increases with increasing temperature.



are shown in Figure 11.24 ▲. The molecules at the high end of the distribution curve have enough energy to break free from the surface—where molecules are held less tightly than in the interior due to fewer neighbor–neighbor interactions—and into the gas state. This transition, from liquid to gas, is called **vaporization**. Some of the water molecules in the gas state, at the low end of the energy distribution curve for the gaseous molecules, plunge back into the water and are captured by intermolecular forces. This transition, from gas to liquid, is the opposite of vaporization and is called **condensation**.

Although both evaporation and condensation occur in a beaker open to the atmosphere, under normal conditions evaporation takes place at a greater rate because most of the newly evaporated molecules escape into the surrounding atmosphere and never come back. The result is a noticeable decrease in the water level within the beaker over time (usually several days).

What happens if we increase the temperature of the water within the beaker? Because of the shift in the energy distribution to higher energies (see Figure 11.24), more molecules now have enough energy to break free and evaporate, so vaporization occurs more quickly. What happens if we spill the water on the table or floor? The same amount of water is now spread over a wider area, resulting in more molecules at the surface of the liquid. Since molecules at the surface have the greatest tendency to evaporate—because they are held less tightly—vaporization also occurs more quickly in this case. You probably know from experience that water in a beaker or glass may take many days to evaporate completely, while the same amount of water spilled on a table or floor typically evaporates within a few hours (depending on the exact conditions).

What happens if the liquid in the beaker is not water, but some other substance with weaker intermolecular forces, such as acetone (the main component in nail polish remover)? The weaker intermolecular forces allow more molecules to evaporate at a given temperature, increasing the rate of vaporization. We call liquids that vaporize easily **volatile**, and those that do not vaporize easily **nonvolatile**. Acetone is more volatile than water. Motor oil is virtually nonvolatile at room temperature.

#### *Summarizing the Process of Vaporization:*

- ▶ The rate of vaporization increases with increasing temperature.
- ▶ The rate of vaporization increases with increasing surface area.
- ▶ The rate of vaporization increases with decreasing strength of intermolecular forces.

### The Energetics of Vaporization

To understand the energetics of vaporization, consider again a beaker of water from the molecular point of view, except now imagine that the beaker is thermally insulated so that heat from the surroundings cannot enter the beaker. What happens to the temperature of the water left in the beaker as molecules evaporate? To answer this question, think about the energy distribution curve again (see Figure 11.24). The molecules that

leave the beaker are the ones at the high end of the energy curve—the most energetic. If no additional heat enters the beaker, the average energy of the entire collection of molecules decreases—much as the class average on an exam goes down if you eliminate the highest-scoring students. So vaporization is an *endothermic* process; it takes energy to vaporize the molecules in a liquid. Another way to understand the endothermicity of vaporization is to remember that vaporization requires overcoming the intermolecular forces that hold liquids together. Since energy is needed to pull the molecules away from one another, the process is endothermic.

Our bodies use the endothermic nature of vaporization for cooling. When we overheat, we sweat, causing our skin to be covered with liquid water. As this water evaporates, it absorbs heat from the body, cooling the skin. A fan makes us feel cooler because it blows newly vaporized water away from our skin, allowing more sweat to vaporize and causing even more cooling. High humidity, on the other hand, slows down the net rate of evaporation, preventing cooling. When the air already contains large amounts of water vapor, the sweat evaporates more slowly, making the body's cooling system less efficient.

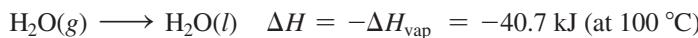
*Condensation*, the opposite of vaporization, is exothermic—heat is released when a gas condenses to a liquid. If you have ever accidentally put your hand above a steaming kettle or opened a bag of microwaved popcorn too soon, you may have experienced a *steam burn*. As the steam condenses to a liquid on your skin, it releases a lot of heat, causing the burn. The condensation of water vapor is also the reason that winter overnight temperatures in coastal regions, which tend to have water vapor in the air, do not get as low as in deserts, which tend to have dry air. As the air temperature in a coastal area drops, water condenses out of the air, releasing heat and preventing the temperature from dropping further. In deserts, the air contains almost no moisture to condense, so the temperature drop is more extreme.

**Heat of Vaporization** The amount of heat required to vaporize one mole of a liquid to gas is its **heat (or enthalpy) of vaporization** ( $\Delta H_{\text{vap}}$ ). The heat of vaporization of water at its normal boiling point of 100 °C is +40.7 kJ/mol:



The heat of vaporization is always positive because the process is endothermic—energy must be absorbed to vaporize a substance. The heat of vaporization is somewhat temperature dependent. For example, at 25 °C the heat of vaporization of water is +44.0 kJ/mol, slightly more than at 100 °C because the water contains less thermal energy at 25 °C. Table 11.7 lists the heats of vaporization of several liquids at their boiling points and at 25 °C.

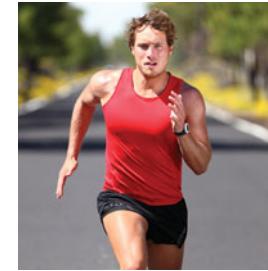
When a substance condenses from a gas to a liquid, the same amount of heat is involved, but the heat is emitted rather than absorbed:



When one mole of water condenses, it releases 40.7 kJ of heat. The sign of  $\Delta H$  in this case is negative because the process is exothermic.

We can use the heat of vaporization of a liquid to calculate the amount of energy required to vaporize a given mass of the liquid (or the amount of heat given off by the condensation of a given mass of liquid), using concepts similar to those covered in Section 6.6 (stoichiometry of  $\Delta H$ ). The heat of vaporization is like a conversion factor between number of moles of a liquid and the amount of heat required to vaporize it (or the amount of heat emitted when it condenses), as demonstrated in Example 11.3.

See Chapter 6 to review endothermic and exothermic processes.



▲ When we sweat, water evaporates from the skin. Since evaporation is endothermic, the result is a cooling effect.

The sign conventions of  $\Delta H$  were introduced in Chapter 6.

**TABLE 11.7 Heats of Vaporization of Several Liquids at Their Boiling Points and at 25 °C**

Liquid	Chemical Formula	Normal Boiling Point (°C)	$\Delta H_{\text{vap}}$ (kJ/mol) at Boiling Point	$\Delta H_{\text{vap}}$ (kJ/mol) at 25 °C
Water	H <sub>2</sub> O	100	40.7	44.0
Rubbing alcohol (isopropyl alcohol)	C <sub>3</sub> H <sub>8</sub> O	82.3	39.9	45.4
Acetone	C <sub>3</sub> H <sub>6</sub> O	56.1	29.1	31.0
Diethyl ether	C <sub>4</sub> H <sub>10</sub> O	34.6	26.5	27.1

### EXAMPLE 11.3 Using the Heat of Vaporization in Calculations



Calculate the mass of water (in g) that can be vaporized at its boiling point with 155 kJ of heat.

**SORT** You are given a certain amount of heat in kilojoules and asked to find the mass of water that can be vaporized.

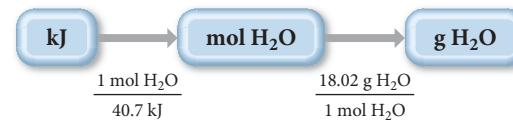
**STRATEGIZE** The heat of vaporization gives the relationship between heat absorbed and moles of water vaporized. Begin with the given amount of heat (in kJ) and convert to moles of water that can be vaporized. Then use the molar mass as a conversion factor to convert from moles of water to mass of water.

**SOLVE** Follow the conceptual plan to solve the problem.

**GIVEN:** 155 kJ

**FIND:** g H<sub>2</sub>O

#### CONCEPTUAL PLAN



#### RELATIONSHIPS USED

$$\Delta H_{\text{vap}} = 40.7 \text{ kJ/mol (at } 100^\circ \text{ C)}$$

$$18.02 \text{ g H}_2\text{O} = 1 \text{ mol H}_2\text{O}$$

#### SOLUTION

$$155 \text{ kJ} \times \frac{1 \text{ mol H}_2\text{O}}{40.7 \text{ kJ}} \times \frac{18.02 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} = 68.6 \text{ g H}_2\text{O}$$

#### FOR PRACTICE 11.3

Calculate the amount of heat (in kJ) required to vaporize 2.58 kg of water at its boiling point.

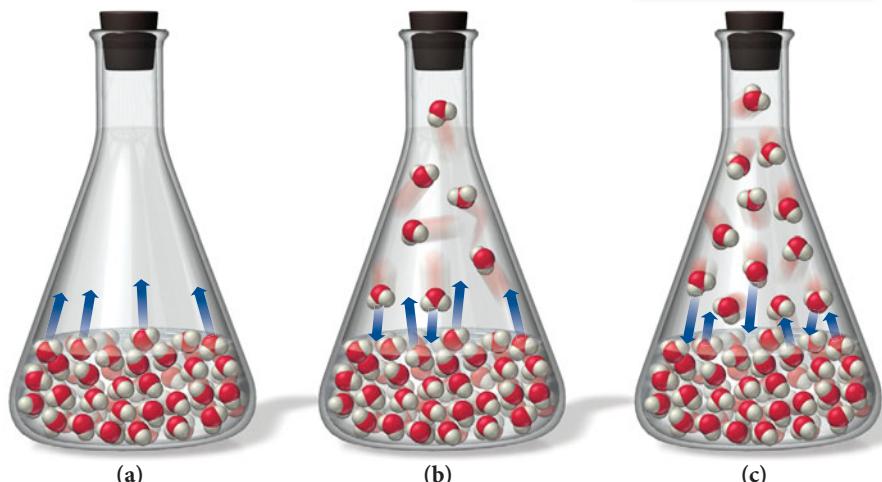
#### FOR MORE PRACTICE 11.3

Suppose that 0.48 g of water at 25 °C condenses on the surface of a 55 g block of aluminum that is initially at 25 °C. If the heat released during condensation goes only toward heating the metal, what is the final temperature (in °C) of the metal block? (The specific heat capacity of aluminum is 0.903 J/g °C.)

### Vapor Pressure and Dynamic Equilibrium

We have already seen that if a container of water is left uncovered at room temperature, the water slowly evaporates away. But what happens if the container is sealed? Imagine a sealed evacuated flask—one from which the air has been removed—containing liquid water, as shown in Figure 11.25 ▶. Initially, the water molecules evaporate, as they did in the open beaker. However, because of the seal, the evaporated molecules cannot escape

Dynamic equilibrium:  
Rate of evaporation =  
rate of condensation



► **FIGURE 11.25** Vaporization in a Sealed Flask (a) When water is in a sealed container, water molecules begin to vaporize. (b) As water molecules build up in the gas state, they begin to recondense into the liquid. (c) When the rate of evaporation equals the rate of condensation, dynamic equilibrium is reached.

into the atmosphere. As water molecules enter the gas state, some start condensing back into the liquid. As the concentration (or partial pressure) of gaseous water molecules increases, the rate of condensation also increases. However, as long as the water remains at a constant temperature, the rate of evaporation remains constant. Eventually the rate of condensation and the rate of vaporization become equal—**dynamic equilibrium** has been reached (Figure 11.26 ▶). Condensation and vaporization continue at equal rates and the concentration of water vapor above the liquid is constant.

The pressure of a gas in dynamic equilibrium with its liquid is called its **vapor pressure**. The vapor pressure of a particular liquid depends on the intermolecular forces present in the liquid and the temperature. Weak intermolecular forces result in volatile substances with high vapor pressures because the intermolecular forces are easily overcome by thermal energy. Strong intermolecular forces result in nonvolatile substances with low vapor pressures.

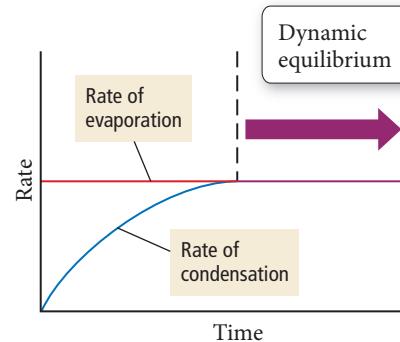
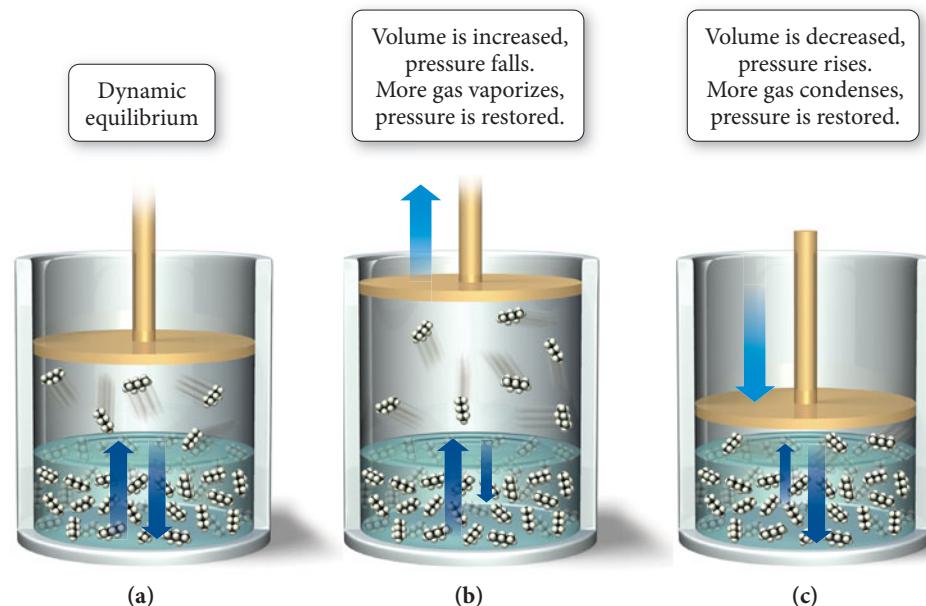
A liquid in dynamic equilibrium with its vapor is a balanced system that tends to return to equilibrium if disturbed. For example, consider a sample of *n*-pentane (a component of gasoline) at 25 °C in a cylinder equipped with a moveable piston (Figure 11.27a ▼). The cylinder contains no other gases except *n*-pentane vapor in dynamic equilibrium with the liquid. Since the vapor pressure of *n*-pentane at 25 °C is 510 mmHg, the pressure in the cylinder is 510 mmHg. Now, what happens when the piston is moved upward to expand the volume within the cylinder? Initially, the pressure in the cylinder drops below 510 mmHg, in accordance with Boyle's law. Then, however, more liquid vaporizes until equilibrium is reached once again (Figure 11.27b). If the volume of the cylinder is expanded again, the same thing happens—the pressure initially drops and more *n*-pentane vaporizes to bring the system back into equilibrium. Further expansion will cause the same result *as long as some liquid n-pentane remains in the cylinder*.

Conversely, what happens if the piston is lowered, decreasing the volume in the cylinder? Initially, the pressure in the cylinder rises above 510 mmHg, but then some of the gas condenses into liquid until equilibrium is reached again (Figure 11.27c).

We can describe the tendency of a system in dynamic equilibrium to return to equilibrium with the following general statement:

**When a system in dynamic equilibrium is disturbed, the system responds so as to minimize the disturbance and return to a state of equilibrium.**

If the pressure above a liquid–vapor system in equilibrium decreases, some of the liquid evaporates, restoring the equilibrium pressure. If the pressure increases, some of the vapor condenses, bringing the pressure back down to the equilibrium pressure. This basic principle—Le Châtelier's principle—is applicable to any chemical system in equilibrium, as we shall see in Chapter 14.



▲ FIGURE 11.26 Dynamic Equilibrium

Dynamic equilibrium occurs when the rate of condensation is equal to the rate of evaporation.

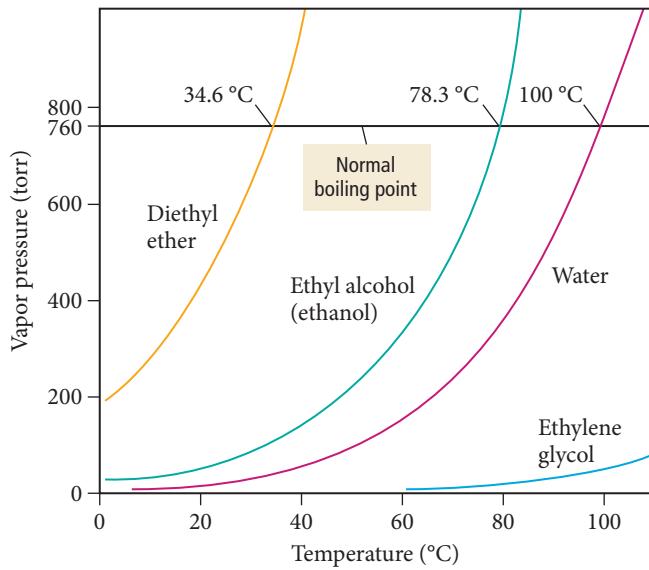
| Boyle's law is discussed in Section 5.3.

◀ FIGURE 11.27 Dynamic Equilibrium in n-Pentane (a) Liquid *n*-pentane is in dynamic equilibrium with its vapor. (b) When the volume is increased, the pressure drops and some liquid is converted to gas to bring the pressure back up. (c) When the volume is decreased, the pressure increases and some gas is converted to liquid to bring the pressure back down.

## Conceptual Connection 11.5 Vapor Pressure

What happens to the vapor pressure of a substance when its surface area is increased at constant temperature?

- (a) The vapor pressure increases.
- (b) The vapor pressure remains the same.
- (c) The vapor pressure decreases.



**▲ FIGURE 11.28** Vapor Pressure of Several Liquids at Different Temperatures

At higher temperatures, more molecules have enough thermal energy to escape into the gas state, so vapor pressure increases with increasing temperature.

Sometimes you see bubbles begin to form in hot water below 100 °C. These bubbles are dissolved air—not gaseous water—leaving the liquid. Dissolved air comes out of water as you heat it because the solubility of a gas in a liquid decreases with increasing temperature (as we will see in Chapter 12).

**► FIGURE 11.29** Boiling A liquid boils when thermal energy is high enough to cause molecules in the interior of the liquid to become gaseous, forming bubbles that rise to the surface.

### Temperature Dependence of Vapor Pressure and Boiling Point

When the temperature of a liquid increases, its vapor pressure rises because the higher thermal energy increases the number of molecules that have enough energy to vaporize (see Figure 11.24). Because of the shape of the thermal energy distribution curve, a small change in temperature makes a large difference in the number of molecules that have enough energy to vaporize, which results in a large increase in vapor pressure. For example, the vapor pressure of water at 25 °C is 23.3 torr, while at 60 °C the vapor pressure is 149.4 torr. Figure 11.28 ▲ shows the vapor pressure of water and several other liquids as a function of temperature.

The **boiling point** of a liquid is *the temperature at which the liquid's vapor pressure equals the external pressure*. When a liquid reaches its boiling point, the thermal energy is enough for molecules in the interior of the liquid (not just those at the surface) to break free of their neighbors and enter the gas state (Figure 11.29 ▼). The bubbles in boiling water are pockets of gaseous water that have formed within the liquid water. The bubbles float to the surface and leave as gaseous water or steam.

The **normal boiling point** of a liquid is *the temperature at which its vapor pressure equals 1 atm*. The normal boiling point of pure water is 100 °C. However, at a lower pressure, water boils at a lower temperature. In Denver, Colorado, where the altitude is around 1600 meters (5200 feet) above sea level, for example, the average atmospheric pressure is about 83% of what it is at sea level, and water boils at approximately 94 °C. For this reason, it takes slightly longer to cook food in boiling water in Denver than in San Francisco (which is at sea level). Table 11.8 shows the boiling point of water at several locations of varied altitudes.

Once the boiling point of a liquid is reached, additional heating only causes more rapid boiling; it does not raise the temperature of the liquid above its boiling point, as



**TABLE 11.8 Boiling Points of Water at Several Locations of Varied Altitudes**

Location	Elevation (ft)	Approximate Pressure (atm)*	Approximate Boiling Point of Water (°C)
Mt. Everest, Tibet (highest mountain peak on Earth)	29,035	0.32	78
Mt. McKinley (Denali), Alaska (highest mountain peak in North America)	20,320	0.46	83
Mt. Whitney, California (highest mountain peak in 48 contiguous U.S. states)	14,495	0.60	87
Denver, Colorado (mile high city)	5,280	0.83	94
Boston, Massachusetts (sea level)	20	1.0	100

\*The atmospheric pressure in each of these locations is subject to weather conditions and can vary significantly from these values.

shown in the *heating curve* in Figure 11.30 ►. Therefore, at 1 atm, boiling water always has a temperature of 100 °C. As long as liquid water is present, its temperature cannot rise above its boiling point. After all the water has been converted to steam, the temperature of the steam can continue to rise beyond 100 °C.

**The Clausius–Clapeyron Equation** Now, let's return our attention to Figure 11.28. As we can see from the graph, the vapor pressure of a liquid increases with increasing temperature. However, *the relationship is not linear*. In other words, doubling the temperature results in more than a doubling of the vapor pressure. The relationship between vapor pressure and temperature is exponential, and can be expressed as follows:

$$P_{\text{vap}} = \beta \exp\left(\frac{-\Delta H_{\text{vap}}}{RT}\right) \quad [11.1]$$

In this expression  $P_{\text{vap}}$  is the vapor pressure,  $\beta$  is a constant that depends on the gas,  $\Delta H_{\text{vap}}$  is the heat of vaporization,  $R$  is the gas constant (8.314 J/mol·K), and  $T$  is the temperature in kelvins. We can rearrange Equation 11.1 by taking the natural logarithm of both sides:

$$\ln P_{\text{vap}} = \ln \left[ \beta \exp\left(\frac{-\Delta H_{\text{vap}}}{RT}\right) \right] \quad [11.2]$$

Because  $\ln AB = \ln A + \ln B$ , we can rearrange the right side of Equation 11.2:

$$\ln P_{\text{vap}} = \ln \beta + \ln \left[ \exp\left(\frac{-\Delta H_{\text{vap}}}{RT}\right) \right] \quad [11.3]$$

Because  $\ln e^x = x$  (see Appendix IB), we can simplify Equation 11.3:

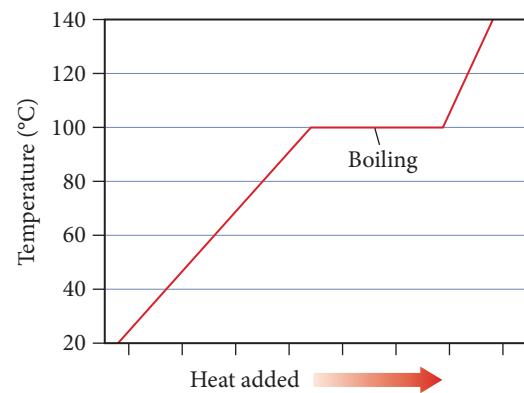
$$\ln P_{\text{vap}} = \ln \beta + \frac{-\Delta H_{\text{vap}}}{RT} \quad [11.4]$$

A slight additional rearrangement gives the following important result:

$$\ln P_{\text{vap}} = \frac{-\Delta H_{\text{vap}}}{R} \left( \frac{1}{T} \right) + \ln \beta \quad \text{Clausius–Clapeyron equation}$$

$$y = m(x) + b \quad (\text{equation for a line})$$

Notice the parallel relationship between the **Clausius–Clapeyron equation** and the equation for a straight line. Just as a plot of  $y$  versus  $x$  yields a straight line with slope  $m$  and intercept  $b$ , so a plot of  $\ln P_{\text{vap}}$  (equivalent to  $y$ ) versus  $1/T$  (equivalent to  $x$ ) gives a straight line with slope  $-\Delta H_{\text{vap}}/R$  (equivalent to  $m$ ) and  $y$ -intercept  $\ln \beta$  (equivalent to  $b$ ), as shown in Figure 11.31 ►. The Clausius–Clapeyron equation gives a linear relationship—not between the vapor pressure and the temperature (which have an

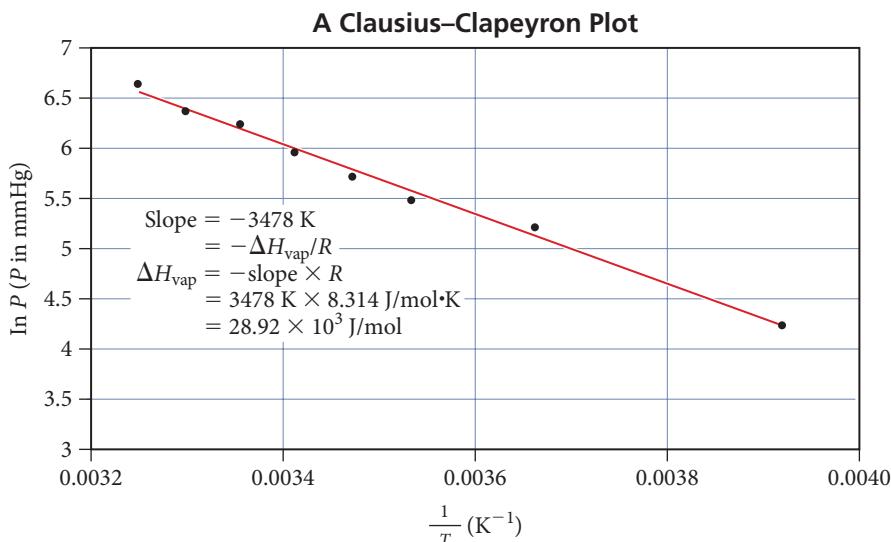


▲ **FIGURE 11.30** The Temperature during Boiling The temperature of water during boiling remains at 100 °C.

Using the Clausius–Clapeyron equation in this way ignores the relatively small temperature dependence of  $\Delta H_{\text{vap}}$ .

**► FIGURE 11.31** A Clausius–Clapeyron Plot

Plot for Diethyl Ether ( $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ )  
A plot of the natural log of the vapor pressure versus the inverse of the temperature in K yields a straight line with slope  $-\Delta H_{\text{vap}}/R$ .



exponential relationship)—but between the *natural log* of the vapor pressure and the *inverse* of temperature. This is a common technique in the analysis of chemical data. If two variables are not linearly related, it is often convenient to find ways to graph *functions of those variables* that are linearly related.

The Clausius–Clapeyron equation leads to a convenient way to measure the heat of vaporization in the laboratory. We simply measure the vapor pressure of a liquid as a function of temperature and create a plot of the natural log of the vapor pressure versus the inverse of the temperature. We can then determine the slope of the line to find the heat of vaporization, as shown in Example 11.4.

### EXAMPLE 11.4 Using the Clausius–Clapeyron Equation to Determine Heat of Vaporization from Experimental Measurements of Vapor Pressure

The vapor pressure of dichloromethane was measured as a function of temperature, and the following results were obtained:

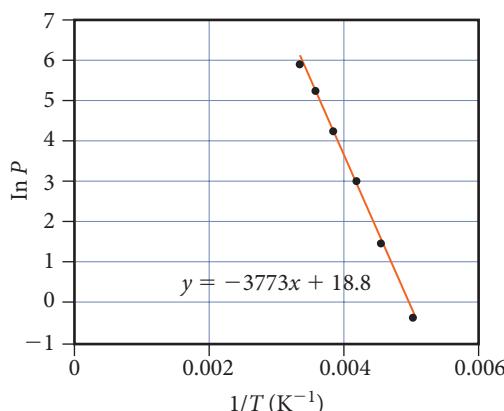
Temperature (K)	Vapor Pressure (torr)
200	0.8
220	4.5
240	21
260	71
280	197
300	391

Determine the heat of vaporization of dichloromethane.

#### SOLUTION

To find the heat of vaporization, use an Excel spreadsheet or a graphing calculator to make a plot of the natural log of vapor pressure ( $\ln P$ ) as a function of the inverse of the temperature in kelvins ( $1/T$ ). Then fit the points to a line and determine the slope of the line. The slope of the best-fitting line is  $-3773 \text{ K}$ . Since the slope equals  $-\Delta H_{\text{vap}}/R$ , we find the heat of vaporization as follows:

$$\begin{aligned} \text{slope} &= -\Delta H_{\text{vap}}/R \\ \Delta H_{\text{vap}} &= -\text{slope} \times R \\ &= -(3773 \text{ K})(8.314 \text{ J/mol} \cdot \text{K}) \\ &= 3.14 \times 10^4 \text{ J/mol} \\ &= 31.4 \text{ kJ/mol} \end{aligned}$$



**FOR PRACTICE 11.4**

The vapor pressure of carbon tetrachloride was measured as a function of the temperature, and the following results were obtained:

Temperature (K)	Vapor Pressure (torr)
255	11.3
265	21.0
275	36.8
285	61.5
295	99.0
300	123.8

Determine the heat of vaporization of carbon tetrachloride.

The Clausius–Clapeyron equation can also be expressed in a two-point form that we can use with just two measurements of vapor pressure and temperature to determine the heat of vaporization.

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad \text{Clausius–Clapeyron equation (two-point form)}$$

We can use this form of the equation to predict the vapor pressure of a liquid at any temperature if we know the enthalpy of vaporization and the normal boiling point (or the vapor pressure at some other temperature), as shown in Example 11.5.

The two-point method is generally inferior to plotting multiple points because fewer data points result in more chance for error.

### EXAMPLE 11.5 Using the Two-Point Form of the Clausius–Clapeyron Equation to Predict the Vapor Pressure at a Given Temperature



Methanol has a normal boiling point of 64.6 °C and a heat of vaporization ( $\Delta H_{\text{vap}}$ ) of 35.2 kJ/mol. What is the vapor pressure of methanol at 12.0 °C?

**SORT** You are given the normal boiling point of methanol (the temperature at which the vapor pressure is 760 mmHg) and the heat of vaporization. You are asked to find the vapor pressure at a specified temperature that is also given.

**GIVEN:**  $T_1(\text{°C}) = 64.6 \text{ °C}$

$P_1 = 760 \text{ torr}$

$\Delta H_{\text{vap}} = 35.2 \text{ kJ/mol}$

$T_2(\text{°C}) = 12.0 \text{ °C}$

**FIND:**  $P_2$

**STRATEGIZE** The conceptual plan is essentially the Clausius–Clapeyron equation, which relates the given and find quantities.

**CONCEPTUAL PLAN**

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

(Clausius–Clapeyron equation, two-point form)

**SOLVE** First, convert  $T_1$  and  $T_2$  from °C to K.

**SOLUTION**

$$\begin{aligned} T_1(\text{K}) &= T_1(\text{°C}) + 273.15 \\ &= 64.6 + 273.15 \\ &= 337.8 \text{ K} \end{aligned}$$

$$\begin{aligned} T_2(\text{K}) &= T_2(\text{°C}) + 273.15 \\ &= 12.0 + 273.15 \\ &= 285.2 \text{ K} \end{aligned}$$

Then, substitute the required values into the Clausius–Clapeyron equation and solve for  $P_2$ .

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{P_2}{P_1} = \frac{-35.2 \times 10^3 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}} \left( \frac{1}{285.2 \text{ K}} - \frac{1}{337.8 \text{ K}} \right)$$

$$= -2.31$$

$$\frac{P_2}{P_1} = e^{-2.31}$$

$$\begin{aligned} P_2 &= P_1(e^{-2.31}) \\ &= 760 \text{ torr}(0.0993) \\ &= 75.4 \text{ torr} \end{aligned}$$

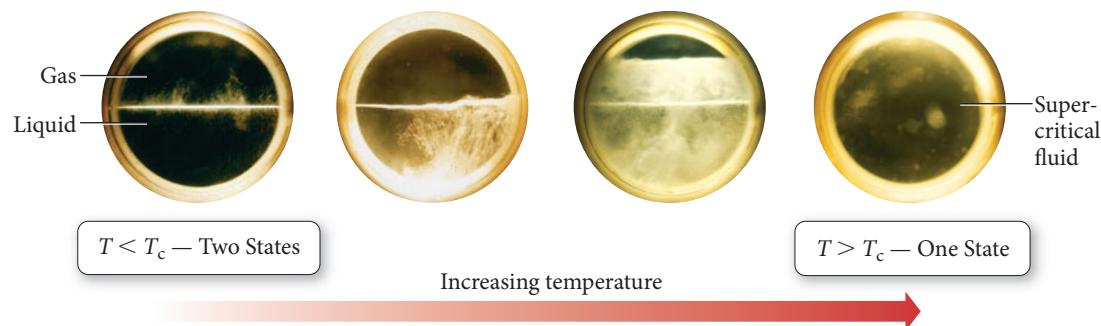
**CHECK** The units of the answer are correct. The magnitude of the answer makes sense because vapor pressure should be significantly lower at the lower temperature.

#### FOR PRACTICE 11.5

Propane has a normal boiling point of  $-42.0^\circ\text{C}$  and a heat of vaporization ( $\Delta H_{\text{vap}}$ ) of 19.04 kJ/mol. What is the vapor pressure of propane at  $25.0^\circ\text{C}$ ?

### The Critical Point: The Transition to an Unusual State of Matter

We have considered the vaporization of a liquid in a container open to the atmosphere with and without heating, and the vaporization of a liquid in a *sealed* container without heating. We now examine the vaporization of a liquid in a *sealed* container *during heating*. Consider liquid *n*-pentane in equilibrium with its vapor in a sealed container initially at  $25^\circ\text{C}$ . At this temperature, the vapor pressure of *n*-pentane is 0.67 atm. What happens if we heat the liquid? As the temperature rises, more *n*-pentane vaporizes and the pressure within the container increases. At  $100^\circ\text{C}$ , the pressure is 5.5 atm, and at  $190^\circ\text{C}$  the pressure is 29 atm. As the temperature and pressure increase, more and more gaseous *n*-pentane is forced into the same amount of space, and the density of the *gas* gets higher and higher. At the same time, the increasing temperature causes the density of the *liquid* to become lower and lower. At  $197^\circ\text{C}$ , the meniscus between the liquid and gaseous *n*-pentane disappears and the gas and liquid states commingle to form a *supercritical fluid* (Figure 11.32 ▶). For any substance, the *temperature* at which this transition occurs is the **critical temperature ( $T_c$ )**. The liquid cannot exist (regardless of pressure) above this temperature. The *pressure* at which this transition occurs is the **critical pressure ( $P_c$ )**.



**▲ FIGURE 11.32 Critical Point Transition** As *n*-pentane is heated in a sealed container, it undergoes a transition to a supercritical fluid. At the critical point, the meniscus separating the liquid and gas disappears, and the fluid becomes supercritical—neither a liquid nor a gas.

Researchers are interested in supercritical fluids because of their unique properties. A supercritical fluid has properties of both liquids and gases—it is in some sense intermediate between the two. Supercritical fluids can act as good solvents, selectively dissolving a number of compounds. For example, supercritical carbon dioxide is used as a solvent to extract caffeine from coffee beans. The caffeine dissolves in the supercritical carbon dioxide, but other substances—such as those responsible for the flavor of coffee—do not. Consequently, the caffeine is removed without substantially altering the coffee's flavor. The supercritical carbon dioxide is easily removed from the mixture by simply lowering the pressure below the critical pressure, at which point the carbon dioxide evaporates, leaving no residue.

## 11.6 Sublimation and Fusion

In Section 11.5, we examined a beaker of liquid water at room temperature from the molecular viewpoint. Now, let's examine a block of ice at  $-10\text{ }^{\circ}\text{C}$  from the same molecular perspective, paying close attention to two common processes: sublimation and fusion.

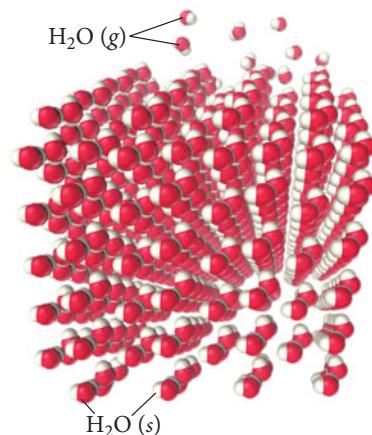
### Sublimation

Even though a block of ice is solid, the water molecules have thermal energy, which causes each one to vibrate about a fixed point. The motion is much less vigorous than in a liquid, but it is significant nonetheless. As in liquids, at any instant some molecules in the block of ice have more thermal energy than the average and some have less. The molecules with high enough thermal energy can break free from the ice surface—where, as in liquids, molecules are held less tightly than in the interior due to fewer neighbor–neighbor interactions—and go directly into the gas state (Figure 11.33 ►). This process is **sublimation**, the transition from solid to gas. Some of the water molecules in the gas state (those at the low end of the energy distribution curve for the gaseous molecules) collide with the surface of the ice and are captured by the intermolecular forces with other molecules. This process—the opposite of sublimation—is **deposition**, the transition from gas to solid. As is the case with liquids, the pressure of a gas in dynamic equilibrium with its solid is the vapor pressure of the solid.

Although both sublimation and deposition occur on the surface of an ice block open to the atmosphere at  $-10\text{ }^{\circ}\text{C}$ , sublimation usually occurs at a greater rate because most of the newly sublimed molecules escape into the surrounding atmosphere and never come back. The result is a noticeable decrease in the size of the ice block over time (even though the temperature is below the melting point).

If you live in a cold climate, you may have noticed the disappearance of ice and snow from the ground even though the temperature remains below  $0\text{ }^{\circ}\text{C}$ . Similarly, ice cubes left in the freezer for a long time slowly shrink, even though the freezer is always below  $0\text{ }^{\circ}\text{C}$ . In both cases, the ice is *subliming*, turning directly into water vapor. Ice also sublimes out of frozen foods. You may have noticed, for example, the gradual growth of ice crystals on the *inside* of airtight plastic food-storage bags in a freezer. The ice crystals are composed of water that has sublimed out of the food and redeposited on the surface of the bag or on the surface of the food. For this reason, food that remains frozen for too long becomes dried out. Such dehydration can be avoided to some degree by freezing foods to colder temperatures, a process called deep-freezing. The colder temperature lowers the vapor pressure of ice and preserves the food longer. Freezer burn on meats is another common manifestation of sublimation. When you improperly store meat (for example, in a container that is not airtight) sublimation continues unabated. The result is the dehydration of the surface of the meat, which becomes discolored and loses flavor and texture.

A substance commonly associated with sublimation is solid carbon dioxide or dry ice, which does not melt under atmospheric pressure no matter what the temperature is. However, at  $-78\text{ }^{\circ}\text{C}$  the  $\text{CO}_2$  molecules have enough energy to leave the surface of the dry ice and become gaseous through sublimation.



**▲ FIGURE 11.33** The Sublimation of Ice  
The water molecules at the surface of an ice cube can sublime directly into the gas state.



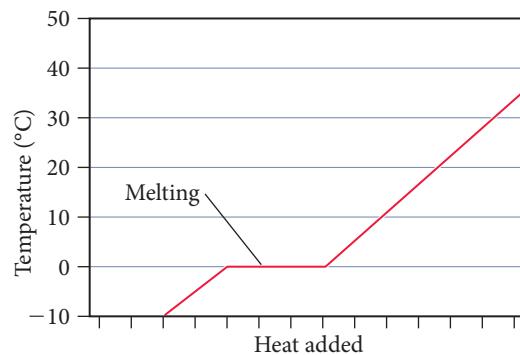
**▲ Dry ice (solid  $\text{CO}_2$ ) sublimes but does not melt at atmospheric pressure.**

## Fusion

Let's return to our ice block and examine what happens at the molecular level as we increase its temperature. The increasing thermal energy causes the water molecules to vibrate faster and faster. At the **melting point** (0 °C for water), the molecules have enough thermal energy to overcome the intermolecular forces that hold the molecules at their stationary points, and the solid turns into a liquid. This process is **melting** or **fusion**, the transition from solid to liquid. The opposite of melting is **freezing**, the transition from liquid to solid. Once the melting point of a solid is reached, additional heating only causes more rapid melting; it does not raise the temperature of the solid above its melting point (Figure 11.34). Only after all of the ice has melted will additional heating raise the temperature of the liquid water past 0 °C. A mixture of water *and* ice always has a temperature of 0 °C (at 1 atm pressure).

The term fusion is used for melting because if we heat several crystals of a solid, they *fuse* into a continuous liquid upon melting.

► **FIGURE 11.34** Temperature during Melting The temperature of water during melting remains at 0.0 °C as long as both solid and liquid water remain.



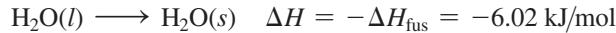
## Energetics of Melting and Freezing

The most common way to cool a beverage quickly is to drop several ice cubes into it. As the ice melts, the drink cools because melting is endothermic—the melting ice absorbs heat from the liquid. The amount of heat required to melt 1 mol of a solid is called the **heat of fusion** ( $\Delta H_{\text{fus}}$ ). The heat of fusion for water is 6.02 kJ/mol:



The heat of fusion is positive because melting is endothermic.

Freezing, the opposite of melting, is exothermic—heat is released when a liquid freezes into a solid. For example, as water in the freezer turns into ice, it releases heat, which must be removed by the refrigeration system of the freezer. If the refrigeration system did not remove the heat, the water would not completely freeze into ice. The heat released as the water began to freeze would warm the freezer, preventing further freezing. The change in enthalpy for freezing has the same magnitude as the heat of fusion but the opposite sign:



Different substances have different heats of fusion as shown in Table 11.9.

TABLE 11.9 Heats of Fusion of Several Substances

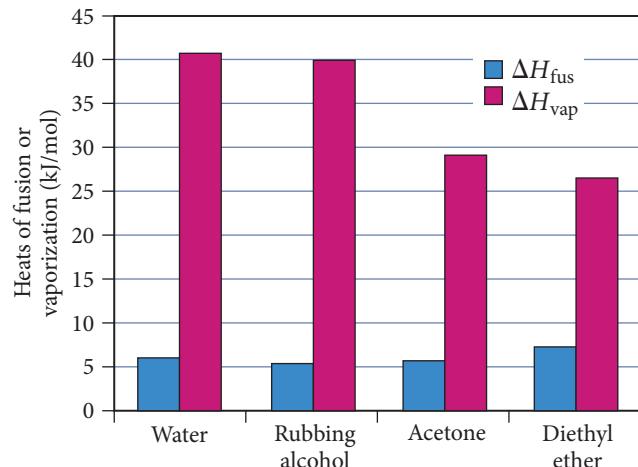
Liquid	Chemical Formula	Melting Point (°C)	$\Delta H_{\text{fus}}(\text{kJ/mol})$
Water	H <sub>2</sub> O	0.00	6.02
Rubbing alcohol (isopropyl alcohol)	C <sub>3</sub> H <sub>8</sub> O	-89.5	5.37
Acetone	C <sub>3</sub> H <sub>6</sub> O	-94.8	5.69
Diethyl ether	C <sub>3</sub> H <sub>10</sub> O	-116.3	7.27

In general, the heat of fusion for a substance is significantly less than its heat of vaporization, as shown in Figure 11.35 ▶. We have already seen that the solid and liquid states are closer to each other in many ways than they are to the gas state. It takes less energy to melt 1 mol of ice into liquid than it does to vaporize 1 mol of liquid water into gas because vaporization requires complete separation of molecules from one another, so the intermolecular forces must be completely overcome. Melting, however, requires that intermolecular forces be only partially overcome, allowing molecules to move around one another while still remaining in contact.

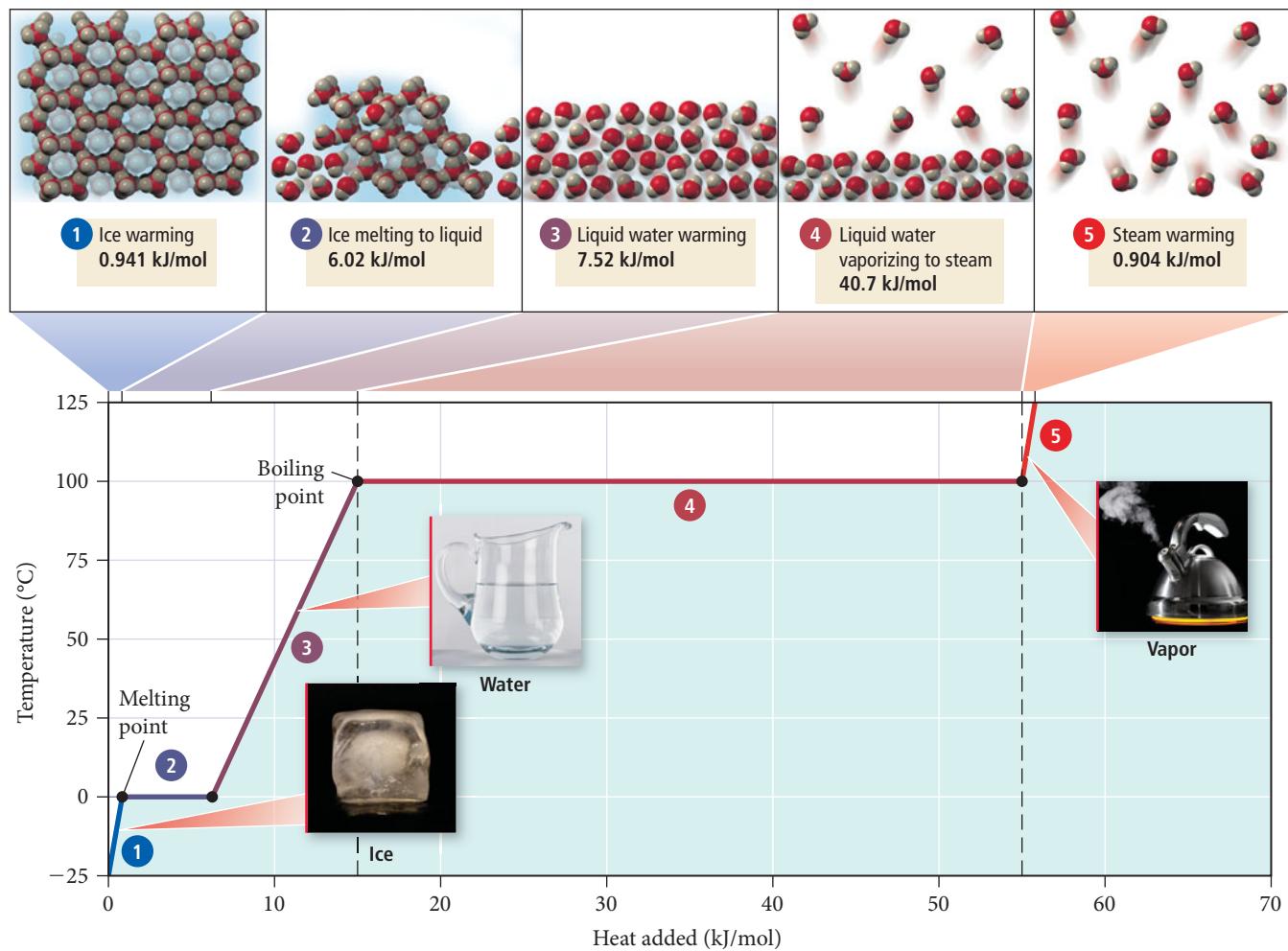
## 11.7 Heating Curve for Water

We can combine and build on the concepts from the Sections 11.5 and 11.6 by examining the *heating curve* for 1.00 mol of water at 1.00 atm pressure shown in Figure 11.36 ▼. The y-axis of the heating curve represents the temperature of the water sample. The x-axis represents the amount of heat added (in kilojoules) during heating. In the diagram, we divide the process into five segments: (1) ice warming; (2) ice melting into liquid water; (3) liquid water warming; (4) liquid water vaporizing into steam; and (5) steam warming.

In two of these segments (2 and 4) the temperature is constant as heat is added because the added heat goes into producing the transition between states, not into increasing the temperature. The two states are in equilibrium during the transition and the temperature remains constant. The amount of heat required to achieve the state change is given by  $q = n\Delta H$ .



▲ FIGURE 11.35 Heat of Fusion and Heat of Vaporization Typical heats of fusion are significantly less than heats of vaporization.



▲ FIGURE 11.36 Heating Curve for Water

In the other three segments (1, 3, and 5), temperature increases linearly. These segments represent the heating of a single state in which the deposited heat raises the temperature in accordance with the substance's heat capacity ( $q = mC_s \Delta T$ ). We examine each of these segments individually.

**Segment 1** In segment 1, solid ice is warmed from  $-25^\circ\text{C}$  to  $0^\circ\text{C}$ . Since no transition between states occurs here, the amount of heat required to heat the solid ice is given by  $q = mC_s \Delta T$  (see Section 6.4), where  $C_s$  is the specific heat capacity of ice ( $C_{s,\text{ice}} = 2.09 \text{ J/g} \cdot {}^\circ\text{C}$ ). For 1.00 mol of water (18.0 g), we calculate the amount of heat as follows:

$$\begin{aligned} q &= mC_{s,\text{ice}} \Delta T \\ &= 18.0 \text{ g} \left( 2.09 \frac{\text{J}}{\text{g} \cdot {}^\circ\text{C}} \right) [0.0 {}^\circ\text{C} - (-25.0 {}^\circ\text{C})] \\ &= 941 \text{ J} = 0.941 \text{ kJ} \end{aligned}$$

So in segment 1, 0.941 kJ of heat is added to the ice, warming it from  $-25^\circ\text{C}$  to  $0^\circ\text{C}$ .

**Segment 2** In segment 2, the added heat does not change the temperature of the ice and water mixture because the heat is absorbed by the transition from solid to liquid. The amount of heat required to convert the ice to liquid water is given by  $q = n \Delta H_{\text{fus}}$ , where  $n$  is the number of moles of water and  $\Delta H_{\text{fus}}$  is the heat of fusion (see Section 11.6):

$$\begin{aligned} q &= n \Delta H_{\text{fus}} \\ &= 1.00 \text{ mol} \left( \frac{6.02 \text{ kJ}}{\text{mol}} \right) \\ &= 6.02 \text{ kJ} \end{aligned}$$

In segment 2, 6.02 kJ is added to the ice, melting it into liquid water. Notice that the temperature does not change during melting. The liquid and solid coexist at  $0^\circ\text{C}$  as the melting occurs.

**Segment 3** In segment 3, the liquid water is warmed from  $0^\circ\text{C}$  to  $100^\circ\text{C}$ . Since no transition between states occurs here, the amount of heat required to heat the liquid water is given by  $q = mC_s \Delta T$ , as in segment 1. However, now we must use the heat capacity of liquid water (not ice) for the calculation. For 1.00 mol of water (18.0 g), we calculate the amount of heat as follows:

$$\begin{aligned} q &= mC_{s,\text{liq}} \Delta T \\ &= 18.0 \text{ g} \left( 4.18 \frac{\text{J}}{\text{g} \cdot {}^\circ\text{C}} \right) (100.0 {}^\circ\text{C} - 0.0 {}^\circ\text{C}) \\ &= 7.52 \times 10^3 \text{ J} = 7.52 \text{ kJ} \end{aligned}$$

So in segment 3, 7.52 kJ of heat is added to the liquid water, warming it from  $0^\circ\text{C}$  to  $100^\circ\text{C}$ .

**Segment 4** In segment 4, the water undergoes a second transition between states, this time from liquid to gas. The amount of heat required to convert the liquid to gas is given by  $q = n \Delta H_{\text{vap}}$ , where  $n$  is the number of moles and  $\Delta H_{\text{vap}}$  is the heat of vaporization (see Section 11.5):

$$\begin{aligned} q &= n \Delta H_{\text{vap}} \\ &= 1.00 \text{ mol} \left( \frac{40.7 \text{ kJ}}{\text{mol}} \right) \\ &= 40.7 \text{ kJ} \end{aligned}$$

Thus, in segment 4, 40.7 kJ is added to the water, vaporizing it into steam. Notice that the temperature does not change during boiling. The liquid and gas coexist at  $100^\circ\text{C}$  as the boiling occurs.

**Segment 5** In segment 5, the steam is warmed from  $100^\circ\text{C}$  to  $125^\circ\text{C}$ . Since no transition between states occurs here, the amount of heat required to heat the steam is given by

$q = mC_s \Delta T$  (as in segments 1 and 3) except that we must use the heat capacity of steam ( $2.01 \text{ J/g} \cdot \text{ }^\circ\text{C}$ ):

$$\begin{aligned} q &= mC_{s, \text{steam}} \Delta T \\ &= 18.0 \text{ g} \left( 2.01 \frac{\text{J}}{\text{g} \cdot \text{ }^\circ\text{C}} \right) (125.0 \text{ }^\circ\text{C} - 100.0 \text{ }^\circ\text{C}) \\ &= 904 = 0.904 \text{ kJ} \end{aligned}$$

So in segment 5, 0.904 kJ of heat is added to the steam, warming it from  $100 \text{ }^\circ\text{C}$  to  $125 \text{ }^\circ\text{C}$ .

## Conceptual Connection 11.6 Cooling of Water with Ice

You just saw that the heat capacity of ice is  $C_{s, \text{ice}} = 2.09 \text{ J/g} \cdot \text{ }^\circ\text{C}$  and that the heat of fusion of ice is  $6.02 \text{ kJ/mol}$ . When a small ice cube at  $-10 \text{ }^\circ\text{C}$  is put into a cup of water at room temperature, which of the following plays a greater role in cooling the liquid water: the warming of the ice from  $-10 \text{ }^\circ\text{C}$  to  $0 \text{ }^\circ\text{C}$ , or the melting of the ice?

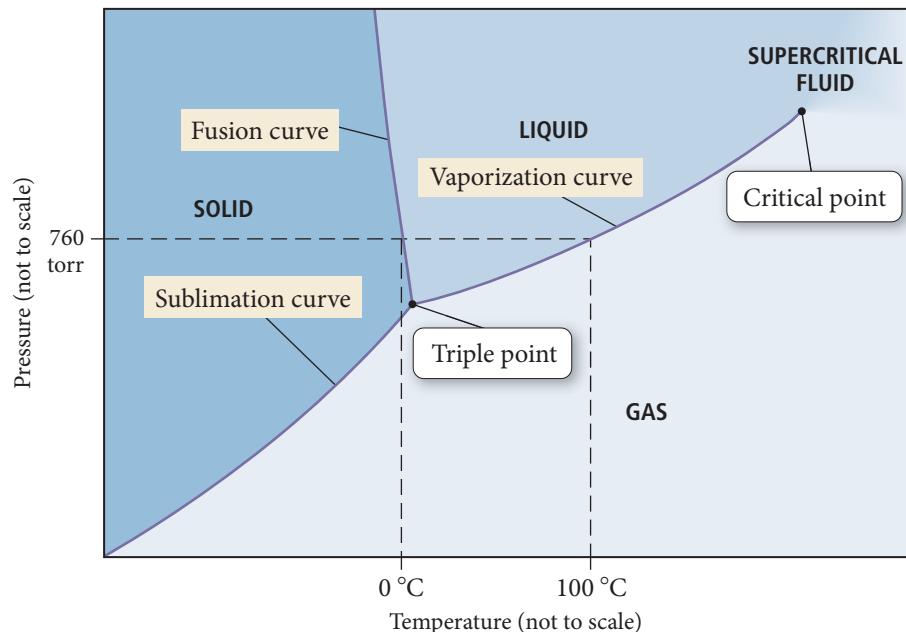
## 11.8 Phase Diagrams

Throughout most of this chapter, we have examined how the state of a substance changes with temperature and pressure. We can combine both the temperature dependence and pressure dependence of the state of a particular substance in a graph called a *phase diagram*. A **phase diagram** is a map of the state or *phase* of a substance as a function of pressure (on the *y*-axis) and temperature (on the *x*-axis). We first examine the major features of a phase diagram, then turn to navigating within a phase diagram, and finally examine and compare the phase diagrams of selected substances.

### The Major Features of a Phase Diagram

We can introduce the major features of a phase diagram by examining the phase diagram for water as an example (Figure 11.37 ▼). The *y*-axis displays the pressure in torr and the *x*-axis displays the temperature in degrees Celsius. We categorize the main features of the phase diagram as regions, lines, and points.

Phase Diagram for Water



◀ FIGURE 11.37 Phase Diagram for Water

**Regions** Any of the three main regions—solid, liquid, and gas—in the phase diagram represent conditions where that particular state is stable. For example, under any of the temperatures and pressures within the liquid region in the phase diagram of water, the liquid is the stable state. Notice that the point 25 °C and 760 torr falls within the liquid region, as we know from everyday experience. In general, low temperature and high pressure favor the solid state, high temperature and low pressure favor the gas state, and intermediate conditions favor the liquid state. A sample of matter that is not in the state indicated by its phase diagram for a given set of conditions converts to that state when those conditions are imposed. For example, steam that is cooled to room temperature at 1 atm condenses to liquid.

**Lines** Each of the lines (or curves) in the phase diagram represents a set of temperatures and pressures at which the substance is in equilibrium between the two states on either side of the line. In the phase diagram for water, consider the curved line beginning just beyond 0 °C separating the liquid from the gas. This line is the vaporization curve (also called the vapor pressure curve) for water that we examined in Section 11.5. At any of the temperatures and pressures that fall along this line, the liquid and gas states of water are equally stable and in equilibrium. For example, at 100 °C and 760 torr pressure, water and its vapor are in equilibrium—they are equally stable and will coexist. The other two major lines in a phase diagram are the sublimation curve (separating the solid and the gas) and the fusion curve (separating the solid and the liquid).

The triple point of a substance such as water can be reproduced anywhere to calibrate a thermometer or pressure gauge with a known temperature and pressure.

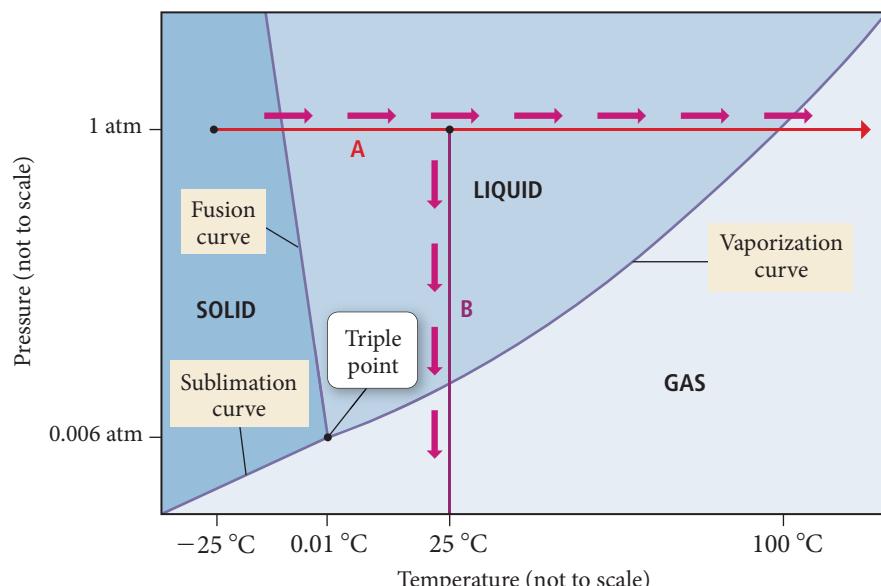
**The Triple Point** The **triple point** in a phase diagram represents the unique set of conditions at which the three states are equally stable and in equilibrium. In the phase diagram for water, the triple point occurs at 0.0098 °C and 4.58 torr. Under these unique conditions (and only under these conditions), the solid, liquid, and gas states of water are equally stable and will coexist in equilibrium.

**The Critical Point** As we discussed in Section 11.5, at the critical temperature and pressure, the liquid and gas states coalesce into a *supercritical fluid*. The **critical point** in a phase diagram represents the temperature and pressure above which a supercritical fluid exists.

## Navigation within a Phase Diagram

We can represent changes in the temperature or pressure of a sample of water as movement within the phase diagram. For example, suppose we heat a block of ice initially at 1.0 atm and –25 °C. We represent the change in temperature at constant pressure as movement along the line marked A in Figure 11.38 ▶. As the temperature rises, we move to the right along the

### Navigation within a Phase Diagram



► FIGURE 11.38 Navigation on the Phase Diagram for Water

line. At the fusion curve, the temperature stops rising and melting occurs until the solid ice is completely converted to liquid water. Crossing the fusion curve requires the complete transition from solid to liquid. Once the ice has completely melted, the temperature of the liquid water can begin to rise until the vaporization curve is reached. At this point, the temperature again stops rising and boiling occurs until all the liquid is converted to gas.

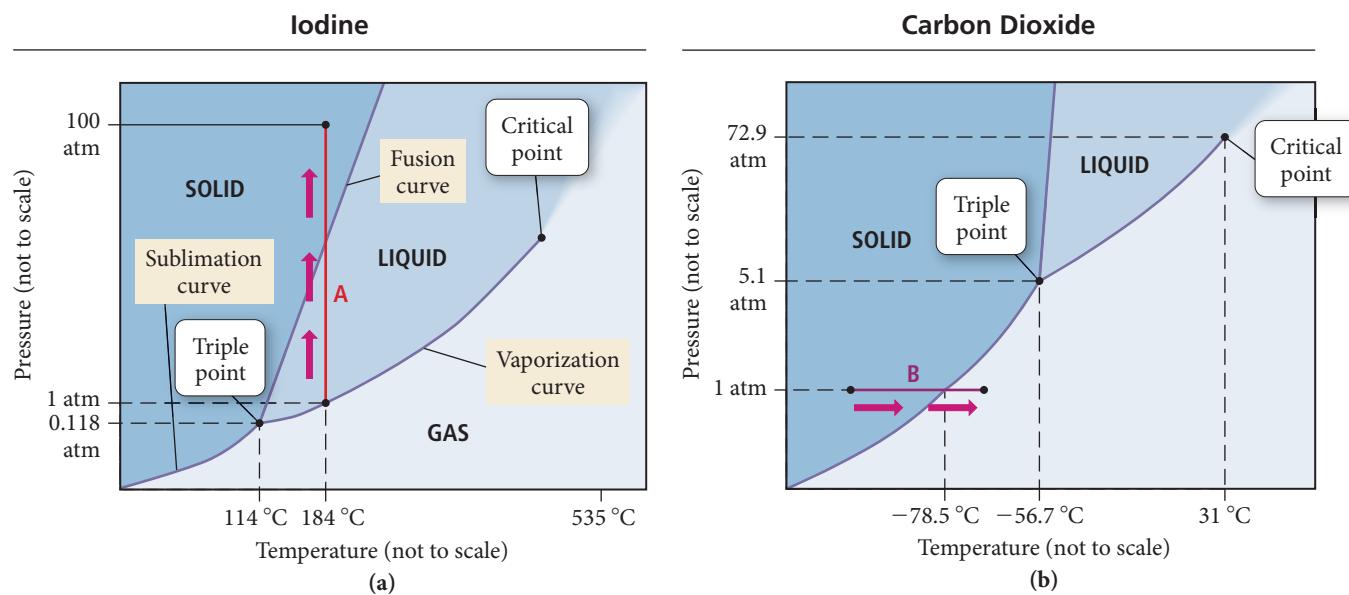
We can represent a change in pressure with a vertical line on the phase diagram. For example, suppose we lower the pressure above a sample of water initially at 1.0 atm and 25 °C. We represent the change in pressure at constant temperature as movement along the line marked B in Figure 11.38. As the pressure drops, we move down the line and approach the vaporization curve. At the vaporization curve, the pressure stops dropping and vaporization occurs until the liquid is completely converted to vapor. Crossing the vaporization curve requires the complete transition from liquid to gas. Only after the liquid has all vaporized can the pressure continue to drop.

## The Phase Diagrams of Other Substances

Examine the phase diagrams of iodine and carbon dioxide, shown in Figure 11.39 ▼. The phase diagrams are similar to that of water in most of their general features, but some significant differences exist.

The fusion curves for both carbon dioxide and iodine have a positive slope—as the temperature increases the pressure also increases—in contrast to the fusion curve for water, which has a negative slope. The behavior of water is atypical. The fusion curve within the phase diagrams for most substances has a positive slope because increasing pressure favors the denser state, which for most substances is the solid state. For example, suppose we increase the pressure on a sample of iodine from 1 atm to 100 atm at 184 °C, as shown by line A in Figure 11.39(a). Notice that this change crosses the fusion curve, converting the liquid into a solid. In contrast, a pressure increase from 1 atm to 100 atm at −0.1 °C in water causes a state transition from solid to liquid. Unlike most substances, the liquid state of water is actually denser than the solid state.

Both water and iodine have stable solid, liquid, and gaseous states at a pressure of 1 atm. However, notice that carbon dioxide has no stable liquid state at a pressure of 1 atm. If we increase the temperature of a block of solid carbon dioxide (dry ice) at 1 atm, as indicated by line B in Figure 11.39(b), we cross the sublimation curve at −78.5 °C. At this temperature, the solid sublimes to a gas, which is one reason that dry ice is useful (it does not melt into a liquid at atmospheric pressure). Carbon dioxide will form a liquid only above pressures of 5.1 atm.



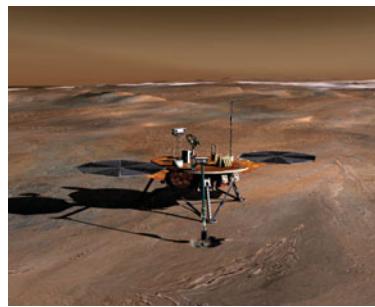
▲ FIGURE 11.39 Phase Diagrams for Other Substances (a) Iodine, (b) Carbon dioxide.

## Conceptual Connection 11.7 Phase Diagrams

A substance has a triple point at  $-24.5^{\circ}\text{C}$  and 225 mm Hg. What is most likely to happen to a solid sample of the substance as it is warmed from  $-35^{\circ}\text{C}$  to  $0^{\circ}\text{C}$  at a pressure of 220 mm Hg?

- (a) The solid will melt into a liquid.
- (b) The solid will sublime into a gas.
- (c) Nothing (the solid will remain as a solid).

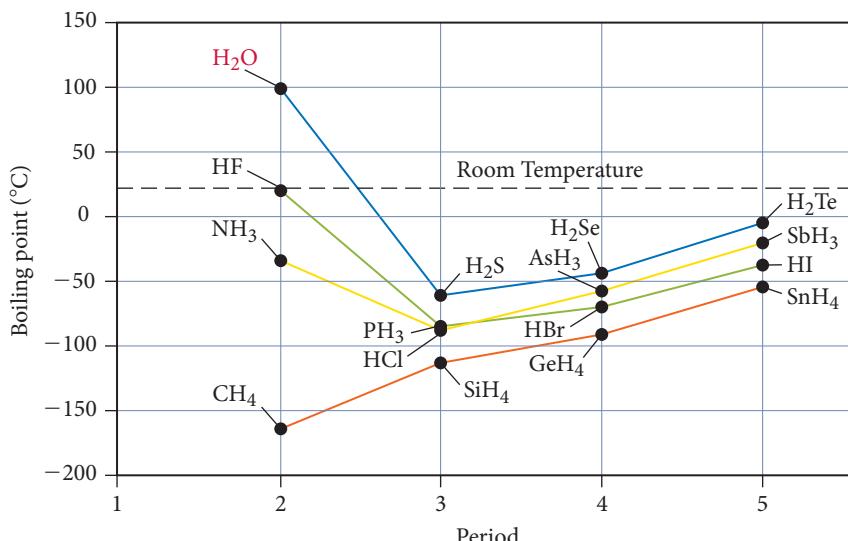
## 11.9 Water: An Extraordinary Substance



▲ The *Phoenix Mars Lander* is looking for evidence of life in frozen water that lies below the surface of Mars's north polar region.

Water is the most common and important liquid on Earth. It fills our oceans, lakes, and streams. In its solid form, it caps our mountains, and in its gaseous form, it humidifies our air. We drink water, we sweat water, and we excrete bodily wastes dissolved in water. Indeed, the majority of our body mass *is* water. Life is impossible without water, and in most places on Earth where liquid water exists, life exists. Recent evidence for the past existence of water on Mars has fueled hopes of finding life or evidence of past life there. And though it may not be obvious to us (because we take water for granted), this familiar substance has many remarkable properties.

Among liquids, water is unique. It has a low molar mass (18.02 g/mol), yet it is a liquid at room temperature. Other main-group hydrides have higher molar masses but lower boiling points, as shown in Figure 11.40 ▼. No other substance of similar molar mass (except for HF) comes close to being a liquid at room temperature. We can understand water's high boiling point (in spite of its low molar mass) by examining its molecular structure. The bent geometry of the water molecule and the highly polar nature of the O—H bonds result in a molecule with a significant dipole moment. Water's two O—H bonds (hydrogen directly bonded to oxygen) allow a water molecule to form strong hydrogen bonds with four other water molecules (Figure 11.41 ►), resulting in a relatively high boiling point. Water's high polarity also allows it to dissolve many other polar and ionic compounds and even a number of nonpolar gases such as oxygen and carbon dioxide (by inducing a dipole moment in their molecules). Consequently, water is the main solvent within living organisms, transporting nutrients and other important compounds throughout the body. Water is the main solvent in our environment as well, allowing aquatic animals, for example, to survive by breathing dissolved oxygen and allowing aquatic plants to survive by using dissolved carbon dioxide for photosynthesis.

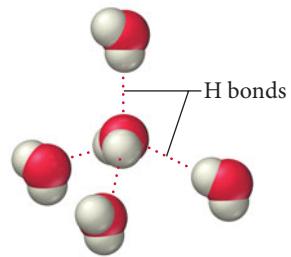


▲ FIGURE 11.40 Boiling Points of Main Group Hydrides Water is the only common main-group hydride that is a liquid at room temperature.

We have already seen in Section 6.4 that water has an exceptionally high specific heat capacity, which has a moderating effect on the climate of coastal cities. In some cities, such as San Francisco, for example, the daily fluctuation in temperature can be less than 10 °C. This same moderating effect occurs over the entire planet, two-thirds of which is covered by water. Without water, the daily temperature fluctuations on our planet might be more like those on Mars, where temperature fluctuations of 63 °C (113 °F) occur between midday and early morning. Imagine awakening to below freezing temperatures, only to bake at summer desert temperatures in the afternoon! The presence of water on Earth and water's uniquely high specific heat capacity are largely responsible for our planet's much smaller daily fluctuations.

As we have seen, the way water freezes is also unique. Unlike other substances, which contract upon freezing, water expands upon freezing. Consequently, ice is less dense than liquid water, which is why ice floats. This seemingly trivial property has significant consequences. The frozen layer of ice at the surface of a winter lake insulates the water in the lake from further freezing. If this ice layer sank, it would kill bottom-dwelling aquatic life and possibly allow the lake to freeze solid, eliminating virtually all life in the lake.

The expansion of water upon freezing, however, is one reason that most organisms do not survive freezing. When the water within a cell freezes, it expands and often ruptures the cell, just as water freezing within a pipe bursts the pipe. Many foods, especially those with high water content, do not survive freezing very well either. Have you ever tried, for example, to freeze your own vegetables? If you put lettuce or spinach in the freezer, it will be limp and damaged upon thawing. The frozen-food industry gets around this problem by *flash freezing* vegetables and other foods. In this process, foods are frozen nearly instantaneously, which prevents water molecules from settling into their preferred crystalline structure. Consequently, the water does not expand very much and the food remains largely undamaged.



**▲ FIGURE 11.41** Hydrogen Bonding in Water A water molecule can form four strong hydrogen bonds with four other water molecules.



**▲** When lettuce freezes, the water within its cells expands, rupturing them.



## Chemistry in the Environment

### Water Pollution

Water quality is critical to human health. Many human diseases—especially in developing nations—are caused by poor water quality. Several kinds of pollutants, including biological and chemical contaminants, can enter water supplies.



**▲** Uncontaminated, sanitary water supplies are critical to human health.

Biological contaminants are microorganisms that cause diseases such as hepatitis, cholera, dysentery, and typhoid. They get into drinking water primarily when human or animal waste is dumped into bodies of water. Drinking water in developed nations is usually chemically treated to kill microorganisms. Water containing biological contaminants poses an immediate danger to human health and should not be consumed. Boiling eliminates most biological contaminants from untreated water.

Chemical contaminants enter drinking water supplies as a result of industrial dumping, pesticide and fertilizer use, and household dumping. These contaminants include organic compounds, such as carbon tetrachloride and dioxin, and inorganic elements and compounds, such as mercury, lead, and nitrates. Since many chemical contaminants are neither volatile nor alive (like biological contaminants are), they are usually *not* eliminated through boiling.

The U.S. Environmental Protection Agency (EPA), under the Safe Drinking Water Act of 1974 and its amendments, sets standards that specify the maximum contamination level (MCL) of nearly 100 biological and chemical contaminants in water. Water providers that serve more than 25 people must periodically test the water they deliver to their consumers for these contaminants. If levels exceed the standards set by the EPA, the water provider must notify consumers and take appropriate measures to remove the contaminant from the water. According to the EPA, water from providers that serve more than 25 people should be safe to consume over a lifetime. If it is not safe to drink for a short period of time, providers must notify consumers.

### Question

Why doesn't boiling eliminate nonvolatile contaminants such as lead?



▲ The well-defined angles and smooth faces of crystalline solids reflect the underlying order of the atoms composing them.

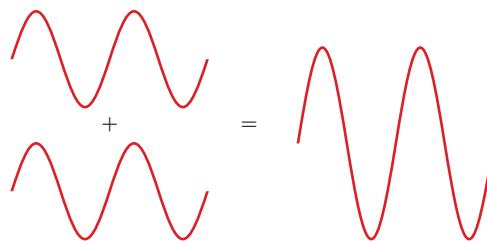


▲ The hexagonal shape of a snowflake derives from the hexagonal arrangement of water molecules in crystalline ice.

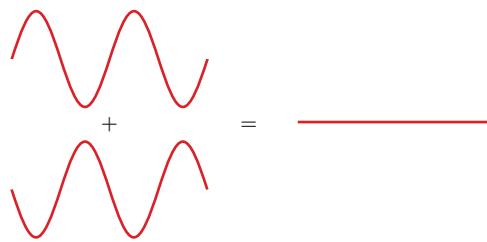
## 11.10 Crystalline Solids: Determining Their Structure by X-Ray Crystallography

Recall that crystalline solids are composed of atoms or molecules arranged in structures with long-range order (see Section 11.2). If you have ever visited the mineral section of a natural history museum and seen crystals with smooth faces and well-defined angles between them, or if you have carefully observed the hexagonal shapes of snowflakes, you have witnessed some of the effects of the underlying order in crystalline solids. The often beautiful geometric shapes that you see on the macroscopic scale are the result of specific structural patterns on the molecular and atomic scales. But how do we study these patterns? How do we look into the atomic and molecular world to determine the arrangement of the atoms and measure the distances between them? In this section, we examine **X-ray diffraction**, a powerful laboratory technique that enables us to do exactly that.

In Section 7.2 we saw that electromagnetic (or light) waves interact with each other in a characteristic way called *interference*: they can cancel each other out or reinforce each other, depending on the alignment of their crests and troughs. *Constructive interference* occurs when two waves interact with their crests and troughs in alignment. *Destructive interference* occurs when two waves interact with the crests of one aligning with the troughs of the other. Recall also that when light encounters two slits separated by a distance comparable to the wavelength of the light, constructive and destructive interference between the resulting beams produces a characteristic *interference pattern*, consisting of alternating bright and dark lines.



Constructive interference

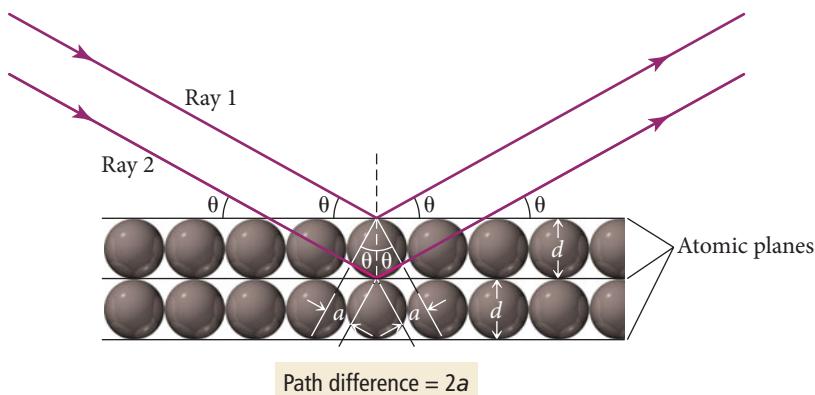


Destructive interference

Atoms within crystal structures have spacings between them on the order of  $10^2$  pm, so light of similar wavelength (which happens to fall in the X-ray region of the electromagnetic spectrum) forms interference patterns or *diffraction patterns* when it interacts with those atoms. The exact pattern of diffraction reveals the spacings between planes of atoms. Consider two planes of atoms within a crystalline lattice separated by a distance  $d$ , as shown in Figure 11.42 ▶. If two rays of light with wavelength  $\lambda$  that are initially in phase (that is, the crests of one wave are aligned with the crests of the other) diffract from the two planes, the diffracted rays may interfere with each other constructively or destructively, depending on the difference between the path lengths traveled by each ray. If the difference between the two path lengths ( $2a$ ) is an integral number ( $n$ ) of wavelengths, then the interference will be constructive:

$$n\lambda = 2a \quad (\text{criterion for constructive interference})$$

[11.5]



**◀ FIGURE 11.42 Diffraction from a Crystal** When X-rays strike parallel planes of atoms in a crystal, constructive interference occurs if the difference in path length between beams reflected from adjacent planes is an integral number of wavelengths.

Using trigonometry, we can see that the angle of reflection ( $\theta$ ) is related to the distance  $a$  and the separation between layers ( $d$ ) by the following relation:

$$\sin \theta = \frac{a}{d} \quad [11.6]$$

Rearranging, we get:

$$a = d \sin \theta \quad [11.7]$$

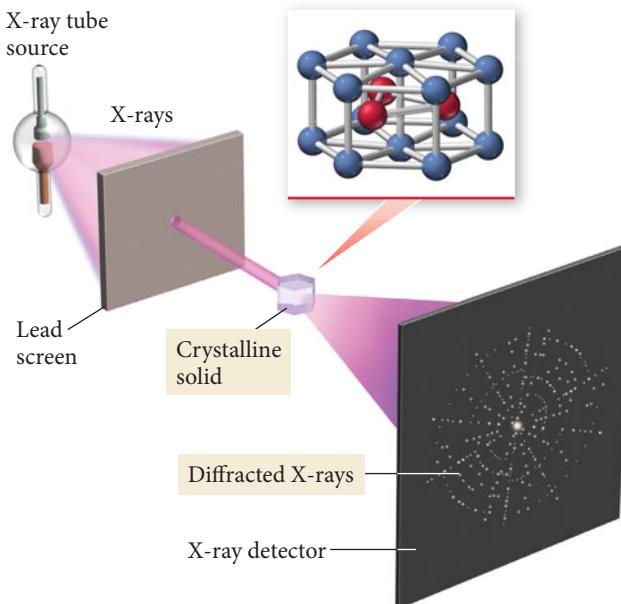
By substituting Equation 11.7 into Equation 11.5, we arrive at the following important relationship:

$$n\lambda = 2d \sin \theta \quad \text{Bragg's law}$$

This equation is known as *Bragg's law*. For a given wavelength of light incident on atoms arranged in layers, we can measure the angle that produces constructive interference (which appears as a bright spot on the X-ray diffraction pattern) and then calculate  $d$ , the distance between the atomic layers:

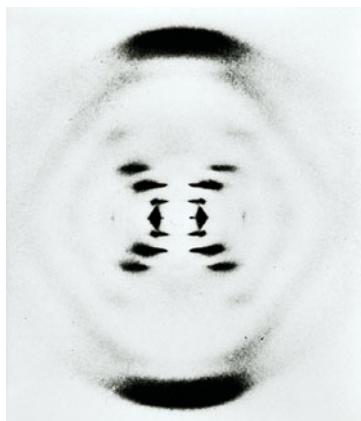
$$d = \frac{n\lambda}{2 \sin \theta} \quad [11.8]$$

In a modern X-ray diffractometer (Figure 11.43 ▶), the diffraction pattern from a crystal is collected and analyzed by a computer. By rotating the crystal and collecting the resulting diffraction patterns at different angles, the distances between various crystalline planes can be measured, eventually yielding the entire crystalline structure. This process is called X-ray crystallography. Researchers use X-ray crystallography to determine not



**◀ FIGURE 11.43 X-Ray Diffraction**

**Analysis** In X-ray crystallography, an X-ray beam is passed through a sample, which is rotated to allow diffraction from different crystalline planes. The resulting patterns, representing constructive interference from various planes, are analyzed to determine crystalline structure.



only the structures of simple atomic lattices, but also the structures of proteins, DNA, and other biologically important molecules. For example, the famous X-ray diffraction photograph shown at left, obtained by Rosalind Franklin and Maurice Wilkins, helped Watson and Crick determine the double-helical structure of DNA. Recall from Section 9.1 that researchers also used X-ray diffraction to determine the structure of HIV protease, a protein critical to the reproduction of HIV and the development of AIDS. That structure was then used to design drug molecules that would inhibit the action of HIV protease, thus halting the advance of the disease.

### EXAMPLE 11.6 Using Bragg's Law

When an X-ray beam of  $\lambda = 154 \text{ pm}$  was incident on the surface of an iron crystal, it produced a maximum reflection at an angle of  $\theta = 32.6^\circ$ . Assuming  $n = 1$ , calculate the separation between layers of iron atoms in the crystal.

#### SOLUTION

To solve this problem, use Bragg's law in the form given by Equation 11.8. The distance,  $d$ , is the separation between layers in the crystal.

$$\begin{aligned} d &= \frac{n\lambda}{2 \sin \theta} \\ &= \frac{154 \text{ pm}}{2 \sin(32.6^\circ)} \\ &= 143 \text{ pm} \end{aligned}$$

#### FOR PRACTICE 11.6

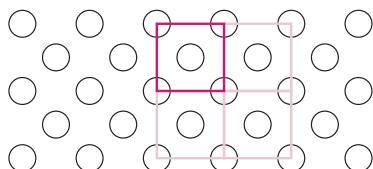
The spacing between layers of molybdenum atoms is 157 pm. Calculate the angle at which 154 pm X-rays produce a maximum reflection for  $n = 1$ .

## 11.11 Crystalline Solids: Unit Cells and Basic Structures

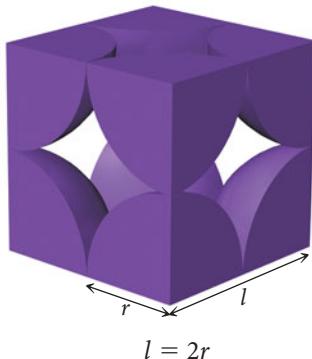
X-Ray crystallography allows us to determine the regular arrangements of atoms within a crystalline solid. This arrangement is called the **crystalline lattice**. The crystalline lattice of any solid is nature's way of aggregating the particles to minimize their energy. We can represent the crystalline lattice with a small collection of atoms, ions, or molecules called the **unit cell**. When the unit cell is repeated over and over—like the tiles of a floor or the pattern in a wallpaper design, but in three dimensions—the entire lattice is reproduced. For example, consider the two-dimensional crystalline lattice shown at left. The unit cell for this lattice is the dark-colored square. Each circle represents a *lattice point*, a point in space occupied by an atom, ion, or molecule. Repeating the pattern in the square throughout the two-dimensional space generates the entire lattice.

Many different unit cells exist, and we often classify unit cells by their symmetry. In this book, we focus primarily on *cubic unit cells* (although we look at one hexagonal unit cell). Cubic unit cells are characterized by equal edge lengths and  $90^\circ$  angles at their corners. The three cubic unit cells—simple cubic, body-centered cubic, and face-centered cubic—along with some of their basic characteristics, are presented in Figure 11.44 ►. There are two colors in this figure to help you visualize the different positions of the atoms; the colors *do not* represent different *kinds* of atoms. For these unit cells, *each atom in any one structure is identical to the other atoms in that structure*.

The **simple cubic** unit cell (Figure 11.45 ►) consists of a cube with one atom at each corner. The atoms touch along each edge of the cube, so the edge length is twice the radius of the atoms ( $l = 2r$ ). Even though it may seem like the unit cell contains eight atoms, it actually contains only one. Each corner atom is shared by eight other unit cells. In other words, any one unit cell actually contains only one-eighth of each of the eight atoms at its corners, for a total of only one atom per unit cell.



Simple cubic



▲ In the simple cubic lattice, the atoms touch along each edge so that the edge length is  $2r$ .

Cubic Cell Name	Atoms per Unit Cell	Structure	Coordination Number	Edge Length in terms of $r$	Packing Efficiency (fraction of volume occupied)
Simple Cubic	1		6	$2r$	52%
Body-Centered Cubic	2		8	$\frac{4r}{\sqrt{3}}$	68%
Face-Centered Cubic	4		12	$2\sqrt{2}r$	74%

A characteristic feature of any unit cell is the **coordination number**, the number of atoms with which each atom is in *direct contact*. The coordination number is the number of atoms with which a particular atom can strongly interact. The simple cubic unit cell has a coordination number of 6; any one atom touches only six others, as you can see in Figure 11.45. A quantity closely related to the coordination number is the **packing efficiency**, the percentage of the volume of the unit cell occupied by the spheres. The higher the coordination number, the greater the packing efficiency. The simple cubic unit cell has a packing efficiency of 52%—the simple cubic unit cell contains a lot of empty space.

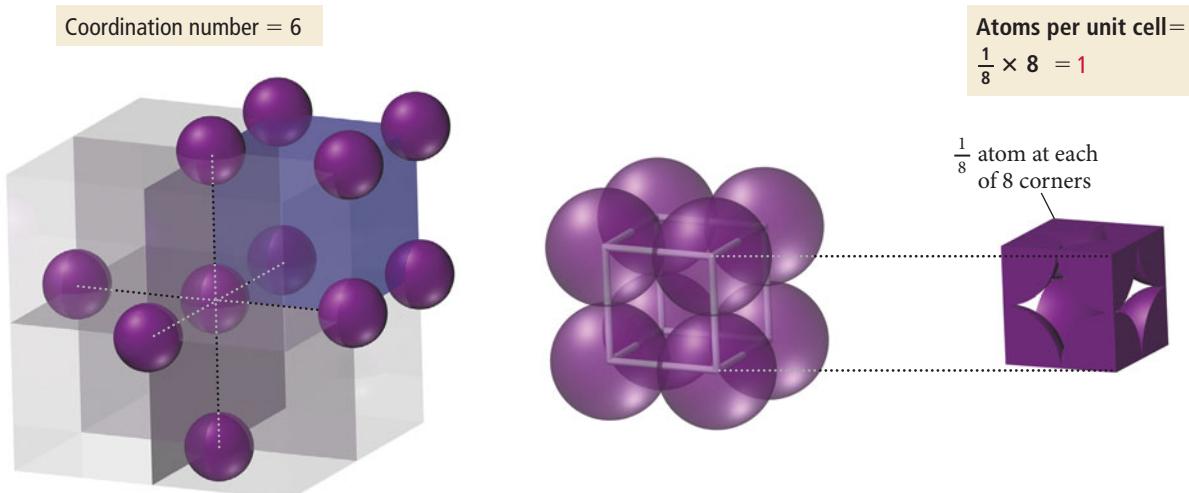
The **body-centered cubic** unit cell (Figure 11.46 ►) consists of a cube with one atom at each corner and one atom (of the same kind) in the very center of the cube. Note that in the body-centered unit cell, the atoms *do not* touch along each edge of the cube, but instead along the diagonal line that runs from one corner, through the middle of the cube, to the

▲ **FIGURE 11.44** The Cubic Crystalline Lattices The different colors used for the atoms in this figure are for clarity only. All atoms within each structure are identical.

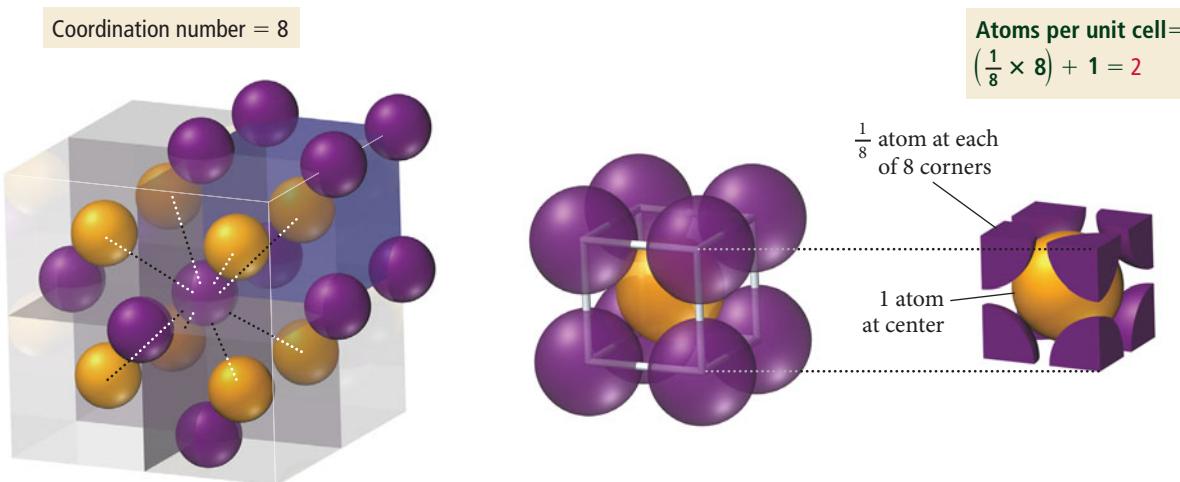
Unit cells, such as the cubic ones shown here, are customarily portrayed with “whole” atoms, even though only a part of the whole atom may actually be in the unit cell.

▼ **FIGURE 11.45** Simple Cubic Crystal Structure

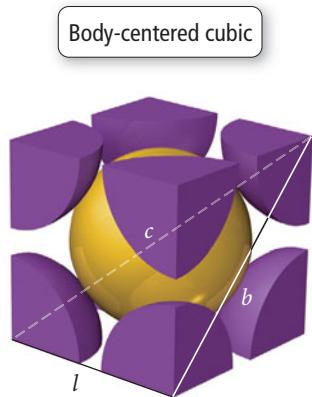
### Simple Cubic Unit Cell



### Body-Centered Cubic Unit Cell



▲ **FIGURE 11.46** Body-Centered Cubic Crystal Structure The different colors used for the atoms in this figure are for clarity only. All atoms within the structure are identical.



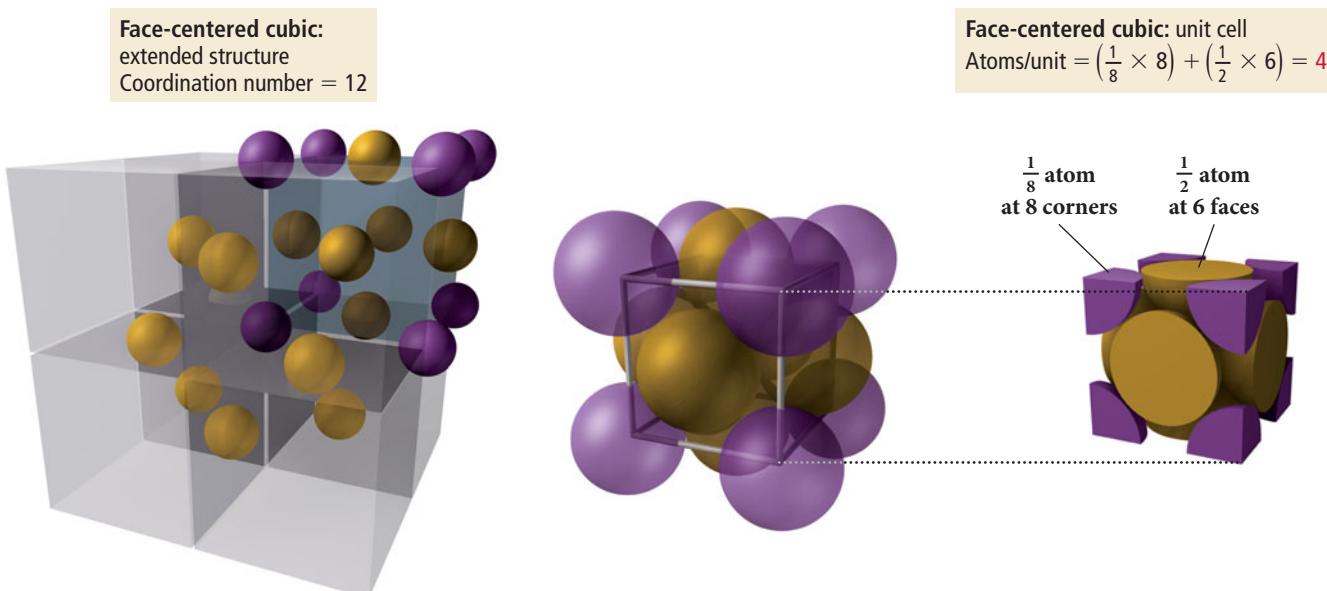
$$\begin{aligned}
 c^2 &= b^2 + l^2 & b^2 &= l^2 + l^2 \\
 c &= 4r & b^2 &= 2l^2 \\
 (4r)^2 &= 2l^2 + l^2 \\
 (4r)^2 &= 3l^2 \\
 l^2 &= \frac{(4r)^2}{3} \\
 l &= \frac{4r}{\sqrt{3}}
 \end{aligned}$$

▲ In the body-centered cubic lattice, the atoms touch only along the cube diagonal. The edge length is  $4r/\sqrt{3}$ .

opposite corner. The edge length in terms of the atomic radius is therefore  $l = 4r/\sqrt{3}$  as shown in the diagram at left. The body-centered unit cell contains two atoms per unit cell because the center atom is not shared with any other neighboring cells. The coordination number of the body-centered cubic unit cell is 8, which we can see by examining the atom in the very center of the cube, which touches eight atoms at the corners. The packing efficiency is 68%, significantly higher than for the simple cubic unit cell. Each atom in this structure strongly interacts with more atoms than each atom in the simple cubic unit cell.

The **face-centered cubic** unit cell (Figure 11.47 ▼) is a cube with one atom at each corner and one atom (of the same kind) in the center of each cube face. Note

### Face-Centered Cubic Unit Cell

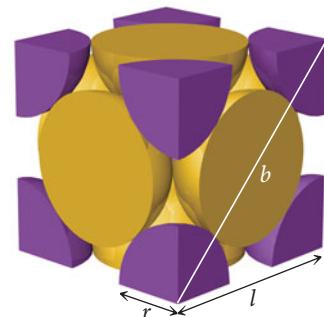


▲ **FIGURE 11.47** Face-Centered Cubic Crystal Structure The different colors used on the atoms in this figure are for clarity only. All atoms within the structure are identical.

that in the face-centered unit cell (like the body-centered unit cell), the atoms *do not* touch along each edge of the cube. Instead, the atoms touch *along the diagonal face*. The edge length in terms of the atomic radius is therefore  $l = 2\sqrt{2}r$ , as shown in the figure at right. The face-centered unit cell contains four atoms per unit cell because the center atoms on each of the six faces are shared between two unit cells. There are  $\frac{1}{2} \times 6 = 3$  face-centered atoms plus  $1/8 \times 8 = 1$  corner atoms, for a total of four atoms per unit cell. The coordination number of the face-centered cubic unit cell is 12 and its packing efficiency is 74%. In this structure, any one atom strongly interacts with more atoms than in either the simple cubic unit cell or the body-centered cubic unit cell.

Face-centered cubic

$$\begin{aligned} b^2 &= l^2 + l^2 = 2l^2 \\ b &= 4r \\ (4r)^2 &= 2l^2 \\ l^2 &= \frac{(4r)^2}{2} \\ l &= \frac{4r}{\sqrt{2}} \\ &= 2\sqrt{2}r \end{aligned}$$



▲ In the face-centered cubic lattice, the atoms touch along a face diagonal. The edge length is  $2\sqrt{2}r$ .

### EXAMPLE 11.7 Relating Density to Crystal Structure

Aluminum crystallizes with a face-centered cubic unit cell. The radius of an aluminum atom is 143 pm. Calculate the density of solid crystalline aluminum in g/cm<sup>3</sup>.

**SORT** You are given the radius of an aluminum atom and its crystal structure. You are asked to find the density of solid aluminum.

**STRATEGIZE** The conceptual plan is based on the definition of density.

Since the unit cell has the physical properties of the entire crystal, you can find the mass and volume of the unit cell and use these to calculate its density.

**SOLVE** Begin by finding the mass of the unit cell. Determine the mass of an aluminum atom from its molar mass. Since the face-centered cubic unit cell contains four atoms per unit cell, multiply the mass of aluminum by 4 to get the mass of a unit cell.

Next, calculate the edge length ( $l$ ) of the unit cell (in m) from the atomic radius of aluminum. For the face-centered cubic structure,  $l = 2\sqrt{2}r$ .

Calculate the volume of the unit cell (in cm) by converting the edge length to cm and cubing the edge length. (Use centimeters because you will want to report the density in units of g/cm<sup>3</sup>.)

Finally, calculate the density by dividing the mass of the unit cell by the volume of the unit cell.

**GIVEN:**  $r = 143$  pm, face-centered cubic

**FIND:**  $d$

#### CONCEPTUAL PLAN

$$d = m/V$$

$m$  = mass of unit cell

= number of atoms in unit cell  $\times$  mass of each atom

$V$  = volume of unit cell

$$= (\text{edge length})^3$$

#### SOLUTION

$$\begin{aligned} m(\text{Al atom}) &= 26.98 \frac{\text{g}}{\text{mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} \\ &= 4.480 \times 10^{-23} \text{ g/atom} \end{aligned}$$

$$\begin{aligned} m(\text{unit cell}) &= 4 \text{ atoms} (4.480 \times 10^{-23} \text{ g/atoms}) \\ &= 1.792 \times 10^{-22} \text{ g} \end{aligned}$$

$$l = 2\sqrt{2}r$$

$$= 2\sqrt{2}(143 \text{ pm})$$

$$= 2\sqrt{2}(143 \times 10^{-12} \text{ m})$$

$$= 4.045 \times 10^{-10} \text{ m}$$

$$V = l^3$$

$$\begin{aligned} &= \left( 4.045 \times 10^{-10} \text{ m} \times \frac{1 \text{ cm}}{10^{-2} \text{ m}} \right)^3 \\ &= 6.618 \times 10^{-23} \text{ cm}^3 \end{aligned}$$

$$\begin{aligned} d &= \frac{m}{V} = \frac{1.792 \times 10^{-22} \text{ g}}{6.618 \times 10^{-23} \text{ cm}^3} \\ &= 2.71 \text{ g/cm}^3 \end{aligned}$$

**CHECK**

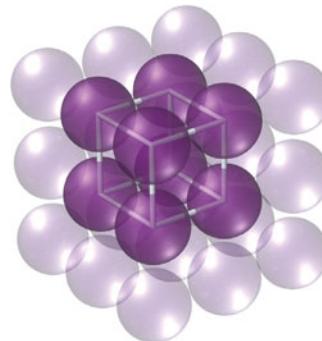
The units of the answer are correct. The magnitude of the answer is reasonable because the density is greater than  $1 \text{ g/cm}^3$  (as you would expect for metals), but still not too high (because aluminum is a low-density metal).

**FOR PRACTICE 11.7**

Chromium crystallizes with a body-centered cubic unit cell. The radius of a chromium atom is 125 pm. Calculate the density of solid crystalline chromium in  $\text{g/cm}^3$ .

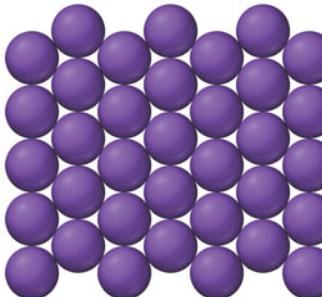
**Closest-Packed Structures**

Another way to envision crystal structures, especially useful in metals where bonds are not usually directional, is to think of the atoms as stacking in layers, much as fruit is stacked at the grocery store. For example, the simple cubic structure can be envisioned as one layer of atoms arranged in a square pattern with the next layer stacking directly over the first, so that the atoms in one layer align exactly on top of the atoms in the layer beneath it, as shown here:

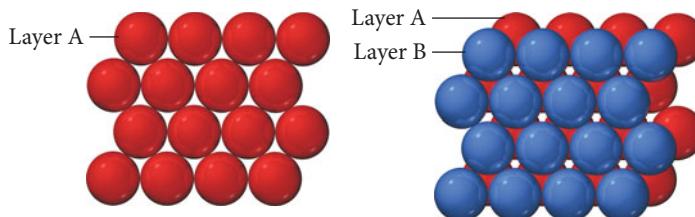


As we saw previously, this crystal structure has a great deal of empty space—only 52% of the volume is occupied by the spheres, and the coordination number is 6.

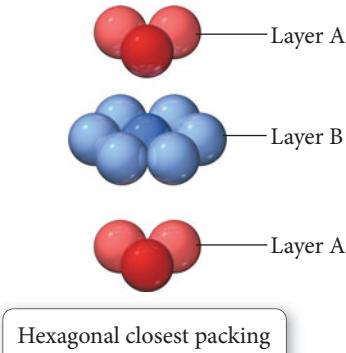
More space-efficient packing can be achieved by aligning neighboring rows of atoms in a pattern with one row offset from the next by one-half a sphere, as shown here:



In this way, the atoms pack more closely to each other in any one layer. We can further increase the packing efficiency by placing the next layer *not directly on top of the first*, but again offset so that any one atom actually sits in the indentation formed by three atoms in the layer beneath it, as shown here:

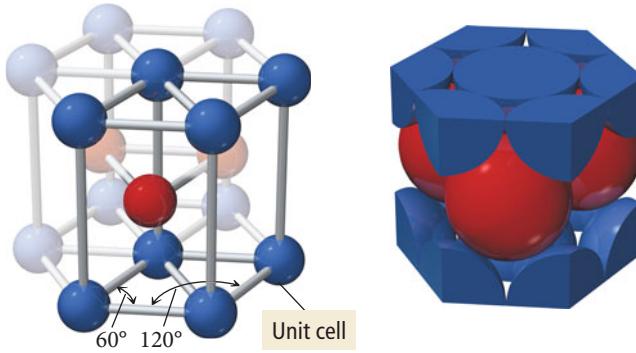


This kind of packing leads to two different crystal structures called *closest-packed structures*, both of which have a packing efficiency of 74% and a coordination number of 12. In the first of these two closest-packed structures—called **hexagonal closest packing**—the third layer of atoms aligns exactly on top of the first, as shown here:



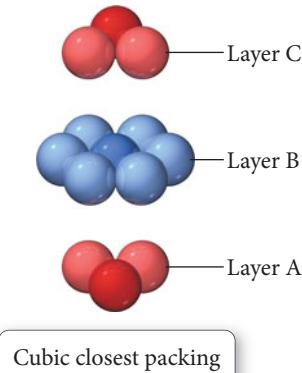
The pattern from one layer to the next is ABAB, with the third layer aligning exactly above the first. Notice that the central atom in layer B of this structure is touching six atoms in its own layer, three atoms in the layer above it, and three atoms in the layer below, for a coordination number of 12. The unit cell for this crystal structure is not a cubic unit cell, but a hexagonal one, as shown in Figure 11.48 ▶.

### Hexagonal Closest Packing



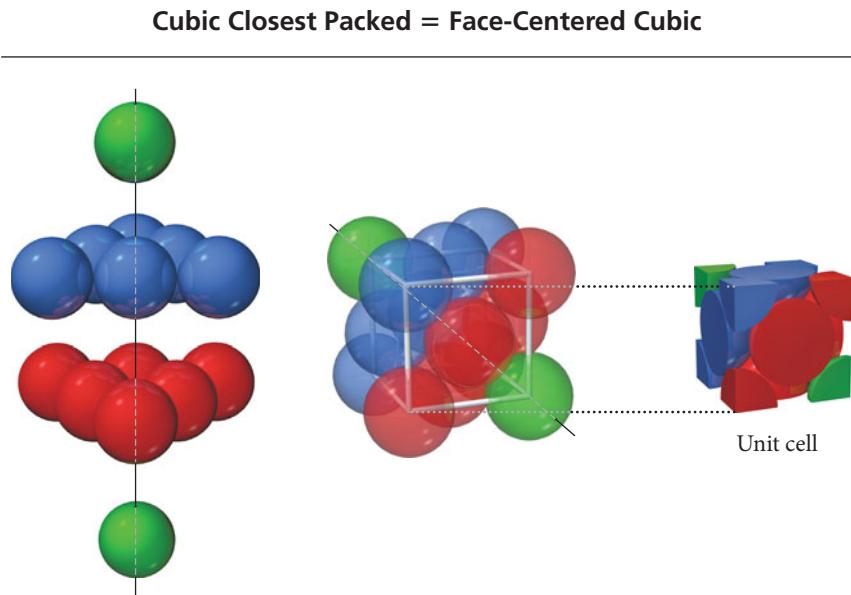
◀ **FIGURE 11.48** Hexagonal Closest Packing Crystal Structure The unit cell is outlined in bold.

In the second of the two closest-packed structures—called **cubic closest packing**—the third layer of atoms is offset from the first, as shown here:



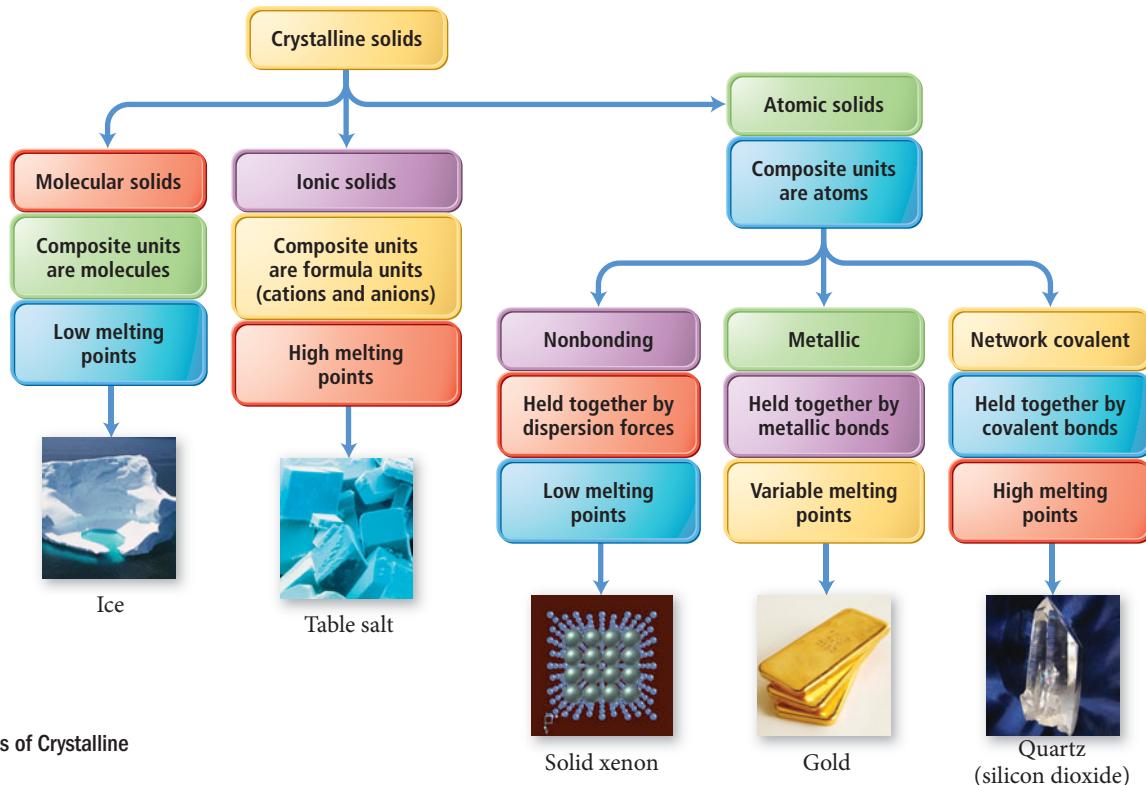
The pattern from one layer to the next is ABCABC, with every fourth layer aligning with the first. Although not simple to visualize, the unit cell for cubic closest packing is the face-centered cubic unit cell, as shown in Figure 11.49 ►. The cubic closest-packed structure is identical to the face-centered cubic unit cell structure.

**► FIGURE 11.49** Cubic Closest-Packing Crystal Structure The unit cell of the cubic closest-packed structure is face-centered cubic.



## 11.12 Crystalline Solids: The Fundamental Types

As we discussed in Section 11.2, solids may be crystalline (comprising a well-ordered array of atoms or molecules) or amorphous (having no long-range order). We can classify crystalline solids into three categories—molecular, ionic, and atomic—based on the individual units that compose the solid. Atomic solids can themselves be classified into three categories—nonbonded, metallic, and network covalent—depending on the types of interactions between atoms within the solid. Figure 11.50 ▼ shows the different categories of crystalline solids.



**► FIGURE 11.50** Types of Crystalline Solids

## Molecular Solids

**Molecular solids** are solids whose composite units are *molecules*. The lattice sites in a crystalline molecular solid are therefore occupied by molecules. Ice (solid H<sub>2</sub>O) and dry ice (solid CO<sub>2</sub>) are examples of molecular solids. Molecular solids are held together by the kinds of intermolecular forces—dispersion forces, dipole–dipole forces, and hydrogen bonding—discussed earlier in this chapter. Molecular solids as a whole tend to have low to moderately low melting points. However, strong intermolecular forces (such as the hydrogen bonds in water) can increase the melting points of some molecular solids.

## Ionic Solids

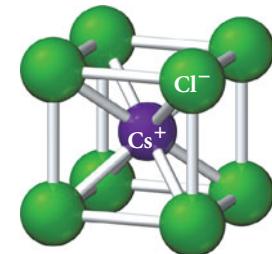
**Ionic solids** are solids whose composite units are ions. Table salt (NaCl) and calcium fluoride (CaF<sub>2</sub>) are examples of ionic solids. Ionic solids are held together by the coulombic interactions that occur between the cations and anions occupying the lattice sites in the crystal. The coordination number of the unit cell for an ionic compound, therefore, represents the number of close cation–anion interactions. Since these interactions lower potential energy, the crystal structure of a particular ionic compound is the one that maximizes the coordination number while accommodating both charge neutrality (each unit cell must be charge neutral) and the different sizes of the cations and anions that compose the particular compound. In general, the more similar the radii of the cation and the anion, the higher the coordination number.

Cesium chloride (CsCl) is a good example of an ionic compound with cations and anions of similar size (Cs<sup>+</sup> radius = 167 pm; Cl<sup>-</sup> radius = 181 pm). In the cesium chloride structure, the chloride ions occupy the lattice sites of a simple cubic cell and one cesium ion lies in the very center of the cell, as shown in Figure 11.51 ►. (In this and subsequent figures of ionic crystal structures, the different colored spheres represent different ions.) The coordination number for cesium chloride is 8, meaning that each cesium ion is in direct contact with eight chloride ions (and vice versa). The cesium chloride unit cell contains one chloride anion ( $8 \times 1/8 = 1$ ) and one cesium cation for a ratio of Cs to Cl of 1:1, as the formula for the compound indicates. (Note that complete chloride ions are shown in Figure 11.51 even though only 1/8 of each ion is in the unit cell.) Calcium sulfide (CaS) has the same structure as cesium chloride.

The crystal structure of sodium chloride must accommodate the more disproportionate sizes of Na<sup>+</sup> (radius = 97 pm) and Cl<sup>-</sup> (radius = 181 pm). If ion size were the only consideration, the larger chloride anion could theoretically fit many of the smaller sodium cations around it, but charge neutrality requires that each sodium cation be surrounded by an equal number of chloride anions. Therefore, the coordination number is limited by the number of chloride anions that can fit around the relatively small sodium cation. The structure that minimizes the energy is shown in Figure 11.52 ► and has a coordination number of 6 (each chloride anion is surrounded by six sodium cations and vice versa). We can visualize this structure, called the *rock salt* structure, as chloride anions occupying the lattice sites of a face-centered cubic structure with the smaller sodium cations occupying the holes between the anions. (Alternatively, we can visualize this structure as the *sodium cations* occupying the lattice sites of a face-centered cubic structure with the *larger chloride anions* occupying the spaces between the cations.) Each unit cell contains four chloride anions [ $(8 \times 1/8) + (6 \times 1/2) = 4$ ] and four sodium cations [ $(12 \times 1/4) + 1 = 4$ ], resulting in a ratio of 1:1, as the formula of the compound specifies. Other compounds exhibiting the sodium chloride structure include LiF, KCl, KBr, AgCl, MgO, and CaO.

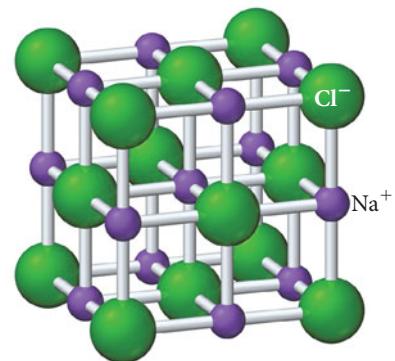
A greater disproportion between the sizes of the cations and anions in a compound makes a coordination number of even 6 physically impossible. For example, in ZnS (Zn<sup>2+</sup> radius = 74 pm; S<sup>2-</sup> radius = 184 pm) the crystal structure, shown in Figure 11.53 ►, has a coordination number of only 4. We can visualize this structure, called the *zinc blende* structure, as sulfide anions occupying the lattice sites of a face-centered cubic structure with the smaller zinc cations occupying four of the eight tetrahedral holes located directly beneath each corner atom. A tetrahedral hole is the

Cesium chloride (CsCl)



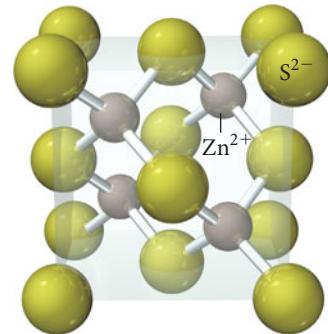
▲ FIGURE 11.51 Cesium Chloride Unit Cell The different colored spheres in this figure represent the different ions in the compound.

Sodium chloride (NaCl)

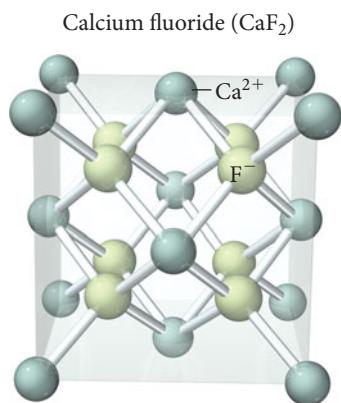
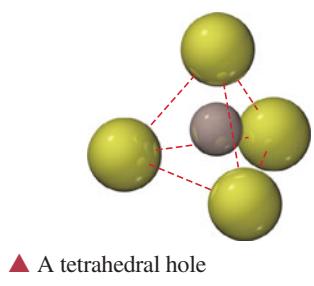


▲ FIGURE 11.52 Sodium Chloride Unit Cell The different colored spheres in this figure represent the different ions in the compound.

Zinc blende (ZnS)

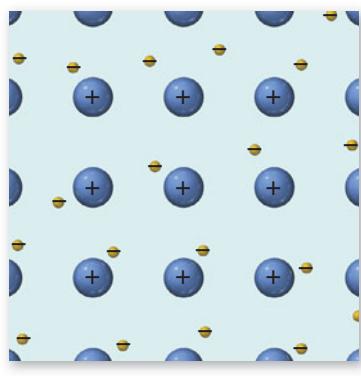


▲ FIGURE 11.53 Zinc Sulfide (Zinc Blende) Unit Cell The different colored spheres in this figure represent the different ions in the compound.



▲ FIGURE 11.54 Calcium Fluoride Unit Cell The different colored spheres in this figure represent the different ions in the compound.

We examine a more sophisticated model for bonding in metals in Section 11.13.



▲ FIGURE 11.55 The Electron Sea Model In the electron sea model for metals, the metal cations exist in a “sea” of electrons.

► FIGURE 11.56 Closest-Packed Crystal Structures in Metals Nickel crystallizes in the cubic closest-packed structure. Zinc crystallizes in the hexagonal closest-packed structure.

empty space that lies in the center of a tetrahedral arrangement of four atoms, as shown at left. Each unit cell contains four sulfide anions [ $(8 \times \frac{1}{8}) + (6 \times \frac{1}{2} = 4)$ ] and four zinc cations (each of the four zinc cations is completely contained within the unit cell), resulting in a ratio of 1:1, just as the formula of the compound indicates. Other compounds exhibiting the zinc blende structure include  $\text{CuCl}$ ,  $\text{AgI}$ , and  $\text{CdS}$ .

When the ratio of cations to anions is not 1:1, the crystal structure must accommodate the unequal number of cations and anions. Many compounds that contain a cation to anion ratio of 1:2 adopt the *fluorite* ( $\text{CaF}_2$ ) structure shown in Figure 11.54 ▲. We can visualize this structure as calcium cations occupying the lattice sites of a face-centered cubic structure with the larger fluoride anions occupying all eight of the tetrahedral holes located directly beneath each corner atom. Each unit cell contains four calcium cations [ $(8 \times \frac{1}{8}) + (6 \times \frac{1}{2}) = 4$ ] and eight fluoride anions (each of the eight fluoride anions is completely contained within the unit cell), resulting in a cation to anion ratio of 1:2, just as in the formula of the compound. Other compounds exhibiting the fluorite structure include  $\text{PbF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaCl}_2$ . Compounds with a cation to anion ratio of 2:1 often exhibit the *antifluorite structure*, in which the anions occupy the lattice sites of a face-centered cubic structure and the cations occupy the tetrahedral holes beneath each corner atom.

The forces holding ionic solids together are strong coulombic forces (or ionic bonds), and since these forces are much stronger than the intermolecular forces, ionic solids tend to have much higher melting points than molecular solids. For example, sodium chloride melts at  $801^\circ\text{C}$ , while carbon disulfide ( $\text{CS}_2$ )—a molecular solid with a higher molar mass—melts at  $-110^\circ\text{C}$ .

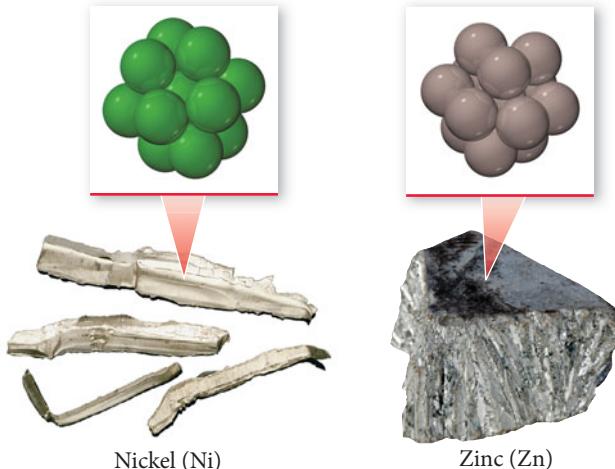
## Atomic Solids

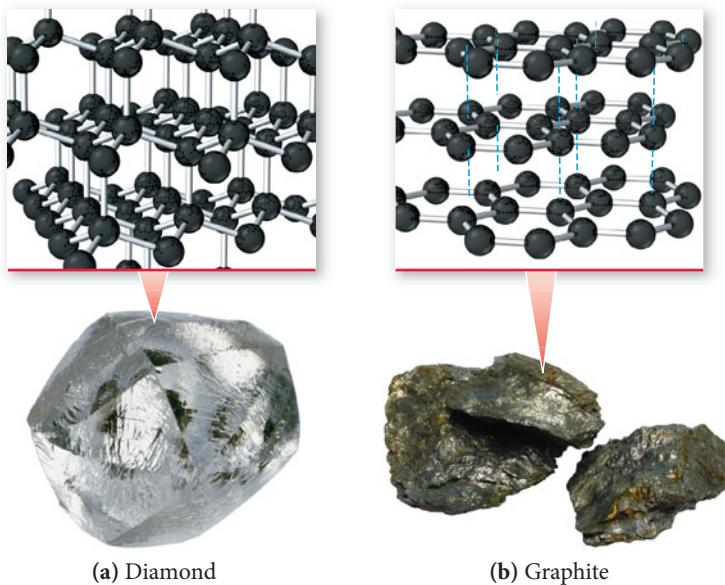
Solids whose composite units are individual atoms are **atomic solids**. Solid xenon ( $\text{Xe}$ ), iron ( $\text{Fe}$ ), and silicon dioxide ( $\text{SiO}_2$ ) are examples of atomic solids. We can classify atomic solids themselves into three categories—*nonbonding atomic solids*, *metallic atomic solids*, and *network covalent atomic solids*—each held together by a different kind of force.

**Nonbonding atomic solids** are held together by relatively weak dispersion forces. In order to maximize these interactions, nonbonding atomic solids form closest-packed structures, maximizing their coordination numbers and minimizing the distance between them. Nonbonding atomic solids have very low melting points that increase uniformly with molar mass. The only nonbonding atomic solids are noble gases in their solid form. Argon, for example, has a melting point of  $-189^\circ\text{C}$  and xenon has a melting point of  $-112^\circ\text{C}$ .

**Metallic atomic solids**, such as iron or gold, are held together by *metallic bonds*, which in the simplest model are represented by the interaction of metal cations with the sea of electrons that surround them, as described in Section 9.11 (Figure 11.55 ▲).

Since metallic bonds are not directional, metals also tend to form closest-packed crystal structures. For example, nickel crystallizes in the cubic closest-packed structure and zinc crystallizes in the hexagonal closest-packed structure (Figure 11.56 ▼). Metallic





**▲ FIGURE 11.57** Network Covalent Atomic Solids (a) In diamond, each carbon atom forms four covalent bonds to four other carbon atoms in a tetrahedral geometry. (b) In graphite, carbon atoms are arranged in sheets. Within each sheet, the atoms are covalently bonded to one another by a network of sigma and pi bonds. Neighboring sheets are held together by dispersion forces.

bonds have varying strengths. Some metals, such as mercury, have melting points below room temperature, whereas other metals, such as iron, have relatively high melting points (iron melts at 1809 °C).

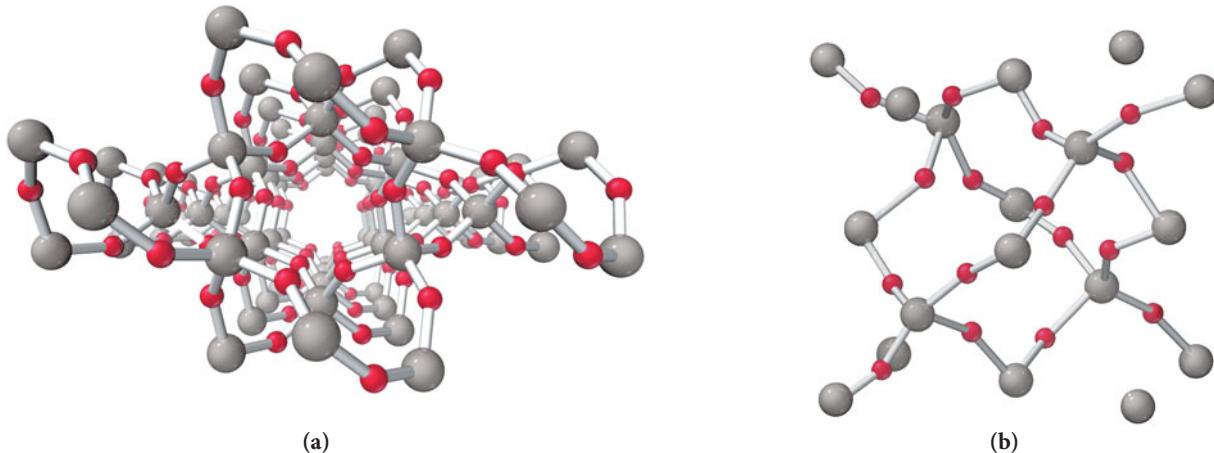
**Network covalent atomic solids**, such as diamond, graphite, and silicon dioxide, are held together by covalent bonds. The crystal structures of these solids are more restricted by the geometrical constraints of the covalent bonds (which tend to be more directional than intermolecular forces, ionic bonds, or metallic bonds) so they *do not* tend to form closest-packed structures.

In diamond (Figure 11.57a ▲), each carbon atom forms four covalent bonds to four other carbon atoms in a tetrahedral geometry. This structure extends throughout the entire crystal, so that a diamond crystal can be thought of as a giant molecule, held together by these covalent bonds. Since covalent bonds are very strong, covalent atomic solids have high melting points. Diamond is estimated to melt at about 3800 °C. The electrons in diamond are confined to the covalent bonds and are not free to flow. Therefore, diamond does not conduct electricity.

In graphite (Figure 11.57b), carbon atoms are arranged in sheets. Within each sheet, carbon atoms are covalently bonded to each other by a network of sigma and pi bonds, similar to those in benzene. Just as the electrons within the pi bonds in benzene are delocalized over the entire molecule, so the pi bonds in graphite are delocalized over the entire sheet, making graphite a good electrical conductor along the sheets. The bond length between carbon atoms *within a sheet* is 142 pm. However, the forces *between* sheets are much different. The separation between sheets is 341 pm. There are no covalent bonds between sheets, only relatively weak dispersion forces. Consequently, the sheets slide past each other relatively easily, which explains the slippery feel of graphite and its extensive use as a lubricant.

**Sigma and pi bonds were discussed in Section 10.7.**

The silicates (extended arrays of silicon and oxygen) are the most common network covalent atomic solids. Geologists estimate that 90% of Earth's crust is composed of silicates; we will cover these in more detail in Chapter 22. The basic silicon–oxygen compound is silica ( $\text{SiO}_2$ ), which in its most common crystalline form is called quartz. The structure of quartz consists of an array of  $\text{SiO}_4$  tetrahedra with shared oxygen atoms, as shown in Figure 11.58a ►. The strong silicon–oxygen covalent bonds that hold quartz together result in its high melting point of about 1600 °C. Common glass is also composed of  $\text{SiO}_2$ , but in its amorphous form (Figure 11.58b).



**▲ FIGURE 11.58** The Structure of Quartz (a) Quartz consists of an array of  $\text{SiO}_4$  tetrahedra with shared oxygen atoms. (b) Glass is amorphous  $\text{SiO}_2$ .

## 11.13 Crystalline Solids: Band Theory

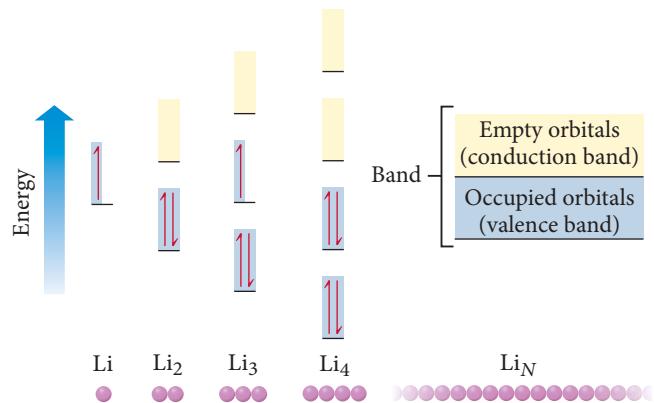
In Section 9.11, we explored a model for bonding in metals called the *electron sea model*. We now turn to a model for bonding in solids that is both more sophisticated and more broadly applicable—it applies to both metallic solids and covalent solids. The model is **band theory** and it grows out of molecular orbital theory, first discussed in Section 10.8.

Recall that in molecular orbital theory, we combine the atomic orbitals of the atoms within a molecule to form molecular orbitals. These molecular orbitals are not localized on individual atoms, but *delocalized over the entire molecule*. Similarly, in band theory, we combine the atomic orbitals of the atoms within a solid crystal to form orbitals that are not localized on individual atoms, but delocalized over the entire *crystal*. In some sense then, the crystal is like a very large molecule, and its valence electrons occupy the molecular orbitals formed from the atomic orbitals of each atom in the crystal.

Consider a series of molecules constructed from individual lithium atoms. The energy levels of the atomic orbitals and resulting molecular orbitals for  $\text{Li}$ ,  $\text{Li}_2$ ,  $\text{Li}_3$ ,  $\text{Li}_4$ , and  $\text{Li}_N$  (where  $N$  is a large number on the order of  $10^{23}$ ) are shown in Figure 11.59 ▼. The lithium atom has a single electron in a single  $2s$  atomic orbital. The  $\text{Li}_2$  molecule contains two electrons and two molecular orbitals. The electrons occupy the lower energy bonding orbital—the higher energy, or antibonding, molecular orbital is empty. The  $\text{Li}_4$  molecule contains four electrons and four molecular orbitals. The electrons occupy the two bonding molecular orbitals—the two antibonding orbitals are completely empty.

The  $\text{Li}_N$  molecule contains  $N$  electrons and  $N$  molecular orbitals. However, because there are so many molecular orbitals, the energy spacings between them are infinitesimally small; they are no longer discrete energy levels, but rather they form a *band* of energy levels. One half of the orbitals in the band ( $N/2$ ) are bonding molecular orbitals and (at 0 K) contain the  $N$  valence electrons. The other  $N/2$  molecular orbitals are antibonding and (at 0 K) are completely empty. If the atoms composing a solid have  $p$  orbitals available, then the same process leads to another band of orbitals at higher energies.

**► FIGURE 11.59** Energy Levels of Molecular Orbitals in Lithium Molecules When many Li atoms are present, the energy levels of the molecular orbitals are so closely spaced that they fuse to form a band. Half of the orbitals are bonding orbitals and contain valence electrons; the other half are antibonding orbitals and are empty.



In band theory, electrons become mobile when they make a transition from the highest occupied molecular orbital into higher energy empty molecular orbitals. For this reason, we call the occupied molecular orbitals the *valence band* and the unoccupied orbitals the *conduction band*. In lithium metal, the highest occupied molecular orbital lies in the middle of a band of orbitals, and the energy difference between it and the next higher energy orbital is infinitesimally small. Therefore, above 0 K, electrons can easily make the transition from the valence band to the conduction band. Since electrons in the conduction band are mobile, lithium, like all metals, is a good electrical conductor. Mobile electrons in the conduction band are also responsible for the thermal conductivity of metals. When a metal is heated, electrons are excited to higher energy molecular orbitals. These electrons can then quickly transport the thermal energy throughout the crystal lattice.

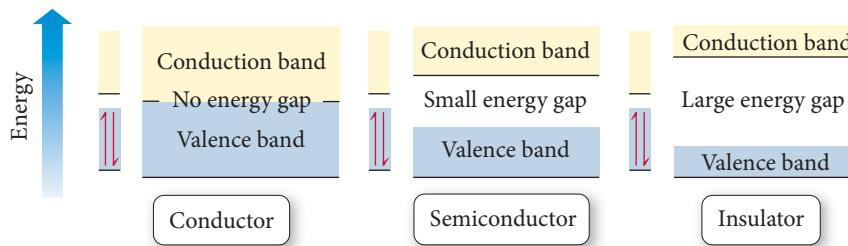
In metals, the valence band and conduction band are energetically continuous—the energy difference between the top of the valence band and the bottom of the conduction band is infinitesimally small. In semiconductors and insulators, however, an energy gap, called the **band gap**, exists between the valence band and conduction band as shown in Figure 11.60 ▼. In insulators, the band gap is large, and electrons are not promoted into the conduction band at ordinary temperatures, resulting in no electrical conductivity. In semiconductors, the band gap is small, allowing some electrons to be promoted at ordinary temperatures and resulting in limited conductivity. However, the conductivity of semiconductors can be increased in a controlled way by adding minute amounts of other substances, called *dopants*, to the semiconductor.

## Doping: Controlling the Conductivity of Semiconductors

Doped semiconductors contain minute amounts of impurities that result in additional electrons in the conduction band or electron “holes” in the valence band. For example, silicon is a group 4A semiconductor. Its valence electrons just fill its valence band. The band gap in silicon is large enough that only a few electrons are promoted into the conduction band at room temperature; therefore, silicon is a poor electrical conductor. However, silicon can be doped with phosphorus, a group 5A element with five valence electrons, to increase its conductivity. The phosphorus atoms are incorporated into the silicon crystal structure, and each phosphorus atom brings with it one additional electron. Since the valence band is completely full, the additional electrons must go into the conduction band. These electrons are then mobile and can conduct electrical current. This type of semiconductor is called an **n-type semiconductor** because the charge carriers are negatively charged electrons in the conduction band.

Silicon can also be doped with a group 3A element, such as gallium, which has only three valence electrons. When gallium is incorporated into the silicon crystal structure, it results in electron “holes,” or empty molecular orbitals, in the valence band. The presence of holes also allows for the movement of electrical current because electrons in the valence band can move between holes. In this way, the holes move in the opposite direction as the electrons. This type of semiconductor is called a **p-type semiconductor** because each hole acts as a positive charge.

The heart of most modern electronic devices are silicon chips containing millions of **p–n junctions**, tiny spots that are p-type on one side and n-type on the other. These junctions can serve a number of functions including acting as **diodes** (circuit elements that allow the flow of electrical current in only one direction) or amplifiers (elements that amplify a small electrical current into a larger one).



◀ FIGURE 11.60 Band Gap In a conductor, there is no energy gap between the valence band and the conduction band. In semiconductors there is a small energy gap, and in insulators there is a large energy gap.

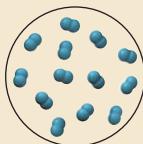
## CHAPTER IN REVIEW

### Self Assessment Quiz

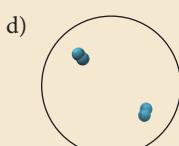
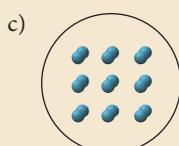
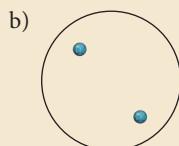
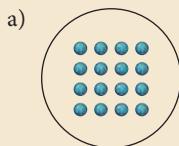
**Q1.** Which state of matter is compressible?

- a) gas
- b) liquid
- c) solid
- d) none of the above

**Q2.** Liquid nitrogen boils at 77 K. The image shown below depicts a sample of liquid nitrogen.



Which image best depicts the nitrogen after it has boiled?



**Q3.** Based on the expected intermolecular forces, which halogen has the highest boiling point?

- a) F<sub>2</sub>
- b) Cl<sub>2</sub>
- c) Br<sub>2</sub>
- d) I<sub>2</sub>

**Q4.** Which substance has dipole–dipole forces?

- a) CCl<sub>4</sub>
- b) NF<sub>3</sub>
- c) CS<sub>2</sub>
- d) SO<sub>3</sub>

**Q5.** One of these substances is a liquid at room temperature. Which one?

- a) CH<sub>3</sub>OH
- b) CF<sub>4</sub>
- c) SiH<sub>4</sub>
- d) CO<sub>2</sub>

**Q6.** Which property of a liquid increases with increasing temperature?

- a) surface tension
- b) viscosity
- c) vapor pressure
- d) none of the above

**Q7.** Determine the amount of heat (in kJ) required to vaporize 1.55 kg of water at its boiling point.

For water,  $\Delta H_{\text{vap}} = 40.7 \text{ kJ/mol}$  (at 100 °C).

- a)  $3.50 \times 10^3 \text{ kJ}$
- b)  $1.14 \times 10^6 \text{ kJ}$
- c) 2.11 kJ
- d) 686 kJ

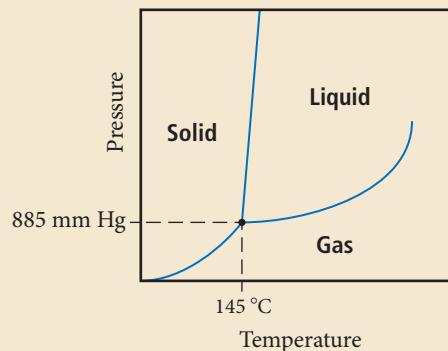
**Q8.** The vapor pressure of a substance is measured over a range of temperatures. A plot of the natural log of the vapor pressure versus the inverse of the temperature (in Kelvin) produces a straight line with a slope of  $-3.46 \times 10^3 \text{ K}$ . Find the enthalpy of vaporization of the substance.

- a)  $2.40 \times 10^{-3} \text{ kJ/mol}$
- b) 28.8 kJ/mol
- c) 0.416 kJ/mol
- d) 3.22 kJ/mol

**Q9.** Acetic acid has a normal boiling point of 118 °C and a  $\Delta H_{\text{vap}}$  of 23.4 kJ/mol. What is the vapor pressure (in mmHg) of acetic acid at 25 °C?

- a)  $2.92 \times 10^{-39} \text{ mmHg}$
- b)  $7.16 \times 10^3 \text{ mmHg}$
- c) 758 mmHg
- d) 80.6 mmHg

**Q10.** Consider the phase diagram shown below. A sample of the substance in the phase diagram is initially at 175 °C and 925 mmHg. What phase transition occurs when the pressure is decreased to 760 mmHg at constant temperature?



- a) solid to liquid
- b) liquid to gas
- c) solid to gas
- d) liquid to solid

**Q11.** How many atoms are in the body-centered cubic unit cell?

- a) 1
- b) 2
- c) 4
- d) 5

- Q12.** Rhodium crystallizes in a face-centered cubic unit cell. The radius of a rhodium atom is 135 pm. Determine the density of rhodium in g/cm<sup>3</sup>.
- 3.07 g/cm<sup>3</sup>
  - 12.4 g/cm<sup>3</sup>
  - 278 g/cm<sup>3</sup>
  - 0.337 g/cm<sup>3</sup>
- Q13.** A mixture containing 21.4 g of ice (at exactly 0.00 °C) and 75.3 g of water (at 55.3 °C) is placed in an insulated container. Assuming no loss of heat to the surroundings, what is the final temperature of the mixture?
- 22.5 °C
  - 25.4 °C
  - 32.6 °C
  - 41.9 °C

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

- Q14.** Which type of solid is dry ice (solid carbon dioxide)?

- ionic
- molecular
- atomic
- none of the above

- Q15.** Which process *releases* the greatest amount of heat?

- the condensation of 10 g of gaseous water
- the freezing of 10 g of liquid water
- the boiling of 10 g of liquid water
- the melting of 10 g of ice

## Key Terms

### Section 11.2

crystalline (485)  
amorphous (485)

### Section 11.3

dispersion force (487)  
dipole–dipole force (490)  
permanent dipole (490)  
miscibility (491)  
hydrogen bonding (492)  
hydrogen bond (493)  
ion–dipole force (495)

### Section 11.4

surface tension (497)  
viscosity (498)  
capillary action (499)

### Section 11.5

vaporization (500)  
condensation (500)

volatile (500)  
nonvolatile (500)  
heat of vaporization  
( $\Delta H_{\text{vap}}$ ) (501)  
dynamic equilibrium (503)  
vapor pressure (503)  
boiling point (504)  
normal boiling point (504)  
Clausius–Clapeyron  
equation (505)  
critical temperature ( $T_c$ ) (508)  
critical pressure ( $P_c$ ) (508)

### Section 11.6

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deposition (509)  
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### Section 11.11

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coordination number (521)  
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body-centered cubic (521)  
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packing (525)  
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## Key Concepts

### Solids, Liquids, and Intermolecular Forces (11.1, 11.2, 11.3)

- The forces that hold molecules or atoms together in a liquid or solid are intermolecular forces. The strength of the intermolecular forces in a substance determines its state.
- Dispersion forces are present in all elements and compounds; they arise from the fluctuations in electron distribution within atoms and molecules. These are the weakest intermolecular forces, but they are significant in molecules with high molar masses.
- Dipole–dipole forces, generally stronger than dispersion forces, are present in all polar molecules.
- Hydrogen bonding occurs in polar molecules that contain hydrogen atoms bonded directly to fluorine, oxygen, or nitrogen. These are the strongest intermolecular forces.
- Ion–dipole forces occur when ionic compounds are mixed with polar compounds, and they are especially important in aqueous solutions.

### Surface Tension, Viscosity, and Capillary Action (11.4)

- Surface tension results from the tendency of liquids to minimize their surface area in order to maximize the interactions between their constituent particles, thus lowering potential energy. Surface tension causes water droplets to form spheres and allows insects and paper clips to “float” on the surface of water.
- Viscosity is the resistance of a liquid to flow. Viscosity increases with increasing strength of intermolecular forces and decreases with increasing temperature.
- Capillary action is the ability of a liquid to flow against gravity up a narrow tube. It is the result of adhesive forces, the attraction between the molecules and the surface of the tube, and cohesive forces, the attraction between the molecules in the liquid.

### Vaporization and Vapor Pressure (11.5, 11.7)

- Vaporization, the transition from liquid to gas, occurs when thermal energy overcomes the intermolecular forces present in a

- liquid. The opposite process is condensation. Vaporization is endothermic and condensation is exothermic.
- The rate of vaporization increases with increasing temperature, increasing surface area, and decreasing strength of intermolecular forces.
  - The heat of vaporization ( $\Delta H_{\text{vap}}$ ) is the heat required to vaporize one mole of a liquid.
  - In a sealed container, a solution and its vapor come into dynamic equilibrium, at which point the rate of vaporization equals the rate of condensation. The pressure of a gas that is in dynamic equilibrium with its liquid is its vapor pressure.
  - The vapor pressure of a substance increases with increasing temperature and with decreasing strength of its intermolecular forces.
  - The boiling point of a liquid is the temperature at which its vapor pressure equals the external pressure.
  - The Clausius–Clapeyron equation expresses the relationship between the vapor pressure of a substance and its temperature and can be used to calculate the heat of vaporization from experimental measurements.
  - When a liquid is heated in a sealed container it eventually forms a supercritical fluid, which has properties intermediate between a liquid and a gas. This occurs at critical temperature and critical pressure.

### Fusion and Sublimation (11.6, 11.7)

- Sublimation is the transition from solid to gas. The opposite process is deposition.
- Fusion, or melting, is the transition from solid to liquid. The opposite process is freezing.
- The heat of fusion ( $\Delta H_{\text{fus}}$ ) is the amount of heat required to melt one mole of a solid. Fusion is endothermic.
- The heat of fusion is generally less than the heat of vaporization because intermolecular forces do not have to be completely overcome for melting to occur.

### Phase Diagrams (11.8)

- A phase diagram is a map of the states of a substance as a function of its pressure (y-axis) and temperature (x-axis).

- The regions in a phase diagram represent conditions under which a single stable state (solid, liquid, gas) exists.
- The lines represent conditions under which two states are in equilibrium.
- The triple point represents the conditions under which all three states coexist.
- The critical point is the temperature and pressure above which a supercritical fluid exists.

### The Uniqueness of Water (11.9)

- Water is a liquid at room temperature despite its low molar mass. Water forms strong hydrogen bonds, resulting in its high boiling point.
- The polarity of water enables it to dissolve many polar and ionic compounds and even nonpolar gases.
- Water expands upon freezing, so ice is less dense than liquid water. Water is critical both to the existence of life and to human health.

### Crystalline Structures (11.10–11.13)

- X-ray crystallography uses the diffraction pattern of X-rays to determine the crystal structure of solids.
- The crystal lattice is represented by a unit cell, a structure that reproduces the entire lattice when repeated in all three dimensions.
- Three basic cubic unit cells are the simple cubic, the body-centered cubic, and the face-centered cubic.
- Some crystal lattices can also be depicted as closest-packed structures, including the hexagonal closest-packing structure (not cubic) and the cubic closest-packing structure (which has a face-centered cubic unit cell).
- The basic types of crystal solids are molecular, ionic, and atomic solids. We divide atomic solids into three different types: nonbonded, metallic, and covalent.
- Band theory is a model for bonding in solids in which the atomic orbitals of the atoms are combined and delocalized over the entire crystal solid.

## Key Equations and Relationships

Clausius–Clapeyron Equation: Relationship between Vapor Pressure ( $P_{\text{vap}}$ ), the Heat of Vaporization ( $\Delta H_{\text{vap}}$ ), and Temperature ( $T$ ) (11.5)

$$\ln P_{\text{vap}} = \frac{-\Delta H_{\text{vap}}}{RT} + \ln \beta \quad (\beta \text{ is a constant})$$

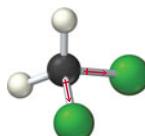
$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

Bragg's Law: Relationship between Light Wavelength ( $\lambda$ ), Angle of Reflection ( $\theta$ ), and Distance ( $d$ ) between the Atomic Layers (11.10)

$$n\lambda = 2d \sin \theta \quad (n = \text{integer})$$

## Key Learning Outcomes

Chapter Objectives	Assessment
Determining Whether a Molecule Has Dipole–Dipole Forces (11.3)	Example 11.1 For Practice 11.1 Exercises 49–60



## Key Learning Outcomes, continued

Determining Whether a Molecule Displays Hydrogen Bonding (11.3)	Example 11.2 For Practice 11.2 Exercises 49–60
Using the Heat of Vaporization in Calculations (11.5)	Example 11.3 For Practice 11.3 For More Practice 11.3 Exercises 71–74
Using the Clausius–Clapeyron Equation (11.5)	Examples 11.4, 11.5 For Practice 11.4, 11.5 Exercises 75–78
Using Bragg's Law in X-Ray Diffraction Calculations (11.10)	Example 11.6 For Practice 11.6 Exercises 95, 96
Relating Density to Crystal Structure (11.11)	Example 11.7 For Practice 11.7 Exercises 99–102



## EXERCISES

### Review Questions

- Explain how a gecko is able to walk on a polished glass surface.
- Why are intermolecular forces important?
- What are the main properties of liquids (in contrast to gases and solids)?
- What are the main properties of solids (in contrast to liquids and gases)?
- What is the fundamental difference between an amorphous solid and a crystalline solid?
- What factors cause transitions between the solid and liquid state? The liquid and gas state?
- Describe the relationship between the state of a substance, its temperature, and the strength of its intermolecular forces.
- From what kinds of interactions do intermolecular forces originate?
- Why are intermolecular forces generally much weaker than bonding forces?
- What is the dispersion force? What does the magnitude of the dispersion force depend on? How can you predict the magnitude of the dispersion force for closely related elements or compounds?
- What is the dipole–dipole force? How can you predict the presence of dipole–dipole forces in a compound?
- How is the miscibility of two liquids related to their polarity?
- What is hydrogen bonding? How can you predict the presence of hydrogen bonding in a compound?
- What is the ion–dipole force? Why is it important?
- What is surface tension? How does surface tension result from intermolecular forces? How is it related to the strength of intermolecular forces?
- What is viscosity? How does viscosity depend on intermolecular forces? What other factors affect viscosity?
- What is capillary action? How does it depend on the relative strengths of adhesive and cohesive forces?
- Explain what happens in the processes of vaporization and condensation. Why does the rate of vaporization increase with increasing temperature and surface area?
- Why is vaporization endothermic? Why is condensation exothermic?
- How is the volatility of a substance related to the intermolecular forces present within the substance?
- What is the heat of vaporization for a liquid and why is it useful?
- Explain the process of dynamic equilibrium. How is dynamic equilibrium related to vapor pressure?
- What happens to a system in dynamic equilibrium when it is disturbed in some way?
- How is vapor pressure related to temperature? What happens to the vapor pressure of a substance when the temperature is increased? Decreased?
- Define the terms *boiling point* and *normal boiling point*.
- What is the Clausius–Clapeyron equation and why is it important?
- Explain what happens to a substance when it is heated in a closed container to its critical temperature.
- What is sublimation? Give a common example of sublimation.
- What is fusion? Is fusion exothermic or endothermic? Why?
- What is the heat of fusion and why is it important?

31. Examine the heating curve for water in Section 11.7 (Figure 11.36). Explain why the curve has two segments in which heat is added to the water but the temperature does not rise.
32. Examine the heating curve for water in Section 11.7 (Figure 11.36). Explain the significance of the slopes of each of the three rising segments. Why are the slopes different?
33. What is a phase diagram? Draw a generic phase diagram and label its important features.
34. What is the significance of crossing a line in a phase diagram?
35. How do the properties of water differ from those of most other substances?
36. Explain the basic principles involved in X-ray crystallography. Include Bragg's law in your explanation.
37. What is a crystalline lattice? How is the lattice represented with the unit cell?
38. Make a drawing of each unit cell: simple cubic, body-centered cubic, and face-centered cubic.
39. For each of the cubic cells in the previous problem, give the coordination number, edge length in terms of  $r$ , and number of atoms per unit cell.
40. What is the difference between hexagonal closest packing and cubic closest packing? What are the unit cells for each of these structures?
41. What are the three basic types of solids and the composite units of each? What types of forces hold each type of solid together?
42. In an ionic compound, how are the relative sizes of the cation and anion related to the coordination number of the crystal structure?
43. Show how the cesium chloride, sodium chloride, and zinc blende unit cells each contain a cation-to-anion ratio of 1:1.
44. Show how the fluorite structure accommodates a cation-to-anion ratio of 1:2.
45. What are the three basic subtypes of atomic solids? What kinds of forces hold each of these subtypes together?
46. In band theory of bonding for solids, what is a *band*? What is the difference between the *valence band* and the *conduction band*?
47. In band theory of bonding for solids, what is a band gap? How does the band gap differ in metals, semiconductors, and insulators?
48. Explain how doping can increase the conductivity of a semiconductor. What is the difference between an n-type semiconductor and a p-type semiconductor?

## Problems by Topic

### Intermolecular Forces

49. Determine the kinds of intermolecular forces that are present in each element or compound.
  - a. N<sub>2</sub>
  - b. NH<sub>3</sub>
  - c. CO
  - d. CCl<sub>4</sub>
50. Determine the kinds of intermolecular forces that are present in each element or compound.
  - a. Kr
  - b. NCl<sub>3</sub>
  - c. SiH<sub>4</sub>
  - d. HF
51. Determine the kinds of intermolecular forces that are present in each element or compound.
  - a. HCl
  - b. H<sub>2</sub>O
  - c. Br<sub>2</sub>
  - d. He
52. Determine the kinds of intermolecular forces that are present in each element or compound.
  - a. PH<sub>3</sub>
  - b. HBr
  - c. CH<sub>3</sub>OH
  - d. I<sub>2</sub>
53. Arrange these compounds in order of increasing boiling point. Explain your reasoning.
  - a. CH<sub>4</sub>
  - b. CH<sub>3</sub>CH<sub>3</sub>
  - c. CH<sub>3</sub>CH<sub>2</sub>Cl
  - d. CH<sub>3</sub>CH<sub>2</sub>OH

54. Arrange these compounds in order of increasing boiling point. Explain your reasoning.
  - a. H<sub>2</sub>S
  - b. H<sub>2</sub>Se
  - c. H<sub>2</sub>O
55. In each pair of compounds, pick the one with the highest boiling point. Explain your reasoning.
  - a. CH<sub>3</sub>OH or CH<sub>3</sub>SH
  - b. CH<sub>3</sub>OCH<sub>3</sub> or CH<sub>3</sub>CH<sub>2</sub>OH
  - c. CH<sub>4</sub> or CH<sub>3</sub>CH<sub>3</sub>
56. In each pair of compounds, pick the one with the higher boiling point. Explain your reasoning.
  - a. NH<sub>3</sub> or CH<sub>4</sub>
  - b. CS<sub>2</sub> or CO<sub>2</sub>
  - c. CO<sub>2</sub> or NO<sub>2</sub>
57. In each pair of compounds, pick the one with the higher vapor pressure at a given temperature. Explain your reasoning.
  - a. Br<sub>2</sub> or I<sub>2</sub>
  - b. H<sub>2</sub>S or H<sub>2</sub>O
  - c. NH<sub>3</sub> or PH<sub>3</sub>
58. In each pair of compounds, pick the one with the higher vapor pressure at a given temperature. Explain your reasoning.
  - a. CH<sub>4</sub> or CH<sub>3</sub>Cl
  - b. CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH or CH<sub>3</sub>OH
  - c. CH<sub>3</sub>OH or H<sub>2</sub>CO
59. Determine if each pair of compounds forms a homogeneous solution when combined. For those that form homogeneous solutions, indicate the type of forces that are involved.
  - a. CCl<sub>4</sub> and H<sub>2</sub>O
  - b. KCl and H<sub>2</sub>O
  - c. Br<sub>2</sub> and CCl<sub>4</sub>
  - d. CH<sub>3</sub>CH<sub>2</sub>OH and H<sub>2</sub>O

60. Determine if each pair of compounds forms a homogeneous solution when combined. For those that form homogeneous solutions, indicate the type of forces that are involved.
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
  - $\text{CBr}_4$  and  $\text{H}_2\text{O}$
  - $\text{LiNO}_3$  and  $\text{H}_2\text{O}$
  - $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

### Surface Tension, Viscosity, and Capillary Action

61. Which compound would you expect to have greater surface tension: acetone [ $(\text{CH}_3)_2\text{CO}$ ] or water ( $\text{H}_2\text{O}$ )? Explain.
62. Water (a) “wets” some surfaces and beads up on others. Mercury (b), in contrast, beads up on almost all surfaces. Explain this difference.

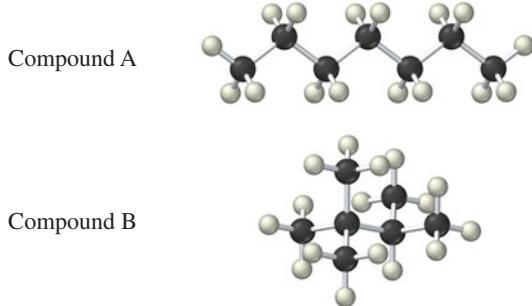


(a)

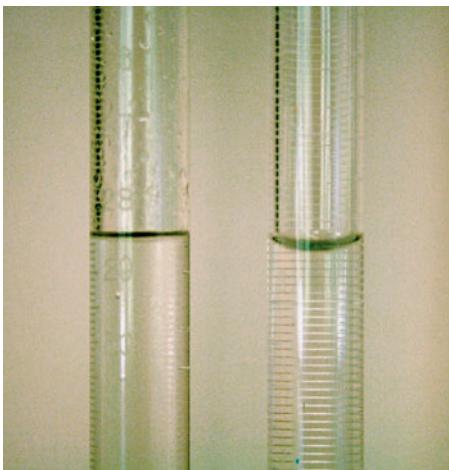


(b)

63. The structures of two isomers of heptane are shown below. Which of these two compounds would you expect to have the greater viscosity?



64. Explain why the viscosity of multigrade motor oils is less temperature-dependent than that of single-grade motor oils.
65. Water in a glass tube that contains grease or oil residue displays a flat meniscus (left), whereas water in a clean glass tube displays a concave meniscus (right). Explain this observation.



66. When a thin glass tube is put into water, the water rises 1.4 cm. When the same tube is put into hexane, the hexane rises only 0.4 cm. Explain.

### Vaporization and Vapor Pressure

67. Which evaporates more quickly: 55 mL of water in a beaker with a diameter of 4.5 cm, or 55 mL of water in a dish with a diameter of 12 cm? Is the vapor pressure of the water different in the two containers? Explain.
68. Which evaporates more quickly: 55 mL of water ( $\text{H}_2\text{O}$ ) in a beaker or 55 mL of acetone [ $(\text{CH}_3)_2\text{CO}$ ] in an identical beaker under identical conditions? Is the vapor pressure of the two substances different? Explain.
69. Spilling room-temperature water over your skin on a hot day cools you down. Spilling room-temperature vegetable oil over your skin on a hot day does not. Explain the difference.
70. Why is the heat of vaporization of water greater at room temperature than it is at its boiling point?
71. The human body obtains 915 kJ of energy from a candy bar. If this energy were used to vaporize water at 100.0 °C, how much water (in liters) could be vaporized? (Assume the density of water is 1.00 g/mL.)
72. A 100.0 mL sample of water is heated to its boiling point. How much heat (in kJ) is required to vaporize it? (Assume a density of 1.00 g/mL.)
73. Suppose that 0.95 g of water condenses on a 75.0 g block of iron that is initially at 22 °C. If the heat released during condensation goes only to warming the iron block, what is the final temperature (in °C) of the iron block? (Assume a constant enthalpy of vaporization for water of 44.0 kJ/mol.)
74. Suppose that 1.15 g of rubbing alcohol ( $\text{C}_3\text{H}_8\text{O}$ ) evaporates from a 65.0 g aluminum block. If the aluminum block is initially at 25 °C, what is the final temperature of the block after the evaporation of the alcohol? Assume that the heat required for the vaporization of the alcohol comes only from the aluminum block and that the alcohol vaporizes at 25 °C.
75. This table displays the vapor pressure of ammonia at several different temperatures. Use the data to determine the heat of vaporization and normal boiling point of ammonia.

Temperature (K)	Pressure (torr)
200	65.3
210	134.3
220	255.7
230	456.0
235	597.0

76. This table displays the vapor pressure of nitrogen at several different temperatures. Use the data to determine the heat of vaporization and normal boiling point of nitrogen.

Temperature (K)	Pressure (torr)
65	130.5
70	289.5
75	570.8
80	1028
85	1718

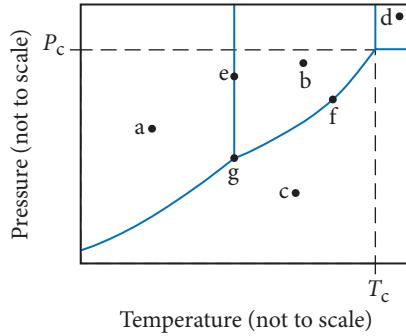
77. Ethanol has a heat of vaporization of 38.56 kJ/mol and a normal boiling point of 78.4 °C. What is the vapor pressure of ethanol at 15 °C?
78. Benzene has a heat of vaporization of 30.72 kJ/mol and a normal boiling point of 80.1 °C. At what temperature does benzene boil when the external pressure is 445 torr?

### Sublimation and Fusion

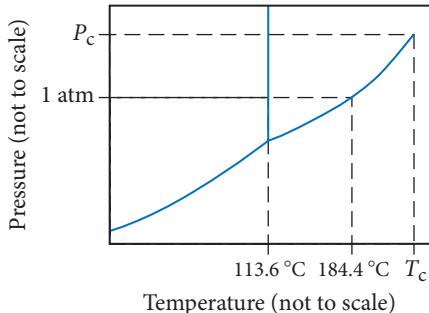
79. How much energy is released when 65.8 g of water freezes?
80. Calculate the amount of heat required to completely sublime 50.0 g of solid dry ice ( $\text{CO}_2$ ) at its sublimation temperature. The heat of sublimation for carbon dioxide is 32.3 kJ/mol.
81. An 8.5 g ice cube is placed into 255 g of water. Calculate the temperature change in the water upon the complete melting of the ice. Assume that all of the energy required to melt the ice comes from the water.
82. How much ice (in grams) would have to melt to lower the temperature of 352 mL of water from 25 °C to 5 °C? (Assume the density of water is 1.0 g/ml.)
83. How much heat (in kJ) is required to warm 10.0 g of ice, initially at  $-10.0\text{ }^\circ\text{C}$ , to steam at  $110.0\text{ }^\circ\text{C}$ ? The heat capacity of ice is  $2.09\text{ J/g}\cdot\text{}^\circ\text{C}$ , and that of steam is  $2.01\text{ J/g}\cdot\text{}^\circ\text{C}$ .
84. How much heat (in kJ) is evolved in converting 1.00 mol of steam at  $145\text{ }^\circ\text{C}$  to ice at  $-50\text{ }^\circ\text{C}$ ? The heat capacity of steam is  $2.01\text{ J/g}\cdot\text{}^\circ\text{C}$ , and that of ice is  $2.09\text{ J/g}\cdot\text{}^\circ\text{C}$ .

### Phase Diagrams

85. Consider the phase diagram shown here. Identify the states present at points *a* through *g*.

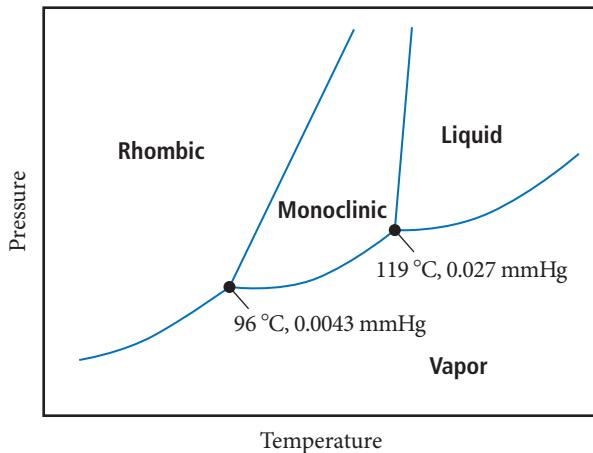


86. Consider the phase diagram for iodine shown here.
- What is the normal boiling point for iodine?
  - What is the melting point for iodine at 1 atm?
  - What state is present at room temperature and normal atmospheric pressure?
  - What state is present at  $186\text{ }^\circ\text{C}$  and 1.0 atm?

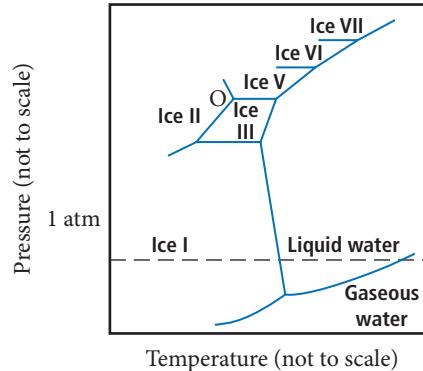


87. Nitrogen has a normal boiling point of  $77.3\text{ K}$  and a melting point (at 1 atm) of  $63.1\text{ K}$ . Its critical temperature is  $126.2\text{ K}$  and critical pressure is  $2.55 \times 10^4\text{ torr}$ . It has a triple point at  $63.1\text{ K}$  and  $94.0\text{ torr}$ . Sketch the phase diagram for nitrogen. Does nitrogen have a stable liquid state at 1 atm?

88. Argon has a normal boiling point of  $87.2\text{ K}$  and a melting point (at 1 atm) of  $84.1\text{ K}$ . Its critical temperature is  $150.8\text{ K}$  and critical pressure is  $48.3\text{ atm}$ . It has a triple point at  $83.7\text{ K}$  and  $0.68\text{ atm}$ . Sketch the phase diagram for argon. Which has the greater density, solid argon or liquid argon?
89. The phase diagram for sulfur is shown here. The rhombic and monoclinic states are two solid states with different structures.
- Below what pressure does solid sulfur sublime?
  - Which of the two solid states of sulfur is most dense?



90. The high-pressure phase diagram of ice is shown here. Notice that, under high pressure, ice can exist in several different solid forms. What three forms of ice are present at the triple point marked O? What is the density of ice II compared to ice I (the familiar form of ice)? Would ice III sink or float in liquid water?



### The Uniqueness of Water

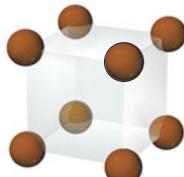
91. Water has a high boiling point given its relatively low molar mass. Why?
92. Water is a good solvent for many substances. What is the molecular basis for this property and why is it significant?
93. Explain the role of water in moderating Earth's climate.
94. How is the density of solid water compared to that of liquid water atypical among substances? Why is this significant?

### Types of Solids and Their Structures

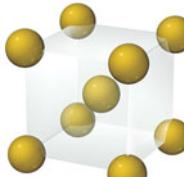
95. An X-ray beam with  $\lambda = 154$  nm incident on the surface of a crystal produced a maximum reflection at an angle of  $\theta = 28.3^\circ$ . Assuming  $n = 1$ , calculate the separation between layers of atoms in the crystal.

96. An X-ray beam of unknown wavelength is diffracted from a NaCl surface. If the interplanar distance in the crystal is 286 pm, and the angle of maximum reflection is found to be  $7.23^\circ$ , what is the wavelength of the X-ray beam? (Assume  $n = 1$ .)

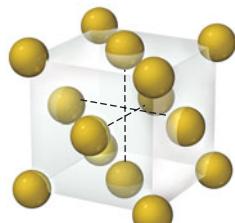
97. Determine the number of atoms per unit cell for each metal.



(a) Polonium

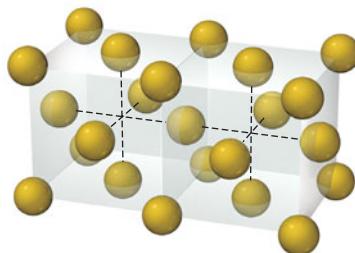


(b) Tungsten

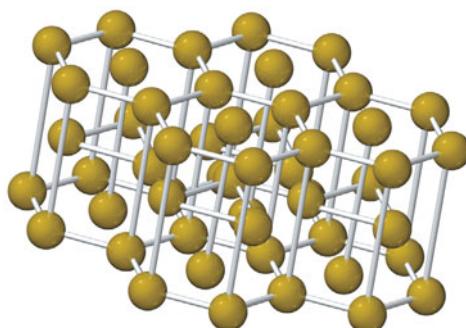


(c) Nickel

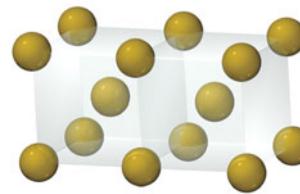
98. Determine the coordination number for each structure.



(a) Gold



(b) Ruthenium



(c) Chromium

99. Platinum crystallizes with the face-centered cubic unit cell. The radius of a platinum atom is 139 pm. Calculate the edge length of the unit cell and the density of platinum in g/cm<sup>3</sup>.

100. Molybdenum crystallizes with the body-centered unit cell. The radius of a molybdenum atom is 136 pm. Calculate the edge length of the unit cell and the density of molybdenum.

101. Rhodium has a density of 12.41 g/cm<sup>3</sup> and crystallizes with the face-centered cubic unit cell. Calculate the radius of a rhodium atom.

102. Barium has a density of 3.59 g/cm<sup>3</sup> and crystallizes with the body-centered cubic unit cell. Calculate the radius of a barium atom.

103. Polonium crystallizes with a simple cubic structure. It has a density of 9.3 g/cm<sup>3</sup>, a radius of 167 pm, and a molar mass of 209 g/mol. Use this data to estimate Avogadro's number (the number of atoms in one mole).

104. Palladium crystallizes with a face-centered cubic structure. It has a density of 12.0 g/cm<sup>3</sup>, a radius of 138 pm, and a molar mass of 106.42 g/mol. Use this data to estimate Avogadro's number.

105. Identify each solid as molecular, ionic, or atomic.

- a. Ar(s)
- b. H<sub>2</sub>O(s)
- c. K<sub>2</sub>O(s)
- d. Fe(s)

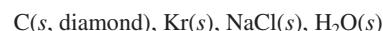
106. Identify each solid as molecular, ionic, or atomic.

- a. CaCl<sub>2</sub>(s)
- b. CO<sub>2</sub>(s)
- c. Ni(s)
- d. I<sub>2</sub>(s)

107. Which solid has the highest melting point? Why?



108. Which solid has the highest melting point? Why?



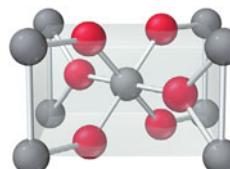
109. Which solid in each pair has the higher melting point and why?

- a. TiO<sub>2</sub>(s) or HOOH(s)
- b. CCl<sub>4</sub>(s) or SiCl<sub>4</sub>(s)
- c. Kr(s) or Xe(s)
- d. NaCl(s) or CaO(s)

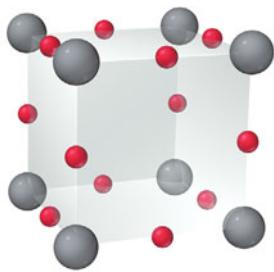
110. Which solid in each pair has the higher melting point and why?

- a. Fe(s) or CCl<sub>4</sub>(s)
- b. KCl(s) or HCl(s)
- c. Ti(s) or Ne(s)
- d. H<sub>2</sub>O(s) or H<sub>2</sub>S(s)

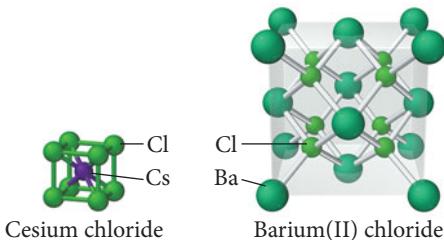
111. An oxide of titanium crystallizes with the unit cell shown here (titanium = gray; oxygen = red). What is the formula of the oxide?



112. An oxide of rhenium crystallizes with the unit cell shown here (rhenium = gray; oxygen = red). What is the formula of the oxide?

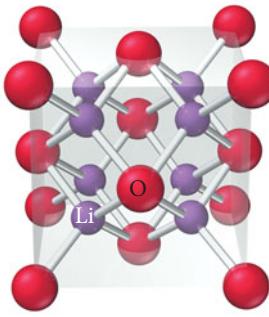


113. The unit cells for cesium chloride and barium(II) chloride are shown here. Show that the ratio of cations to anions in each unit cell corresponds to the ratio of cations to anions in the formula of each compound.

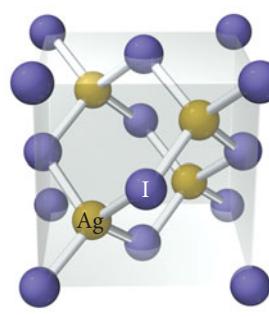


114. The unit cells for lithium oxide and silver iodide are shown here. Show that the ratio of cations to anions in each unit cell

corresponds to the ratio of cations to anions in the formula of each compound.



Lithium oxide



Silver iodide

### Band Theory

115. Which solid would you expect to have little or no band gap?  
 a.  $Zn(s)$       b.  $Si(s)$       c.  $As(s)$
116. How many molecular orbitals are present in the valence band of a sodium crystal with a mass of 5.45 g?
117. Indicate if each solid would form an n-type or a p-type semiconductor.  
 a. germanium doped with gallium  
 b. silicon doped with arsenic
118. Indicate if each solid would form an n-type or a p-type semiconductor.  
 a. silicon doped with gallium  
 b. germanium doped with antimony

## Cumulative Problems

119. Explain the observed trend in the melting points of the hydrogen halides.

HI	-50.8 °C
HBr	-88.5 °C
HCl	-114.8 °C
HF	-83.1 °C

120. Explain the observed trend in the boiling points of these compounds.

$H_2Te$	-2 °C
$H_2Se$	-41.5 °C
$H_2S$	-60.7 °C
$H_2O$	-100 °C

121. The vapor pressure of water at 25 °C is 23.76 torr. If 1.25 g of water is enclosed in a 1.5 L container, will any liquid be present? If so, what mass of liquid?

122. The vapor pressure of  $CCl_3F$  at 300 K is 856 torr. If 11.5 g of  $CCl_3F$  is enclosed in a 1.0 L container, will any liquid be present? If so, what mass of liquid?

123. Examine the phase diagram for iodine shown in Figure 11.39(a). What state transitions occur as we uniformly increase the pressure on a gaseous sample of iodine from 0.010 atm at 185 °C to 100 atm at 185 °C? Make a graph, analogous to the heating curve for water shown in Figure 11.36. Plot pressure versus time during the pressure increase.

124. Carbon tetrachloride displays a triple point at 249.0 K and a melting point (at 1 atm) of 250.3 K. Which state of carbon tetrachloride is more dense, the solid or the liquid? Explain.

125. Four ice cubes at exactly 0 °C with a total mass of 53.5 g are combined with 115 g of water at 75 °C in an insulated container. If no heat is lost to the surroundings, what is the final temperature of the mixture?

126. A sample of steam with a mass of 0.552 g and at a temperature of 100 °C condenses into an insulated container holding 4.25 g of water at 5.0 °C. Assuming that no heat is lost to the surroundings, what is the final temperature of the mixture?

127. Draw a heating curve (such as the one in Figure 11.36) for 1 mole of methanol beginning at 170 K and ending at 350 K. Assume that the values given here are constant over the relevant temperature ranges.

Melting point	176 K
Boiling point	338 K
$\Delta H_{fus}$	2.2 kJ/mol
$\Delta H_{vap}$	35.2 kJ/mol
$C_{s,solid}$	105 J/mol · K
$C_{s,liquid}$	81.3 J/mol · K
$C_{s,gas}$	48 J/mol · K

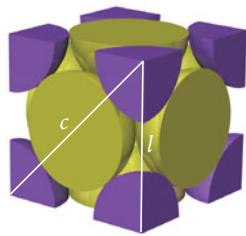
- 128.** Draw a heating curve (such as the one in Figure 11.36) for 1 mole of benzene beginning at 0 °C and ending at 100 °C. Assume that the values given here are constant over the relevant temperature ranges.

Melting point	5.4 °C
Boiling point	90.1 °C
$\Delta H_{\text{fus}}$	9.9 kJ/mol
$\Delta H_{\text{vap}}$	30.7 kJ/mol
$C_{\text{s,solid}}$	118 J/mol · K
$C_{\text{s,liquid}}$	135 J/mol · K
$C_{\text{s,gas}}$	104 J/mol · K

- 129.** Air conditioners not only cool air, but dry it as well. A room in a home measures 6.0 m × 10.0 m × 2.2 m. If the outdoor temperature is 30 °C and the vapor pressure of water in the air is 85% of the vapor pressure of water at this temperature, what mass of water must be removed from the air each time the volume of air in the room is cycled through the air conditioner? The vapor pressure for water at 30 °C is 31.8 torr.
- 130.** A sealed flask contains 0.55 g of water at 28 °C. The vapor pressure of water at this temperature is 28.36 mmHg. What is the minimum volume of the flask in order that no liquid water be present in the flask?

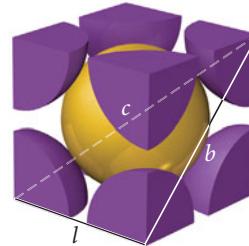
- 131.** Silver iodide crystallizes in the zinc blende structure. The separation between nearest neighbor cations and anions is approximately 325 pm, and the melting point is 558 °C. Cesium chloride, by contrast, crystallizes in the cesium chloride structure shown in Figure 11.51. Even though the separation between nearest neighbor cations and anions is greater (348 pm), the melting point of cesium chloride is higher (645 °C). Explain.
- 132.** Copper iodide crystallizes in the zinc blende structure. The separation between nearest neighbor cations and anions is approximately 311 pm, and the melting point is 606 °C. Potassium chloride, by contrast, crystallizes in the rock salt structure. Even though the separation between nearest neighbor cations and anions is greater (319 pm), the melting point of potassium chloride is higher (776 °C). Explain.

- 133.** Consider the face-centered cubic structure shown here:



- What is the length of the line (labeled *c*) that runs diagonally across one of the faces of the cube in terms of *r* (the atomic radius)?
- Use the answer to part a and the Pythagorean theorem to derive the expression for the edge length (*l*) in terms of *r*.

- 134.** Consider the body-centered cubic structure shown here:



- What is the length of the line (labeled *c*) that runs from one corner of the cube diagonally through the center of the cube to the other corner in terms of *r* (the atomic radius)?
- Use the Pythagorean theorem to derive an expression for the length of the line (labeled *b*) that runs diagonally across one of the faces of the cube in terms of the edge length (*l*).
- Use the answer to parts (a) and (b) along with the Pythagorean theorem to derive the expression for the edge length (*l*) in terms of *r*.

- 135.** The unit cell in a crystal of diamond belongs to a crystal system different from any we discussed in this chapter. The volume of a unit cell of diamond is 0.0454 nm<sup>3</sup> and the density of diamond is 3.52 g/cm<sup>3</sup>. Find the number of carbon atoms in a unit cell of diamond.
- 136.** The density of an unknown metal is 12.3 g/cm<sup>3</sup> and its atomic radius is 0.134 nm. It has a face-centered cubic lattice. Find the atomic mass of this metal.
- 137.** Based on the phase diagram of CO<sub>2</sub> shown in Figure 11.39(b), describe the state changes that occur when the temperature of CO<sub>2</sub> is increased from 190 K to 350 K at a constant pressure of (a) 1 atm, (b) 5.1 atm, (c) 10 atm, (d) 100 atm.
- 138.** Consider a planet where the pressure of the atmosphere at sea level is 2500 mmHg. Does water behave in a way that can sustain life on the planet?
- 139.** An unknown metal is found to have a density of 7.8748 g/cm<sup>3</sup> and to crystallize in a body-centered cubic lattice. The edge of the unit cell is 0.28664 nm. Calculate the atomic mass of the metal.
- 140.** When spheres of radius *r* are packed in a body-centered cubic arrangement, they occupy 68.0% of the available volume. Use the fraction of occupied volume to calculate the value of *a*, the length of the edge of the cube, in terms of *r*.

## Challenge Problems

- 141.** Potassium chloride crystallizes in the rock salt structure. Estimate the density of potassium chloride using the ionic radii provided in Chapter 8.
- 142.** Butane (C<sub>4</sub>H<sub>10</sub>) has a heat of vaporization of 22.44 kJ/mol and a normal boiling point of −0.4 °C. A 250 mL sealed flask contains 0.55 g of butane at −22 °C. How much butane is present as a liquid? If the butane is warmed to 25 °C, how much is present as a liquid?
- 143.** Liquid nitrogen can be used as a cryogenic substance to obtain low temperatures. Under atmospheric pressure, liquid nitrogen boils at 77 K, allowing low temperatures to be reached. However, if the nitrogen is placed in a sealed, insulated container connected to a vacuum pump, even lower temperatures can be reached. Why? If the vacuum pump has sufficient capacity and is left on for an extended period of time, the liquid nitrogen will start to freeze. Explain.
- 144.** Calculate the fraction of empty space in cubic closest packing to five significant figures.

**145.** A tetrahedral site in a closest-packed lattice is formed by four spheres at the corners of a regular tetrahedron. This is equivalent to placing the spheres at alternate corners of a cube. In such a closest-packed arrangement the spheres are in contact, and if the spheres have a radius  $r$ , the diagonal of the face of the cube is  $2r$ . The tetrahedral hole is inside the middle of the cube. Find the length of the body diagonal of this cube and then find the radius of the tetrahedral hole.

**146.** Given that the heat of fusion of water is  $-6.02 \text{ kJ/mol}$ , the heat capacity of  $\text{H}_2\text{O}(l)$  is  $75.2 \text{ J/mol} \cdot \text{K}$ , and the heat capacity of  $\text{H}_2\text{O}(s)$  is  $37.7 \text{ J/mol} \cdot \text{K}$ , calculate the heat of fusion of water at  $-10^\circ\text{C}$ .

**147.** The heat of combustion of  $\text{CH}_4$  is  $890.4 \text{ kJ/mol}$  and the heat capacity of  $\text{H}_2\text{O}$  is  $75.2 \text{ J/mol} \cdot \text{K}$ . Find the volume of methane measured at  $298 \text{ K}$  and  $1.00 \text{ atm}$  required to convert  $1.00 \text{ L}$  of water at  $298 \text{ K}$  to water vapor at  $373 \text{ K}$ .

**148.** Two liquids, A and B, have vapor pressures at a given temperature of  $24 \text{ mmHg}$  and  $36 \text{ mmHg}$ , respectively. We prepare solutions

of A and B at a given temperature and measure the total pressures above the solutions. We obtain this data:

Solution	Amt A (mol)	Amt B (mol)	P (mmHg)
1	1	1	30
2	2	1	28
3	1	2	32
4	1	3	33

Predict the total pressure above a solution of 5 mol A and 1 mol B.

**149.** Three 1.0 L flasks, maintained at  $308 \text{ K}$ , are connected to each other with stopcocks. Initially the stopcocks are closed. One of the flasks contains  $1.0 \text{ atm}$  of  $\text{N}_2$ ; the second,  $2.0 \text{ g}$  of  $\text{H}_2\text{O}$ ; and the third,  $0.50 \text{ g}$  of ethanol,  $\text{C}_2\text{H}_5\text{O}$ . The vapor pressure of  $\text{H}_2\text{O}$  at  $308 \text{ K}$  is  $42 \text{ mmHg}$  and that of ethanol is  $102 \text{ mmHg}$ . The stopcocks are then opened and the contents mix freely. What is the pressure?

## Conceptual Problems

**150.** One prediction of global warming is the melting of global ice, which may result in coastal flooding. A criticism of this prediction is that the melting of icebergs does not increase ocean levels any more than the melting of ice in a glass of water increases the level of liquid in the glass. Is this a valid criticism? Does the melting of an ice cube in a cup of water raise the level of the liquid in the cup? Why or why not? In response to this criticism, scientists have asserted that they are not worried about melting icebergs, but rather the melting of ice sheets that sit on the continent of Antarctica. Would the melting of this ice increase ocean levels? Why or why not?

**151.** The rate of vaporization depends on the surface area of the liquid. However, the vapor pressure of a liquid does not depend on the surface area. Explain.

**152.** Substance A has a smaller heat of vaporization than substance B. Which of the two substances will undergo a larger change in vapor pressure for a given change in temperature?

**153.** The density of a substance is greater in its solid state than in its liquid state. If the triple point in the phase diagram of the substance is below  $1.0 \text{ atm}$ , which will necessarily be at a lower temperature, the triple point or the normal melting point?

**154.** A substance has a heat of vaporization of  $\Delta H_{\text{vap}}$  and heat of fusion of  $\Delta H_{\text{fus}}$ . Express the heat of sublimation in terms of  $\Delta H_{\text{vap}}$  and  $\Delta H_{\text{fus}}$ .

**155.** Examine the heating curve for water in Section 11.7 (Figure 11.36). If heat is added to the water at a constant rate, which of the three segments in which temperature is rising will have the least steep slope? Why?

**156.** A root cellar is an underground chamber used to store fruits, vegetables, and even meats. In extreme cold, farmers put large vats of water into the root cellar to prevent the fruits and vegetables from freezing. Explain why this works.

**157.** Suggest an explanation for the observation that the heat of fusion of a substance is always smaller than its heat of vaporization.

**158.** Refer to Figure 11.36 to answer each question.

a. A sample of steam begins on the line segment labeled 5 on the graph. Is heat absorbed or released in moving from the line segment labeled 5 to the line segment labeled 3? What is the sign of  $q$  for this change?

b. In moving from left to right along the line segment labeled 2 on the graph, heat is absorbed, but the temperature remains constant. Where does the heat go?

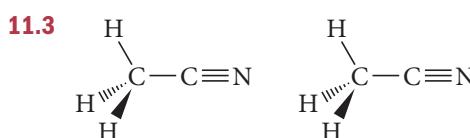
c. How would the graph change if it were for another substance (other than water)?

**159.** The following image is an electrostatic potential map for ethylene oxide,  $(\text{CH}_2)_2\text{O}$ , a polar molecule. Use the electrostatic potential map to predict the geometry for how one ethylene oxide molecule interacts with another. Draw structural formulas, using the 3D bond notation introduced in Section 10.4, to show the geometry of the interaction.



we expect  $\text{I}_2$  to have the greatest dispersion forces and therefore the highest boiling point (and in fact it does).

## Dispersion Forces



### Inter Molecular Forces and Boiling Point

**11.4** (a) CH<sub>3</sub>OH. The compounds all have similar molar masses, so the dispersion forces are similar in all three. CO is polar, but because CH<sub>3</sub>OH contains H directly bonded to O, it has hydrogen bonding, resulting in the highest boiling point.

### Vapor Pressure

**11.5** (b) Although the *rate of vaporization* increases with increasing surface area, the *vapor pressure* of a liquid is independent of surface area. An increase in surface area increases both the rate of vaporization and the rate of condensation—the effects exactly cancel and the vapor pressure does not change.

### Cooling of Water with Ice

**11.6** The warming of the ice from  $-10\text{ }^{\circ}\text{C}$  to  $0\text{ }^{\circ}\text{C}$  absorbs only  $20.9\text{ J/g}$  of ice. The melting of the ice, however, absorbs about  $334\text{ J/g}$  of ice. (You can obtain this value by dividing the heat of fusion of water by its molar mass.) Therefore, the melting of the ice produces a larger temperature decrease in the water than does the warming of the ice.

### Phase Diagrams

**11.7** (b) The solid will sublime into a gas. Since the pressure is below the triple point, the liquid state is not stable.

# 12

## Solutions

*One molecule of nonsaline substance (held in the solvent) dissolved in 100 molecules of any volatile liquid decreases the vapor pressure of this liquid by a nearly constant fraction, nearly 0.0105.*

—François-Marie Raoult (1830–1901)

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**12.6** Colligative Properties: Vapor Pressure Lowering, Freezing Point Depression, Boiling Point Elevation, and Osmotic Pressure 567

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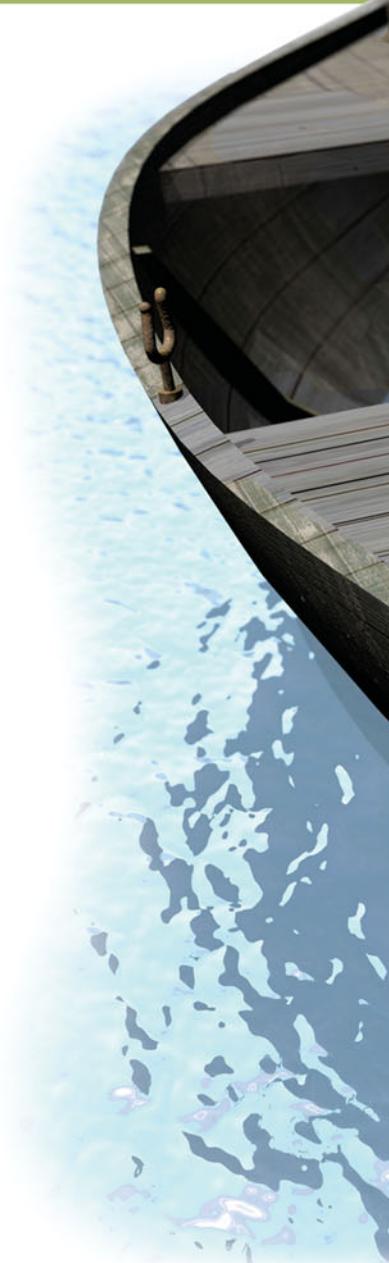
**12.8** Colloids 582

Key Learning Outcomes 587

**W**E LEARNED IN Chapter 1 that most of the matter we encounter is in the form of mixtures. In this chapter, we focus on homogeneous mixtures, known as solutions. Solutions are mixtures in which atoms and molecules intermingle on the molecular and atomic scale. Common examples of solutions include ocean water, gasoline, and air. Why do solutions form? How are their properties different from the properties of the pure substances that compose them? As you read this chapter, keep in mind the large number of solutions that surround you at every moment, including those that exist within your own body.

### 12.1 Thirsty Solutions: Why You Shouldn't Drink Seawater

In the popular novel *Life of Pi* by Yann Martel, the main character (whose name is Pi) is stranded on a lifeboat with a Bengal tiger in the middle of the Pacific Ocean for 227 days. He survives in part by rigging a solar still to distill seawater for drinking. However, in the first three days of his





predicament (before he rigs the still) he becomes severely dehydrated from lack of water. He is surrounded by seawater, but drinking *that* water would only have made his condition worse. Why? Seawater actually draws water *out of the body* as it passes through the stomach and intestines, resulting in diarrhea and further dehydration. We can think of seawater as a *thirsty solution*—one that draws more water to itself. Consequently, seawater should never be consumed as drinking water.

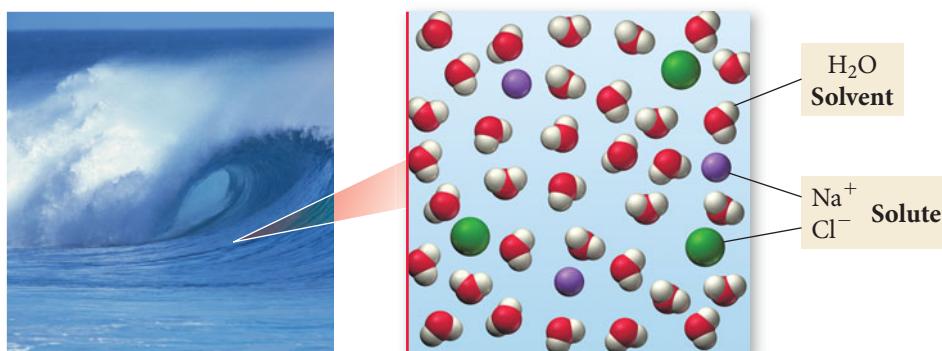
Seawater is a **solution**, a homogeneous mixture of two or more substances or components as shown in Figure 12.1 ►. The majority component is typically called the **solvent** and the minority component is called the **solute**. In seawater, water is the solvent and sodium chloride is the primary solute. Solutions form in part because of the intermolecular forces we discussed in Chapter 11. In most solutions, the particles of the solute interact with the particles of the solvent through intermolecular forces.

The reason that seawater draws water to itself is related to nature's tendency toward spontaneous mixing, which we discuss in more detail later in this chapter and in Chapter 17. For now, we simply observe that, unless it is highly unfavorable energetically,

*Drinking seawater causes dehydration because seawater draws water out of body tissues.*

In some cases, the concepts of solute and solvent are not useful. For example, a homogeneous mixture of water and ethanol can contain equal amounts of both components and neither component can then be identified as the solvent.

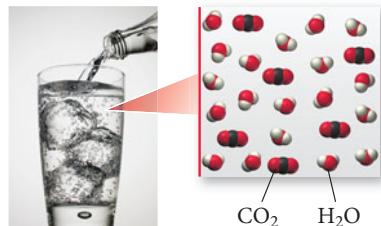
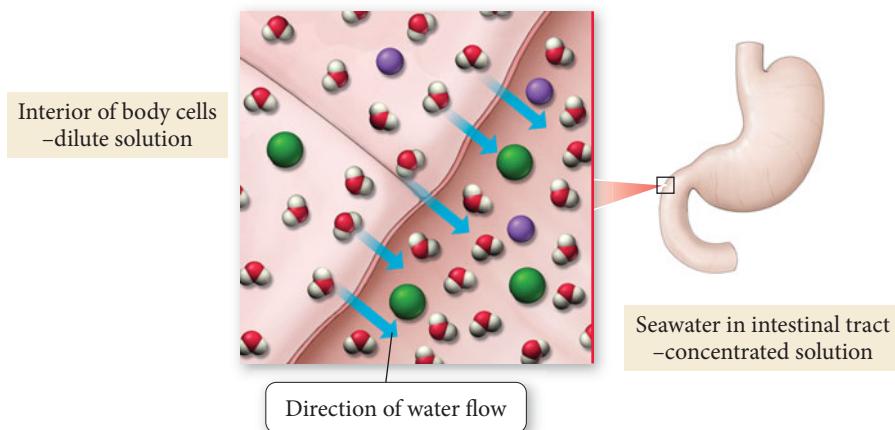
► **FIGURE 12.1 A Typical Solution** In seawater, sodium chloride is the primary solute. Water is the solvent.



substances tend to combine into uniform mixtures, not separate into pure substances. For example, suppose pure water and a sodium chloride solution are in separate compartments with a removable barrier between them, as shown in Figure 12.2(a) ►. If we remove the barrier, the two liquids spontaneously mix, eventually forming a more dilute sodium chloride solution of uniform concentration, as shown in Figure 12.2(b). The tendency toward mixing results in a uniform concentration of the final solution.

Seawater is a *thirsty* solution because of this tendency toward mixing. As seawater moves through the intestine, it flows past cells that line the digestive tract. These cells consist of largely fluid interiors surrounded by membranes. Cellular fluids themselves contain dissolved ions, including sodium and chloride, but the fluids in the cells are more dilute than seawater. Nature's tendency toward mixing (which tends to produce solutions of uniform concentration), together with the selective permeability of the cell membranes (which allows water to flow in and out, but restricts the flow of dissolved solids), cause *a flow of solvent out of the body's cells into the seawater*. In this way, the two solutions become more similar in concentration (as though they had mixed)—the solution in the intestine becomes somewhat more dilute than it was and the solution in the cells becomes somewhat more concentrated. The accumulation of extra fluid in the intestines causes diarrhea, and the decreased fluid in the cells causes dehydration. If Pi had drunk the seawater instead of constructing the solar still, neither he nor his companion, the large Bengal tiger, would have survived his ordeal.

► Seawater is a more concentrated solution than the fluids in body cells. As a result, when seawater flows through the digestive tract, it draws water out of the surrounding tissues.



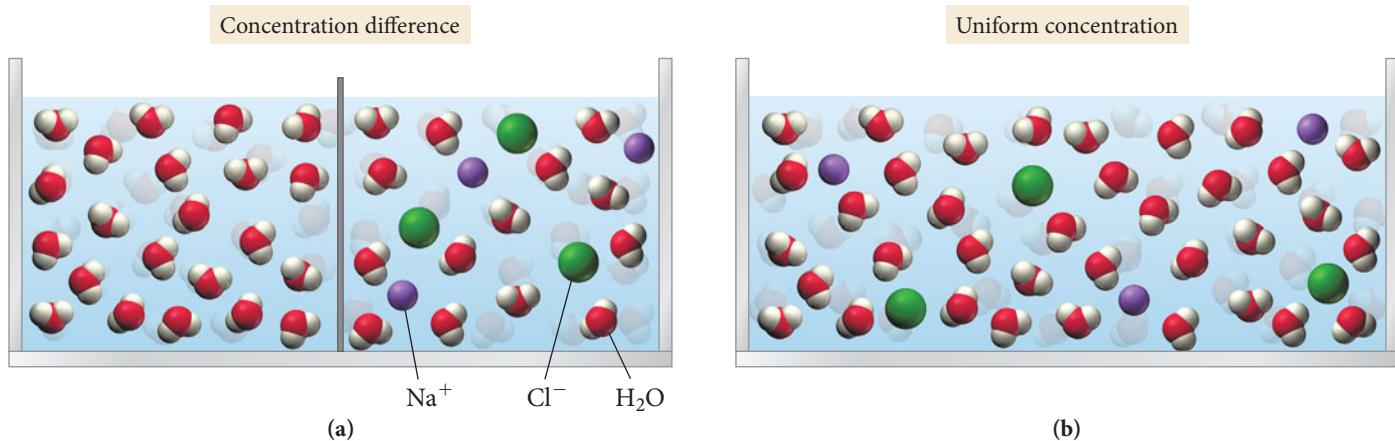
▲ Club soda is a solution of carbon dioxide and water.

## 12.2 Types of Solutions and Solubility

A solution may be composed of a solid and a liquid (such as the salt and water that are the primary components of seawater), but it may also be composed of a gas and a liquid, two different liquids, or other combinations (see Table 12.1). In **aqueous solutions**, water is the solvent, and a solid, liquid, or gas is the solute. For example, sugar water and salt water are both aqueous solutions. Similarly, ethyl alcohol—the alcohol in alcoholic beverages—readily mixes with water to form a solution, and carbon dioxide dissolves in water to form the aqueous solution that we know as club soda.

## Spontaneous Mixing

When the barrier is removed, spontaneous mixing occurs, producing a solution of uniform concentration.



**▲ FIGURE 12.2** The Tendency to Mix (a) Pure water and a sodium chloride solution are separated by a barrier. (b) When the barrier is removed, the two liquids spontaneously mix, producing a single solution of uniform concentration.

**TABLE 12.1 Common Types of Solutions**

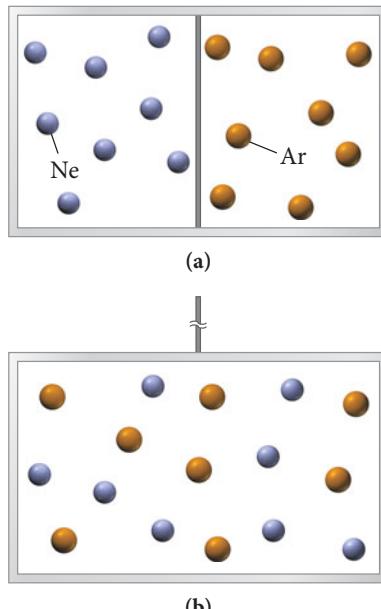
Solution Phase	Solute Phase	Solvent Phase	Example
Gaseous solution	Gas	Gas	Air (mainly oxygen and nitrogen)
Liquid solution	Gas	Liquid	Club soda (CO <sub>2</sub> and water)
	Liquid	Liquid	Vodka (ethanol and water)
	Solid	Liquid	Seawater (salt and water)
Solid solution	Solid	Solid	Brass (copper and zinc) and other alloys

The general solubilities of a number of ionic compounds are described by the solubility rules in Section 4.5.

You probably know from experience that a particular solvent, such as water, does not dissolve all possible solutes. For example, you cannot clean your greasy hands with just water because the water does not dissolve the grease. However, another solvent, such as paint thinner, can easily dissolve the grease. The grease is *insoluble* in water but *soluble* in the paint thinner. The **solubility** of a substance is the amount of the substance that will dissolve in a given amount of solvent. The solubility of sodium chloride in water at 25 °C is 36 g NaCl per 100 g water, while the solubility of grease in water is nearly zero. The solubility of one substance in another depends both on the tendency toward mixing that we discussed in Section 12.1 and on the types of intermolecular forces that we discussed in Chapter 11.

### Nature's Tendency toward Mixing: Entropy

So far in this book, we have seen that many physical systems tend toward lower *potential energy*. For example, two particles with opposite charges (such as a proton and an electron or a cation and an anion) move toward each other because their potential energy decreases as their separation decreases according to Coulomb's law. The formation of a solution, however, *does not necessarily* lower the potential energy of its constituent particles. The clearest example of this phenomenon is the formation of a homogeneous mixture (a *solution*) of two ideal gases. Suppose that we enclose neon and argon in a container with a removable barrier between them, as shown in Figure 12.3(a) ►. As soon as we remove the barrier, the neon and argon mix together to form a solution, as shown in Figure 12.3(b). *Why?*



**▲ FIGURE 12.3** Spontaneous Mixing of Two Ideal Gases (a) Neon and argon are separated by a barrier. (b) When the barrier is removed, the two gases spontaneously mix to form a uniform solution.

At low pressures and moderate temperatures both neon and argon behave as ideal gases—they do not interact with each other in any way (that is, there are no significant intermolecular forces between their constituent particles). When the barrier is removed, the two gases mix, but their potential energy remains unchanged. In other words, we cannot think of the mixing of two ideal gases as lowering their potential energy. Rather, the tendency to mix is related to a concept called *entropy*.

**Entropy** is a measure of *energy randomization* or *energy dispersal* in a system. Recall that a gas at any temperature above 0 K has kinetic energy due to the motion of its atoms. When neon and argon are confined to their individual compartments, their kinetic energies are also confined to those compartments. When the barrier between the compartments is removed, each gas—along with its kinetic energy—becomes *spread out* or *dispersed* over a larger volume. Thus, the mixture of the two gases has greater energy dispersal, or greater *entropy*, than the separated components.

*The pervasive tendency for energy to spread out, or disperse, whenever it is not restrained from doing so* is the reason that two ideal gases mix. Another common example of the tendency toward energy dispersal is the transfer of thermal energy from hot to cold. If we heat one end of an iron rod, the thermal energy deposited at the end of the rod will spontaneously spread along the entire length of the rod. In contrast to the mixing of two ideal gases—where the kinetic energy of the particles becomes dispersed over a larger volume because the particles themselves become dispersed—the thermal energy in the rod, initially concentrated in relatively fewer particles, becomes dispersed by being distributed over a larger number of particles. The tendency for energy to disperse is why thermal energy flows from the hot end of the rod to the cold one, and not the other way around. Imagine a metal rod that became spontaneously hotter on one end and ice cold on the other—this does not happen because energy does not spontaneously concentrate itself. In Chapter 17, we will see that the dispersal of energy is actually the fundamental criterion that ultimately determines the spontaneity of any process.

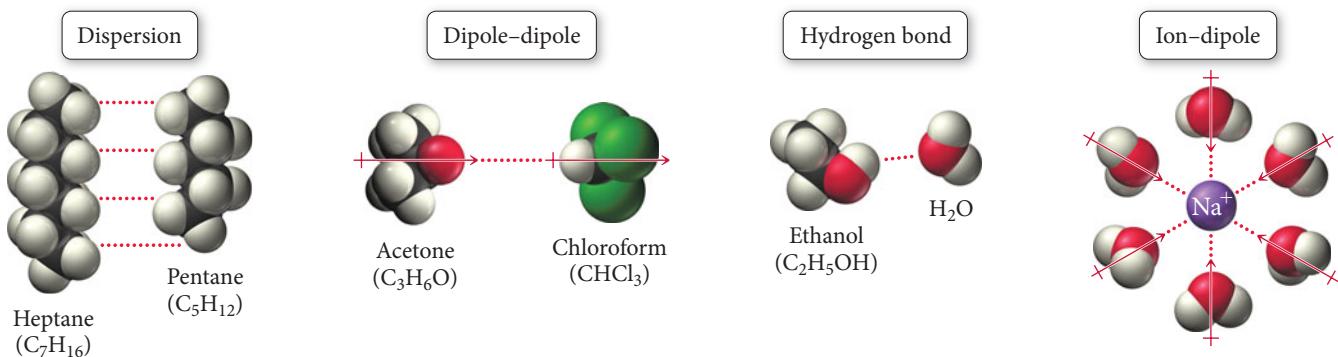
## The Effect of Intermolecular Forces

We have just seen that, in the absence of intermolecular forces, two substances spontaneously mix to form a homogeneous solution. We know from Chapter 11, however, that solids and liquids exhibit a number of different types of intermolecular forces including dispersion forces, dipole–dipole forces, hydrogen bonding, and ion–dipole forces (Figure 12.4) ▶. These forces may promote the formation of a solution or prevent it, depending on the nature of the forces in the particular combination of solute and solvent.

▼ FIGURE 12.4 Intermolecular Forces Involved in Solutions

### Intermolecular Forces

These forces may contribute to or oppose the formation of a solution.



**TABLE 12.2 Relative Interactions and Solution Formation**

Solvent-solute interactions	>	Solvent-solvent and solute-solute interactions	Solution forms
Solvent-solute interactions	=	Solvent-solvent and solute-solute interactions	Solution forms
Solvent-solute interactions	<	Solvent-solvent and solute-solute interactions	Solution may or may not form, depending on relative disparity

Intermolecular forces exist between (a) the solvent and solute particles, (b) the solvent particles themselves, and (c) the solute particles themselves, as shown in Figure 12.5 ▶.

*Solvent–solute interactions:* The interactions between a solvent particle and a solute particle.

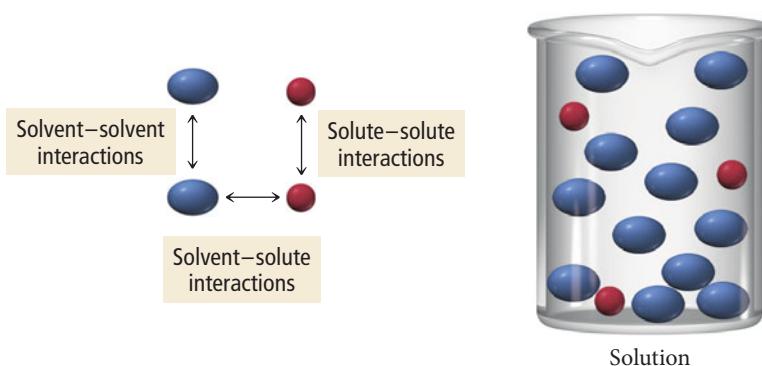
*Solvent–solvent interactions:* The interactions between a solvent particle and another solvent particle.

*Solute–solute interactions:* The interactions between a solute particle and another solute particle.

As shown in Table 12.2, a solution always forms if the solvent–solute interactions are comparable to, or stronger than, the solvent–solvent interactions and the solute–solute interactions. For example, consider mixing the hydrocarbons pentane ( $C_5H_{12}$ ) and heptane ( $C_7H_{16}$ ). The intermolecular forces present within both pentane and heptane are dispersion forces. Similarly, the intermolecular forces present *between* heptane and pentane are also dispersion forces. All three interactions are of similar magnitude so the two substances are soluble in each other in all proportions—they are said to be **miscible**. The formation of the solution is driven by the tendency toward mixing, or toward greater entropy, that we just discussed.

If solvent–solute interactions are weaker than solvent–solvent and solute–solute interactions—in other words, if solvent molecules and solute molecules each interact more strongly with molecules of their own kind than with molecules of the other kind—then a solution may still form, depending on the relative disparities between the interactions. If the disparity is small, the tendency to mix results in the formation of a solution even though the process is energetically uphill. If the disparity is large, however, a solution does not form. For example, consider mixing hexane and water. The water molecules have strong hydrogen-bonding attractions to each other but cannot form hydrogen bonds with hexane. The energy required to pull water molecules away from one another is too

### Solution Interactions



▲ **FIGURE 12.5 Forces in a Solution** The relative strengths of these three interactions determine whether a solution will form.

**TABLE 12.3 Common Laboratory Solvents**

Common Polar Solvents	Common Nonpolar Solvents
Water ( $\text{H}_2\text{O}$ )	Hexane ( $\text{C}_6\text{H}_{14}$ )
Acetone ( $\text{CH}_3\text{COCH}_3$ )	Diethyl ether ( $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ ) <sup>*</sup>
Methanol ( $\text{CH}_3\text{OH}$ )	Toluene ( $\text{C}_7\text{H}_8$ )
Ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ )	Carbon tetrachloride ( $\text{CCl}_4$ )

\*Diethyl ether has a small dipole moment and can be considered intermediate between polar and nonpolar.

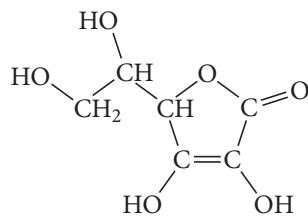
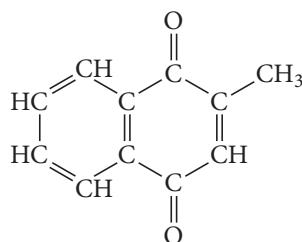
great, and too little energy is returned when the water molecules interact with hexane molecules. As a result, a solution does not form when hexane and water are mixed. Although the tendency to mix is strong, it cannot overcome the large energy disparity between the powerful solvent–solvent interactions and the weak solvent–solute interactions.

In general, we can use the rule of thumb that *like dissolves like* when predicting the formation of solutions. Polar solvents, such as water, tend to dissolve many polar or ionic solutes, and nonpolar solvents, such as hexane, tend to dissolve many nonpolar solutes. Similar kinds of solvents dissolve similar kinds of solutes. Table 12.3 lists some common polar and nonpolar laboratory solvents.

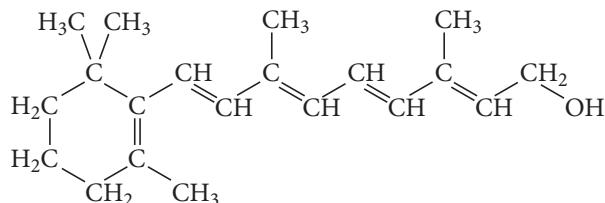
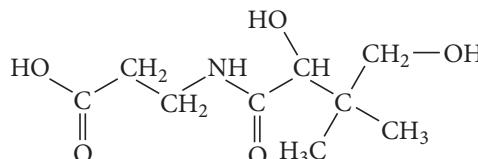
### EXAMPLE 12.1 Solubility

Vitamins are often categorized as either fat soluble or water soluble. Water-soluble vitamins dissolve in body fluids and are easily eliminated in the urine, so there is little danger of overconsumption. Fat-soluble vitamins, on the other hand, can accumulate in the body's fatty deposits. Overconsumption of a fat-soluble vitamin can be dangerous to your health. Examine the structure of each vitamin shown here and classify it as either fat soluble or water soluble.

(a) Vitamin C

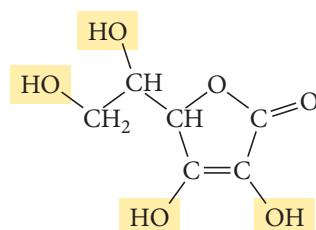
(b) Vitamin K<sub>3</sub>

(c) Vitamin A

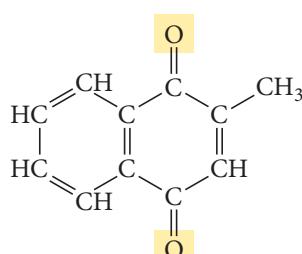
(d) Vitamin B<sub>5</sub>

### SOLUTION

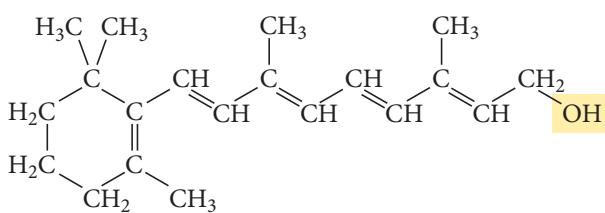
(a) The four —OH bonds in vitamin C make it highly polar and allow it to hydrogen bond with water. Vitamin C is water soluble.



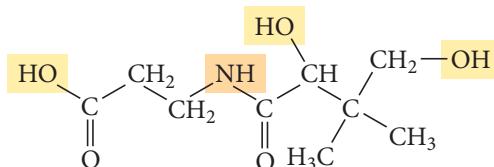
(b) The C—C bonds in vitamin K<sub>3</sub> are nonpolar and the C—H bonds are nearly so. The C=O bonds are polar, but the bond dipoles oppose and largely cancel each other, so the molecule is dominated by the nonpolar bonds. Vitamin K<sub>3</sub> is fat soluble.



(c) The C—C bonds in vitamin A are nonpolar and the C—H bonds are nearly so. The one polar —OH bond may increase its water solubility slightly, but overall vitamin A is nonpolar and therefore fat soluble.



(d) The three —OH bonds and one —NH bond in vitamin B<sub>5</sub> make it highly polar and allow it to hydrogen bond with water. Vitamin B<sub>5</sub> is water soluble.



### FOR PRACTICE 12.1

Determine whether each compound is soluble in hexane.

- |                                |  |
|--------------------------------|--|
| (a) water (H <sub>2</sub> O)   | (b) propane (CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub> ) |
| (c) ammonia (NH <sub>3</sub> ) | (d) hydrogen chloride (HCl)                                    |

### Conceptual Connection 12.1 Solubility

Consider the table listing the solubilities of several alcohols in water and in hexane. Explain the observed trend in terms of intermolecular forces.

Alcohol	Space-Filling Model	Solubility in H <sub>2</sub> O (mol alcohol/100 g H <sub>2</sub> O)	Solubility in Hexane (C <sub>6</sub> H <sub>14</sub> ) (mol alcohol/100 g C <sub>6</sub> H <sub>14</sub> )
Methanol (CH <sub>3</sub> OH)		Miscible	0.12
Ethanol (CH <sub>3</sub> CH <sub>2</sub> OH)		Miscible	Miscible
Propanol (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH)		Miscible	Miscible
Butanol (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH)		0.11	Miscible
Pentanol (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH)		0.030	Miscible

## 12.3 Energetics of Solution Formation

In Chapter 6, we examined the energy changes associated with chemical reactions. Similar energy changes can occur when a solution forms, depending on the magnitude of the interactions between the solute and solvent particles. For example, when we dissolve

sodium hydroxide in water, heat is evolved—the solution process is *exothermic*. In contrast, when we dissolve ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) in water, heat is absorbed—this solution process is *endothermic*. Other solutions, such as sodium chloride in water, barely absorb or evolve heat upon formation. What causes these different behaviors?

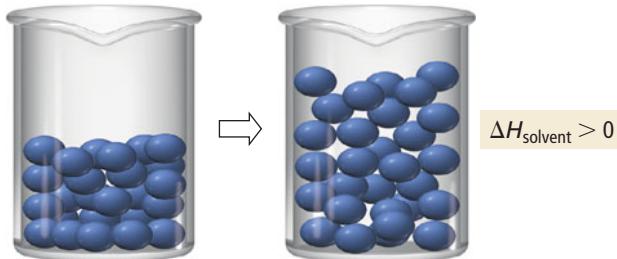
We can understand the energy changes associated with solution formation by envisioning the process as occurring in three steps, each with an associated change in enthalpy:

1. Separating the solute into its constituent particles.



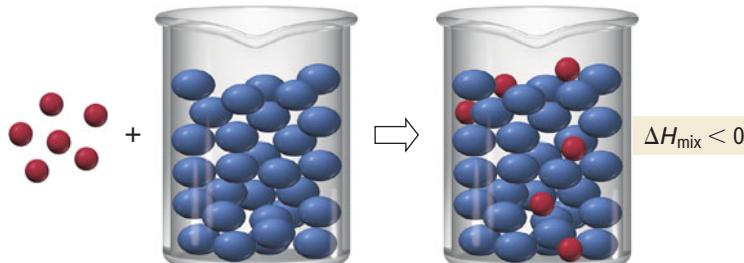
This step is always endothermic (positive  $\Delta H$ ) because energy is required to overcome the forces that hold the solute particles together.

2. Separating the solvent particles from each other to make room for the solute particles.



This step is also endothermic because energy is required to overcome the intermolecular forces among the solvent particles.

3. Mixing the solute particles with the solvent particles.



This step is exothermic because energy is released as the solute particles interact (through intermolecular forces) with the solvent particles.

According to Hess's law, the overall enthalpy change upon solution formation, called the **enthalpy of solution** ( $\Delta H_{\text{soln}}$ ) is the sum of the changes in enthalpy for each step:

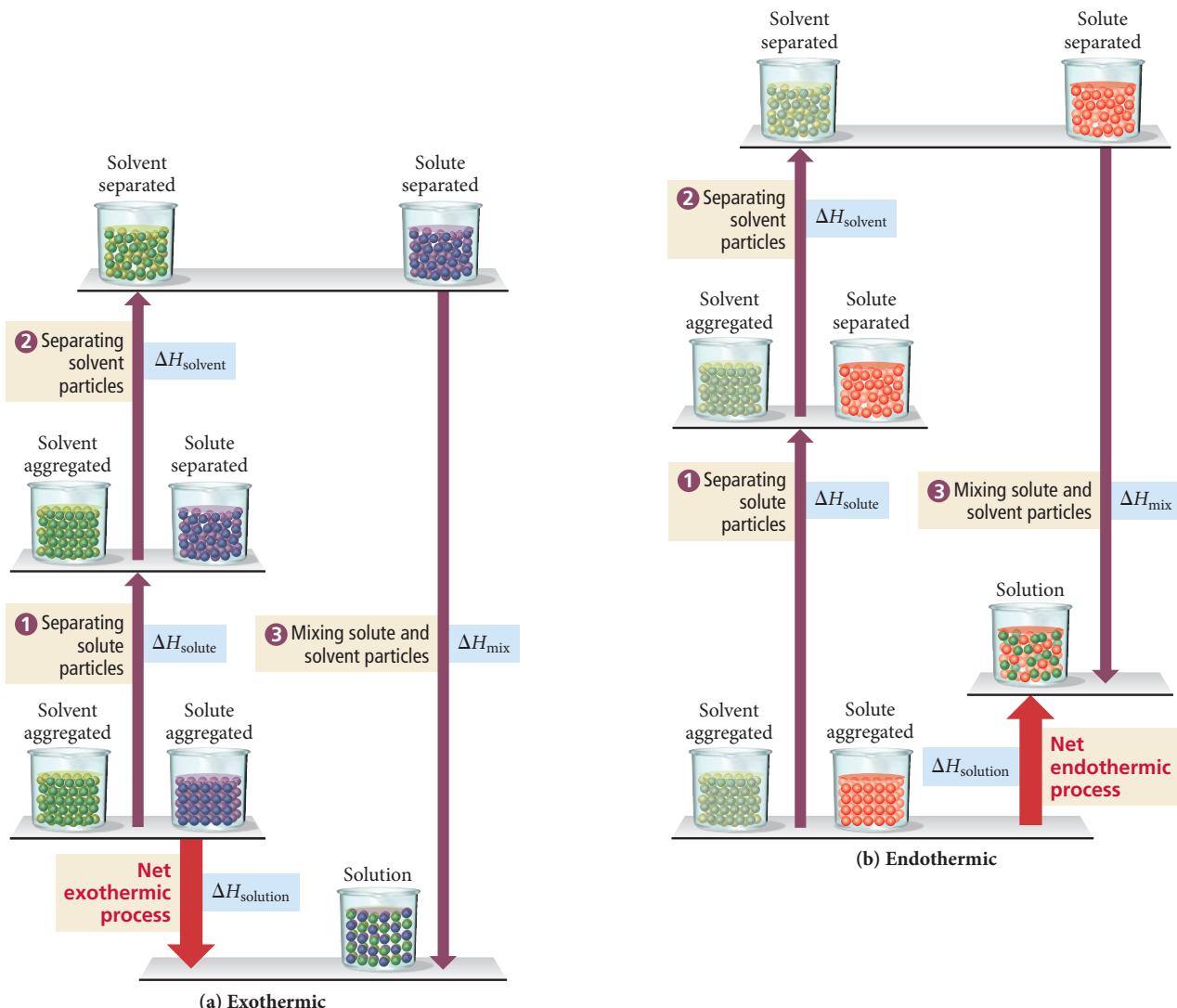
$$\Delta H_{\text{soln}} = \Delta H_{\text{solute}} + \Delta H_{\text{solvent}} + \Delta H_{\text{mix}}$$

endothemic (+)      endothermic (+)      exothermic (-)

Since the first two terms are endothermic (positive  $\Delta H$ ) and the third term is exothermic (negative  $\Delta H$ ), the overall sign of  $\Delta H_{\text{soln}}$  depends on the magnitudes of the individual terms, as shown in Figure 12.6 ►.

1. If the sum of the endothermic terms is approximately equal in magnitude to the exothermic term, then  $\Delta H_{\text{soln}}$  is about zero. The increasing entropy upon mixing drives the formation of a solution while the overall energy of the system remains nearly constant.
2. If the sum of the endothermic terms is smaller in magnitude than the exothermic term, then  $\Delta H_{\text{soln}}$  is negative and the solution process is exothermic. In this case, both the tendency toward lower energy and the tendency toward greater entropy drive the formation of a solution.
3. If the sum of the endothermic terms is greater in magnitude than the exothermic term, then  $\Delta H_{\text{soln}}$  is positive and the solution process is endothermic. In this case, as long as  $\Delta H_{\text{soln}}$  is not too large, the tendency toward greater entropy still drives the formation of a solution. If, on the other hand,  $\Delta H_{\text{soln}}$  is too large, a solution does not form.

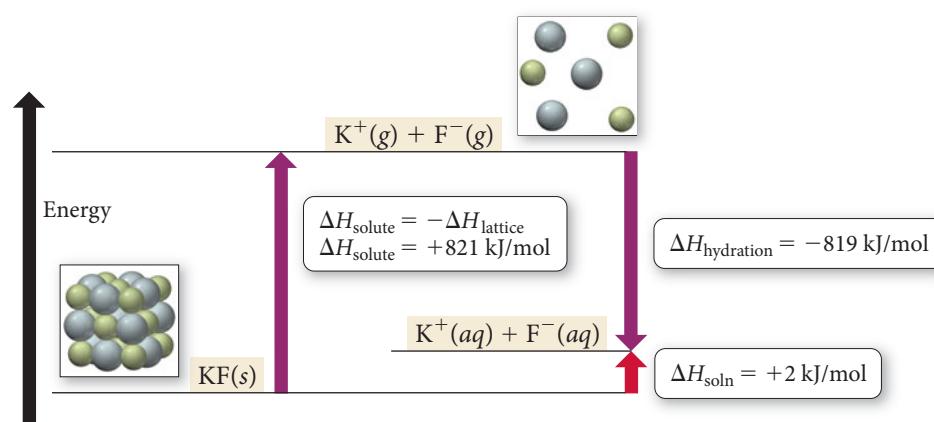
### Energetics of Solution Formation



### Aqueous Solutions and Heats of Hydration

Many common solutions, such as the seawater mentioned in the opening example of this chapter, contain an ionic compound dissolved in water. In these aqueous solutions,  $\Delta H_{\text{solvent}}$  and  $\Delta H_{\text{mix}}$  can be combined into a single term called the **heat of hydration** ( $\Delta H_{\text{hydration}}$ ) (Figure 12.7 ▶). The heat of hydration is the enthalpy change that occurs when 1 mol of the

#### Heat of Hydration



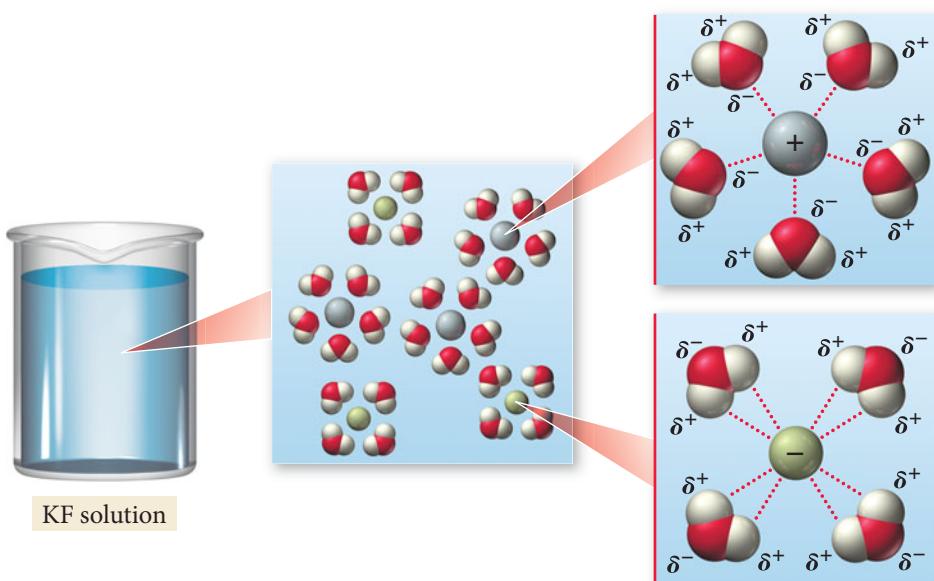
**▲ FIGURE 12.6** Energetics of the Solution Process (a) When  $\Delta H_{\text{mix}}$  is greater in magnitude than the sum of  $\Delta H_{\text{solute}}$  and  $\Delta H_{\text{solvent}}$ , the heat of solution is negative (exothermic). (b) When  $\Delta H_{\text{mix}}$  is smaller in magnitude than the sum of  $\Delta H_{\text{solute}}$  and  $\Delta H_{\text{solvent}}$ , the heat of solution is positive (endothermic).

**◀ FIGURE 12.7** Heat of Hydration and Heat of Solution The heat of hydration is the heat emitted when 1 mol of gaseous solute ions is dissolved in water. The sum of the negative of the lattice energy (which is  $\Delta H_{\text{solute}}$ ) and the heat of hydration is the heat of solution.

**► FIGURE 12.8** Ion-Dipole Interactions

**Interactions** Ion-dipole interactions such as those between potassium ions, fluoride ions, and water molecules cause the heat of hydration to be largely negative (exothermic).

### Ion-Dipole Interactions

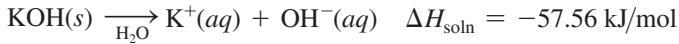
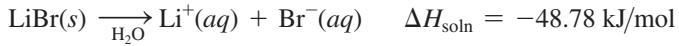


gaseous solute ions is dissolved in water. Because the ion–dipole interactions that occur between a dissolved ion and the surrounding water molecules (Figure 12.8 ▲) are much stronger than the hydrogen bonds in water,  $\Delta H_{\text{hydration}}$  is always largely negative (exothermic) for ionic compounds. Using the heat of hydration, we can write the enthalpy of solution as a sum of just two terms, one endothermic and one exothermic:

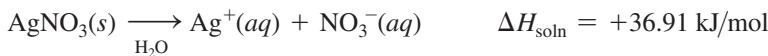
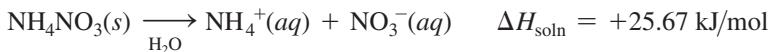
$$\begin{aligned}\Delta H_{\text{soln}} &= \Delta H_{\text{solute}} + \underbrace{\Delta H_{\text{solvent}} + \Delta H_{\text{mix}}}_{\substack{\text{endothermic} \\ (\text{positive})}} \\ \Delta H_{\text{soln}} &= \Delta H_{\text{solute}} + \underbrace{\Delta H_{\text{hydration}}}_{\substack{\text{exothermic} \\ (\text{negative})}}\end{aligned}$$

For ionic compounds,  $\Delta H_{\text{solute}}$ , the energy required to separate the solute into its constituent particles, is the negative of the solute's lattice energy ( $\Delta H_{\text{solute}} = -\Delta H_{\text{lattice}}$ ), discussed in Section 9.4. For ionic aqueous solutions, then, the overall enthalpy of solution depends on the relative magnitudes of  $\Delta H_{\text{solute}}$  and  $\Delta H_{\text{hydration}}$ , with three possible scenarios (in each case we refer to the *magnitude* (*absolute value*) of  $\Delta H$ ):

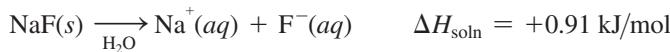
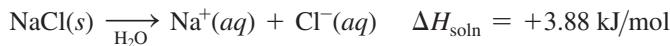
1.  $|\Delta H_{\text{solute}}| < |\Delta H_{\text{hydration}}|$ . The amount of energy required to separate the solute into its constituent ions is less than the energy given off when the ions are hydrated.  $\Delta H_{\text{soln}}$  is therefore negative, and the solution process is exothermic. Solutes with negative enthalpies of solution include lithium bromide and potassium hydroxide. When these solutes dissolve in water, the resulting solutions feel warm to the touch.



2.  $|\Delta H_{\text{solute}}| > |\Delta H_{\text{hydration}}|$ . The amount of energy required to separate the solute into its constituent ions is greater than the energy given off when the ions are hydrated.  $\Delta H_{\text{soln}}$  is therefore positive, and the solution process is endothermic (if a solution forms at all). Solutes that form aqueous solutions with positive enthalpies of solution include ammonium nitrate and silver nitrate. When these solutes dissolve in water, the resulting solutions feel cool to the touch.



3.  $|\Delta H_{\text{solute}}| \approx |\Delta H_{\text{hydration}}|$ . The amount of energy required to separate the solute into its constituent ions is roughly equal to the energy given off when the ions are hydrated.  $\Delta H_{\text{soln}}$  is therefore approximately zero, and the solution process is neither appreciably exothermic nor appreciably endothermic. Solutes with enthalpies of solution near zero include sodium chloride and sodium fluoride. When these solutes dissolve in water, the resulting solutions do not undergo a noticeable change in temperature.



### Conceptual Connection 12.2 Energetics of Aqueous Solution Formation

The enthalpy of solution for cesium fluoride is  $-36.8 \text{ kJ/mol}$ . What can you conclude about the relative magnitudes of  $\Delta H_{\text{solute}}$  and  $\Delta H_{\text{hydration}}$ ?

## 12.4 Solution Equilibrium and Factors Affecting Solubility

The dissolution of a solute in a solvent is an equilibrium process similar to the equilibrium process associated with a phase change (discussed in Chapter 11). Imagine, from a molecular viewpoint, the dissolution of a solid solute such as sodium chloride in a liquid solvent such as water (Figure 12.9 ▶). Initially, water molecules rapidly solvate sodium cations and chloride anions, resulting in a noticeable decrease in the amount of solid sodium chloride in the water. Over time, however, the concentration of dissolved

▼ FIGURE 12.9 Dissolution of NaCl

- (a) When sodium chloride is first added to water, sodium and chloride ions dissolve into the water.
- (b) As the solution becomes more concentrated, some of the sodium and chloride ions can begin to recrystallize as solid sodium chloride.
- (c) When the rate of dissolution equals the rate of recrystallization, dynamic equilibrium is reached.

### Solution Equilibrium



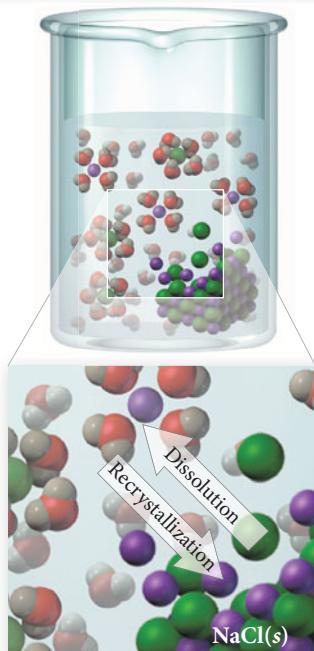
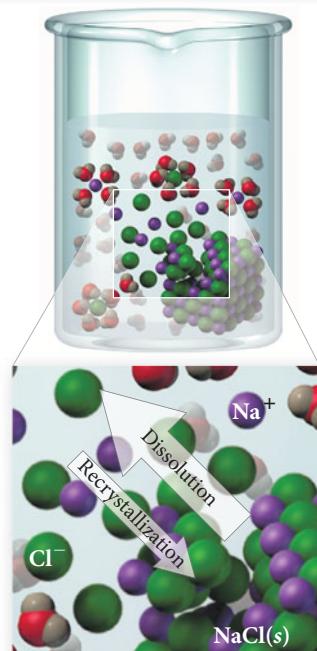
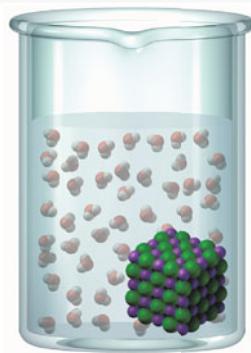
When sodium chloride is first added to water, sodium and chloride ions begin to dissolve into the water.



As the solution becomes more concentrated, some of the sodium and chloride ions can begin to recrystallize as solid sodium chloride.



When the rate of dissolution equals the rate of recrystallization, dynamic equilibrium has been reached.



(a) Initial

Rate of dissolution > Rate of recrystallization

(b) Dissolving

Rate of dissolution = Rate of recrystallization

(c) Dynamic equilibrium

► **FIGURE 12.10** Precipitation from a Supersaturated Solution

When a small piece of solid sodium acetate is added to a supersaturated sodium acetate solution, the excess solid precipitates out of the solution.



sodium chloride in the solution increases. This dissolved sodium chloride then begins to recrystallize as solid sodium chloride. Initially the rate of dissolution far exceeds the rate of recrystallization, but as the concentration of dissolved sodium chloride increases, the rate of recrystallization also increases. Eventually the rates of dissolution and recrystallization become equal—**dynamic equilibrium** has been reached.



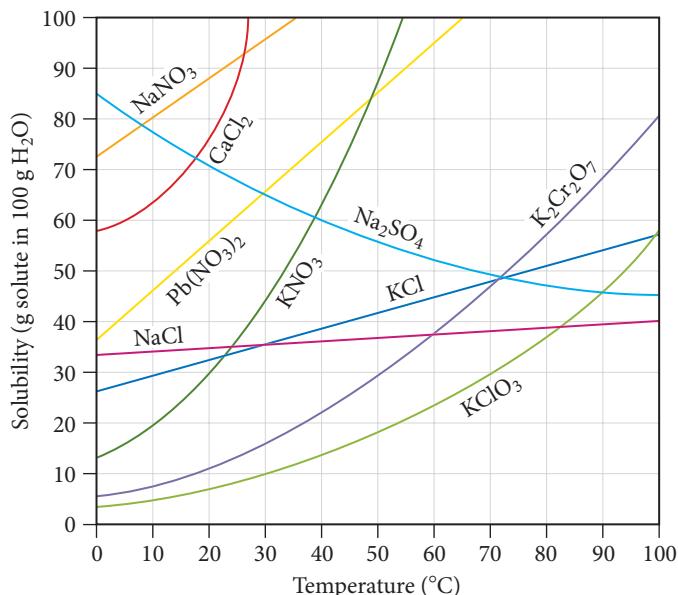
A solution in which the dissolved solute is in dynamic equilibrium with the solid (undissolved) solute is a **saturated solution**. If you add additional solute to a saturated solution, it will not dissolve. A solution containing less than the equilibrium amount of solute is an **unsaturated solution**. If you add additional solute to an unsaturated solution, it will dissolve.

Under certain circumstances, a **supersaturated solution**—one containing more than the equilibrium amount of solute—may form. Supersaturated solutions are unstable and the excess solute normally precipitates out of the solution. However, in some cases, if left undisturbed, a supersaturated solution can exist for an extended period of time. For example, in a common classroom demonstration a tiny piece of solid sodium acetate is added to a supersaturated solution of sodium acetate. This triggers the precipitation of the solute, which crystallizes out of solution in a dramatic and often beautiful way (Figure 12.10 ▲).

## The Temperature Dependence of the Solubility of Solids

In the case of sugar dissolving in water, the higher temperature increases both how fast the sugar dissolves and how much sugar dissolves.

The solubility of solids in water can be highly dependent on temperature. Have you ever noticed how much more sugar you can dissolve in hot tea than in cold tea? Although exceptions exist, the solubility of most solids in water increases with increasing temperature, as shown in Figure 12.11 ▼. For example, the solubility of potassium



► **FIGURE 12.11** Solubility and Temperature

The solubility of most solids increases with increasing temperature.

nitrate ( $\text{KNO}_3$ ) at room temperature is about 37 g  $\text{KNO}_3$  per 100 g of water. At 50 °C, the solubility rises to 88 g  $\text{KNO}_3$  per 100 g of water.

A common way to purify a solid is a technique called **recrystallization**. In this technique, enough solid is added to water (or some other solvent) to create a saturated solution at an elevated temperature. As the solution cools, it becomes supersaturated and the excess solid precipitates out of solution. If the solution cools slowly, the solid forms crystals as it comes out of solution. The crystalline structure tends to reject impurities, resulting in a purer solid.

You can use the temperature dependence of the solubility of solids to make rock candy. Prepare a saturated sucrose (table sugar) solution at an elevated temperature, and allow a string or stick to dangle into the solution for several days. As the solution cools and the solvent evaporates, the solution becomes supersaturated and sugar crystals grow on the string or stick. After several days, beautiful edible crystals or “rocks” of sugar cover the string.



▲ Rock candy is formed by the recrystallization of sugar.

## Factors Affecting the Solubility of Gases in Water

Solutions of gases dissolved in water are common. Club soda, for example, is a solution of carbon dioxide and water, and most liquids exposed to air contain dissolved gases from air. Fish depend on the oxygen dissolved in lake or ocean water for life, and our blood contains dissolved nitrogen, oxygen, and carbon dioxide. Even tap water contains dissolved gases. The solubility of a gas in a liquid is affected by both temperature and pressure.

**The Effect of Temperature** You can observe the effect of temperature on the solubility of a gas in water by heating ordinary tap water on a stove. Before the water reaches its boiling point, small bubbles develop in the water. These bubbles are the dissolved air (mostly nitrogen and oxygen) coming out of solution. (Once the water boils, the bubbling becomes more vigorous—these larger bubbles are composed of water vapor.) The dissolved air comes out of the heated solution because—unlike solids, whose solubility generally increases with increasing temperature—the *solubility of gases in liquids decreases with increasing temperature*.

The inverse relationship between gas solubility and temperature is the reason that warm soda pop bubbles more than cold soda pop when you open it and warm beer goes flat faster than cold beer. More carbon dioxide comes out of these solutions at room temperature than at a lower temperature because the gas is less soluble at room temperature. The decreasing solubility of gases with increasing temperature is also the reason that fish don’t bite much in a warm lake. The warm temperature results in a lower oxygen concentration. With lower oxygen levels, the fish become lethargic and do not strike as aggressively at the lure or bait you cast their way.



Cold soda pop      Warm soda pop  
▲ Warm soda pop bubbles more than cold soda pop because carbon dioxide is less soluble in the warm solution.

## Conceptual Connection 12.3 Solubility and Temperature

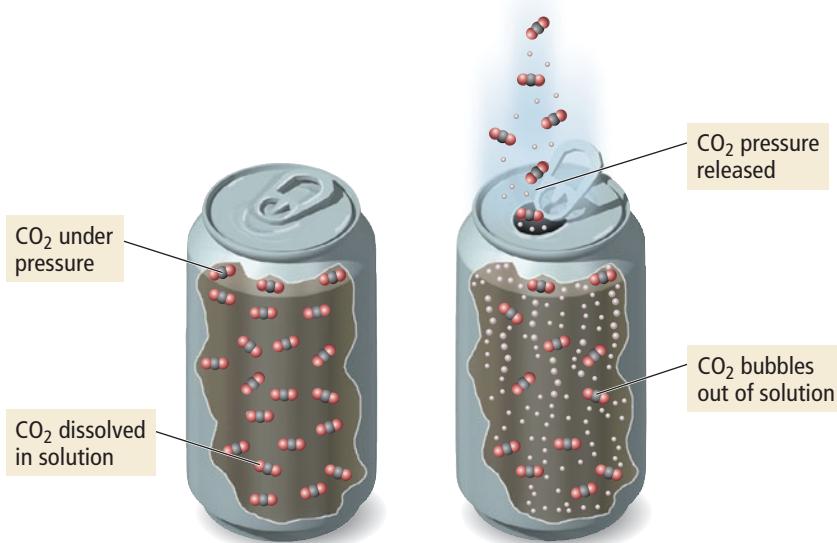
A solution is saturated in both nitrogen gas and potassium bromide at 75 °C. When the solution is cooled to room temperature, what is most likely to happen?

- Some nitrogen gas bubbles out of solution.
- Some potassium bromide precipitates out of solution.
- Some nitrogen gas bubbles out of solution *and* some potassium bromide precipitates out of solution.
- Nothing happens.

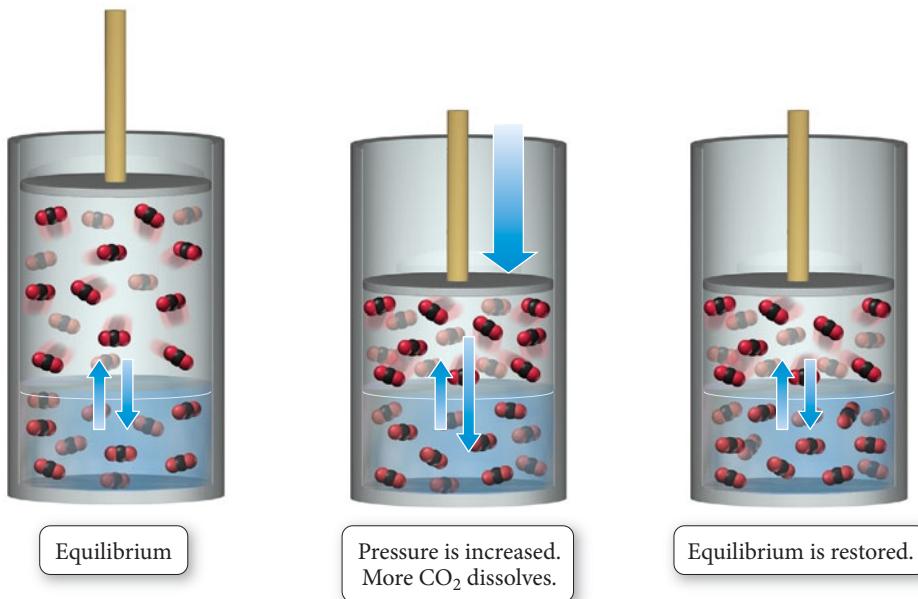
**The Effect of Pressure** The solubility of gases also depends on pressure. The higher the pressure of a gas above a liquid, the more soluble the gas is in the liquid. In a sealed can of soda pop, for example, the carbon dioxide is maintained in solution by a high pressure of carbon dioxide within the can. When the can is opened, this pressure is released and the solubility of carbon dioxide decreases, resulting in bubbling (Figure 12.12 ▶).

► **FIGURE 12.12 Soda Fizz**

The bubbling that occurs when a can of soda is opened results from the reduced pressure of carbon dioxide over the liquid. At lower pressure, the carbon dioxide is less soluble and bubbles out of solution.



The increased solubility of a gas in a liquid can be understood by considering cylinders containing water and carbon dioxide gas.



The first cylinder represents an equilibrium between gaseous and dissolved carbon dioxide—the rate of carbon dioxide molecules entering solution exactly equals the rate of molecules leaving the solution. Now imagine decreasing the volume, as shown in the second cylinder. The pressure of carbon dioxide increases, causing the rate of molecules entering the solution to rise. The number of molecules in solution increases until equilibrium is established again, as shown in the third cylinder. However, the amount of carbon dioxide in solution is now greater.

We can quantify the solubility of gases with increasing pressure with **Henry's law**:

$$S_{\text{gas}} = k_H P_{\text{gas}}$$

where  $S_{\text{gas}}$  is the solubility of the gas (usually in M),  $k_H$  is a constant of proportionality (called the *Henry's law constant*) that depends on the specific solute and solvent and also on temperature, and  $P_{\text{gas}}$  is the partial pressure of the gas (usually in atm). The equation shows that the solubility of a gas in a liquid is directly proportional to the pressure of the gas above the liquid. Table 12.4 lists the Henry's law constants for several common gases.

**TABLE 12.4 Henry's Law Constants for Several Gases in Water at 25 °C**

Gas	$k_H$ (M/atm)
O <sub>2</sub>	$1.3 \times 10^{-3}$
N <sub>2</sub>	$6.1 \times 10^{-4}$
CO <sub>2</sub>	$3.4 \times 10^{-2}$
NH <sub>3</sub>	$5.8 \times 10^1$
He	$3.7 \times 10^{-4}$


**Conceptual Connection 12.4 Henry's Law**

Examine the Henry's law constants in Table 12.4. Why is the constant for ammonia bigger than the others?

**EXAMPLE 12.2 Henry's Law**

What pressure of carbon dioxide is required to keep the carbon dioxide concentration in a bottle of club soda at 0.12 M at 25 °C?

<b>SORT</b> You are given the desired solubility of carbon dioxide and asked to find the pressure required to achieve this solubility.	<b>GIVEN:</b> $s_{\text{CO}_2} = 0.12 \text{ M}$ <b>FIND:</b> $P_{\text{CO}_2}$
<b>STRATEGIZE</b> Use Henry's law to find the required pressure from the solubility. You will need the Henry's law constant for carbon dioxide, which is listed in Table 12.4.	<b>CONCEPTUAL PLAN</b>  $s_{\text{CO}_2} = k_{\text{H}, \text{CO}_2} P_{\text{CO}_2}$ <b>RELATIONSHIPS USED</b> $S_{\text{gas}} = k_{\text{H}} P_{\text{gas}}$ (Henry's law) $k_{\text{H}, \text{CO}_2} = 3.4 \times 10^{-2} \text{ M/atm}$ (from Table 12.4)
<b>SOLVE</b> Solve the Henry's law equation for $P_{\text{CO}_2}$ and substitute the other quantities to calculate it.	<b>SOLUTION</b> $S_{\text{CO}_2} = k_{\text{H}, \text{CO}_2} P_{\text{CO}_2}$ $P_{\text{CO}_2} = \frac{s_{\text{CO}_2}}{k_{\text{H}, \text{CO}_2}}$ $= \frac{0.12 \text{ M}}{3.4 \times 10^{-2} \frac{\text{M}}{\text{atm}}}$ $= 3.5 \text{ atm}$

**CHECK** The answer is in the correct units and seems reasonable. A small answer (for example, less than 1 atm) would be suspect because you know that the soda is under a pressure greater than atmospheric pressure when you open it. A very large answer (for example, over 100 atm) would be suspect because an ordinary can or bottle probably could not sustain such high pressures without bursting.

**FOR PRACTICE 12.2**

Determine the solubility of oxygen in water at 25 °C exposed to air at 1.0 atm. Assume a partial pressure for oxygen of 0.21 atm.

## 12.5 Expressing Solution Concentration

As we have seen, the amount of solute in a solution is an important property of the solution. For example, the amount of sodium chloride in a solution determines whether or not the solution will cause dehydration if consumed. A **dilute solution** contains small quantities of solute relative to the amount of solvent. Drinking a dilute sodium chloride solution will not cause dehydration. A **concentrated solution** contains large quantities of solute relative to the amount of solvent. Drinking a concentrated sodium chloride solution will cause dehydration. Common ways of reporting solution concentration include molarity, molality, parts by mass, parts by volume, mole fraction, and mole



## Chemistry in the Environment

### Lake Nyos

Most people living near Lake Nyos in Cameroon, West Africa, began August 22, 1986, like any other day. Unfortunately, the day ended in tragedy. On that evening, a large cloud of carbon dioxide gas burped up from the depths of Lake Nyos, killing over 1700 people and about 3000 cattle. Two years before, a similar tragedy had occurred in Lake Monoun, just 60 miles away, killing 37 people. Today, scientists have taken steps to prevent these lakes from accumulating the carbon dioxide that caused the disasters.



◀ Lake Nyos, in Cameroon, has a deceptively peaceful appearance; in the summer of 1986, more than 1700 people died around its shores.

Lake Nyos is a water-filled volcanic crater. Some 50 miles beneath the surface of the lake, molten volcanic rock (magma) produces carbon dioxide gas that seeps into the lake. The



◀ A plumbing system slowly vents carbon dioxide from Lake Nyos.

carbon dioxide forms a solution with the lake water. The high pressure at the bottom of the deep lake allows the solution to become highly concentrated in carbon dioxide. The 1986 disaster occurred because over time—either because of the high concentration itself or because of some other natural trigger such as a landslide or small earthquake—some gaseous carbon dioxide escaped. The rising bubbles disrupted the stratified layers of lake water, causing water at the bottom of the lake to rise to a region of lower pressure. The drop in pressure decreased the solubility of the carbon dioxide, so more carbon dioxide bubbles formed. This in turn caused more churning and still more carbon dioxide release. The result was a massive cloud of carbon dioxide gas that escaped from the lake. Since carbon dioxide is heavier than air, the carbon dioxide traveled down the sides of the volcano and into the nearby valley, displacing air and asphyxiating many of the local residents.

In an effort to keep these events from recurring, scientists have constructed a piping system that slowly vents carbon dioxide from the lake bottom, preventing the buildup that led to the tragedy.



### Question

Suppose that the water pressure at the bottom of Lake Nyos is 25 atm. What is the solubility of carbon dioxide at that depth?

percent, as summarized in Table 12.5. We have seen two of these units before: molarity in Section 4.4, and mole fraction in Section 5.6. In the following section, we review the terms we have already covered and introduce the new ones.

### Molarity

The **molarity (M)** of a solution is the amount of solute (in moles) divided by the volume of solution (in liters).

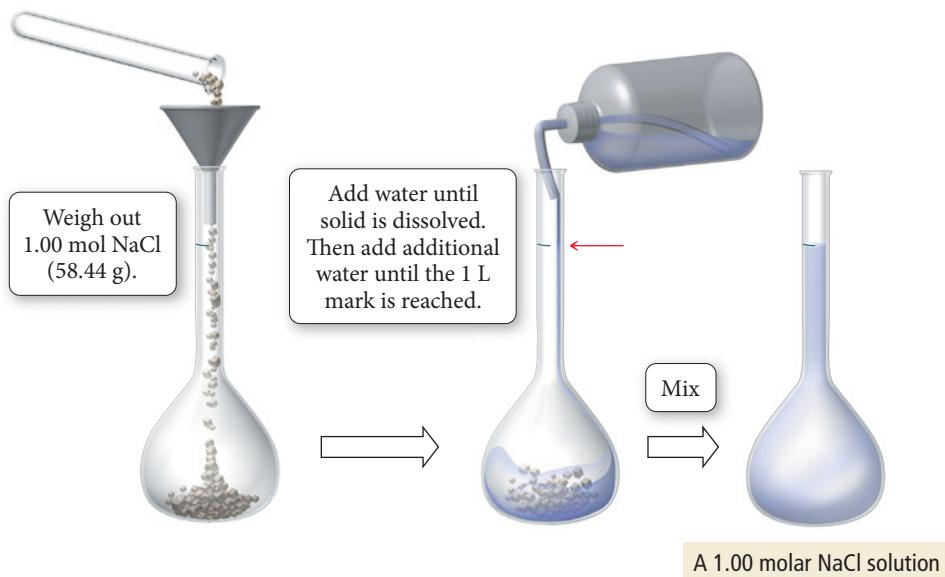
$$\text{Molarity (M)} = \frac{\text{amount solute (in mol)}}{\text{volume solution (in L)}}$$

**TABLE 12.5 Solution Concentration Terms**

Unit	Definition	Units
Molarity (M)	$\frac{\text{amount solute (in mol)}}{\text{volume solution (in L)}}$	$\frac{\text{mol}}{\text{L}}$
Molality ( $m$ )	$\frac{\text{amount solute (in mol)}}{\text{mass solvent (in kg)}}$	$\frac{\text{mol}}{\text{kg}}$
Mole fraction ( $\chi$ )	$\frac{\text{amount solute (in mol)}}{\text{total amount of solute and solvent (in mol)}}$	None
Mole percent (mol %)	$\frac{\text{amount solute (in mol)}}{\text{total amount of solute and solvent (in mol)}} \times 100\%$	%
Parts by mass	$\frac{\text{mass solute}}{\text{mass solution}} \times \text{multiplication factor}$	
Percent by mass (%)	$\text{Multiplication factor} = 100$	%
Parts per million by mass (ppm)	$\text{Multiplication factor} = 10^6$	ppm
Parts per billion by mass (ppb)	$\text{Multiplication factor} = 10^9$	ppb
Parts by volume (%), ppm, ppb	$\frac{\text{volume solute}}{\text{volume solution}} \times \text{multiplication factor}^*$	

\*Multiplication factors for parts by volume are identical to those for parts by mass.

Note that molarity is moles of solute per liter of *solution*, not per liter of solvent. To make a solution of a specified molarity, we usually put the solute into a flask and then add water (or another solvent) to the desired volume of solution, as shown in Figure 12.13 ▼. Molarity is a convenient unit to use when making, diluting, and transferring solutions because it specifies the amount of solute per unit of solution.



▲ **FIGURE 12.13** Preparing a Solution of Known Concentration To make a 1 M NaCl solution, we add 1 mol of the solid to a flask and dilute with water to make 1 L of solution.

Molarity depends on volume, and because volume varies with temperature, molarity also varies with temperature. For example, a 1 M aqueous solution at room temperature will be slightly less than 1 M at an elevated temperature because the volume of the solution is greater at the elevated temperature.