

# *Liquids and Solids*

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Courtesy of the artist and Galerie Lelong, New York

*The total three-dimensional arrangement of particles of a crystal is its crystal structure.*

# Liquids

## SECTION 12-1

### OBJECTIVES

- Describe the motion of particles in liquids and the properties of liquids according to the kinetic-molecular theory.
- Discuss the process by which liquids can change into a gas. Define *vaporization*.
- Discuss the process by which liquids can change into a solid. Define *freezing*.

The water in the waves crashing on a beach and the molten lava rushing down the sides of a volcano are examples of matter in the liquid state. When you think of Earth's oceans, lakes, and rivers and the many liquids you use every day, it is hard to believe that liquids are the *least* common state of matter in the universe. Liquids are less common than solids, gases, and plasmas because a substance in the liquid state can exist only within a relatively narrow range of temperatures and pressures.

In this section, you will examine the properties of the liquid state. You will also compare them with those of the solid state and the gas state. These properties will be discussed in terms of the kinetic-molecular theory.

### Properties of Liquids and the Kinetic-Molecular Theory

A liquid can be described as a form of matter that has a definite volume and takes the shape of its container. The properties of liquids can be understood by applying the kinetic-molecular theory, considering the motion and arrangement of molecules and the attractive forces between them.

As in a gas, particles in a liquid are in constant motion. However, the particles in a liquid are closer together and lower in kinetic energy than those in a gas. Therefore, the attractive forces between particles in a liquid are more effective than those between particles in a gas. This attraction between liquid particles is caused by the intermolecular forces discussed in Chapter 6: dipole-dipole forces, London dispersion forces, and hydrogen bonding.

Liquids are more ordered than gases because of the stronger intermolecular forces and the lower mobility of the liquid particles. According to the kinetic-molecular theory of liquids, the particles are not bound together in fixed positions. Instead, they move about constantly. This particle mobility explains why liquids and gases are referred to as fluids. A **fluid** is a substance that can flow and therefore take the shape of its container. Most liquids naturally flow downhill because of gravity. However, some liquids can flow in other directions as well. For example, liquid helium near absolute zero has the unusual property of being able to flow uphill.

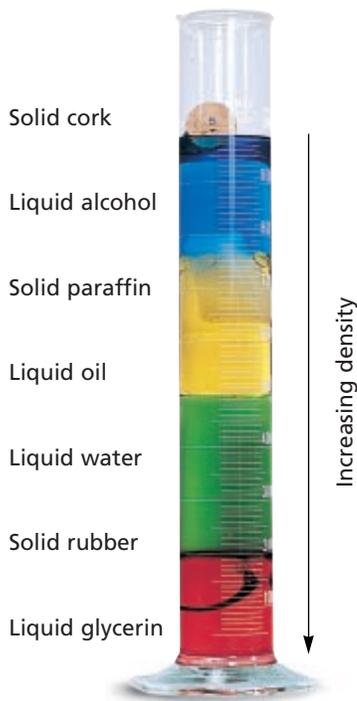


**Module 1:** States of Matter/Classes of Matter

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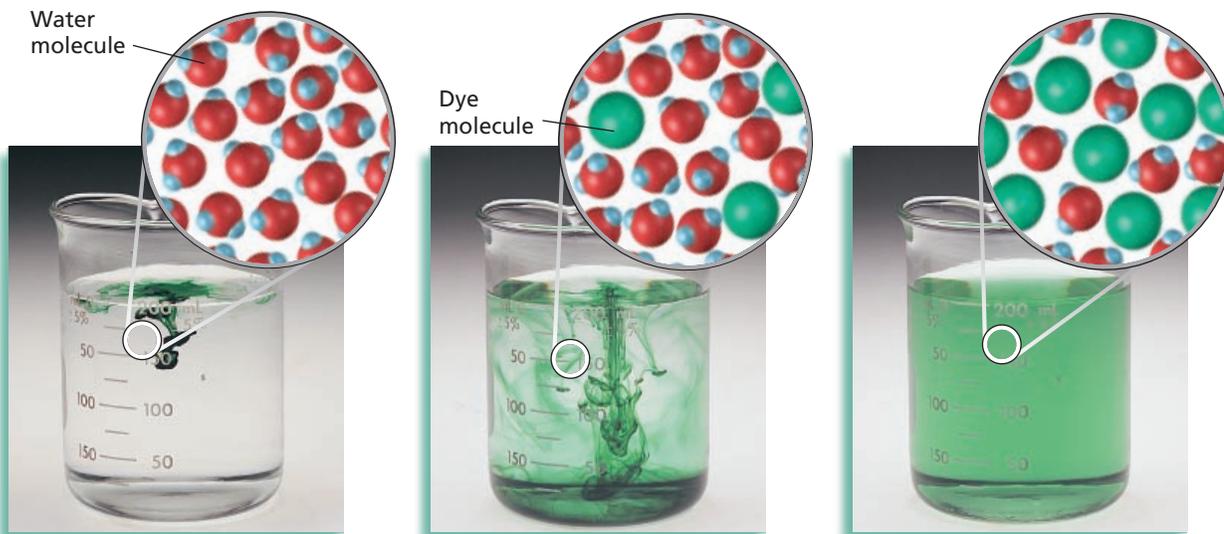
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**FIGURE 12-1** Solids and liquids of different densities are shown. The densest materials are at the bottom. The least dense are at the top. (Dyes have been added to the liquids to make the layers more visible.)

**FIGURE 12-2** Like gases, the two liquids in this beaker diffuse over time. The green liquid food coloring from the drop will eventually form a uniform solution with the water.



## Relatively High Density

At normal atmospheric pressure, most substances are thousands of times denser as liquids than as gases. This higher density is a result of the close arrangement of liquid particles. Most substances are only slightly less dense (about 10%) as liquids than as solids, however. Water is one of the few substances that becomes less dense when it solidifies, as will be discussed further in Section 12-4.

At the same temperature and pressure, different liquids can differ greatly in density. Figure 12-1 shows some liquids and solids with different densities. The densities differ to such an extent that the liquids form layers.

## Relative Incompressibility

When liquid water at 20°C is compressed by a pressure of 1000 atm, its volume decreases by only 4%. Such behavior is typical of all liquids and is similar to the behavior of solids. In contrast, a gas under a pressure of 1000 atm would have only about 1/1000 of its volume at normal atmospheric pressure. Liquids are much less compressible than gases because liquid particles are more closely packed together. In addition, liquids can transmit pressure equally in all directions.

## Ability to Diffuse

As described in Chapter 10, gases diffuse and mix with other gas particles. Liquids also diffuse and mix with other liquids, as shown in Figure 12-2. Any liquid gradually diffuses throughout any other liquid in which it can dissolve. As in gases, diffusion in liquids occurs because of the constant, random motion of particles. Yet diffusion is much slower in liquids than in gases because liquid particles are closer together. Also, the attractive forces between the particles of a liquid slow their movement. As the temperature of a liquid is increased, diffusion occurs more rapidly. That is because the average kinetic energy, and therefore the average speed of the particles, is increased.

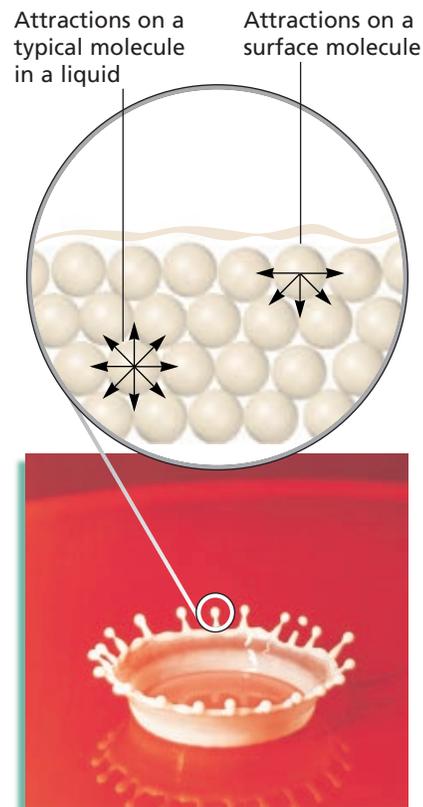
## Surface Tension

A property common to all liquids, **surface tension**, is a force that tends to pull adjacent parts of a liquid's surface together, thereby decreasing surface area to the smallest possible size. Surface tension results from the attractive forces between particles of a liquid. The higher the force of attraction, the higher the surface tension. Water has a higher surface tension than most liquids. This is due to the hydrogen bonds water molecules can form with each other. The molecules at the surface of the water are a special case. They can form hydrogen bonds with the other water molecules beneath them and beside them, but not with the molecules in the air above them. As a result, the surface water molecules are drawn together and toward the body of the liquid, creating a high surface tension. Surface tension causes liquid droplets to take on a spherical shape because a sphere has the smallest possible surface area for a given volume. An example of this phenomenon is shown in Figure 12-3.

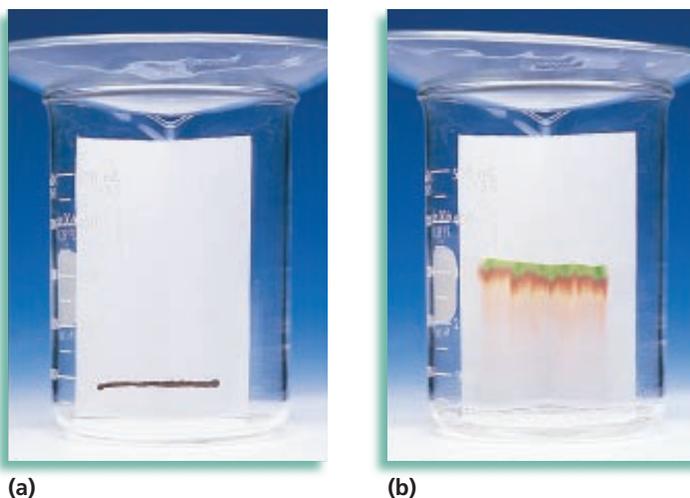
**Capillary action**, the attraction of the surface of a liquid to the surface of a solid, is a property closely related to surface tension. A liquid will rise quite high in a very narrow tube if a strong attraction exists between the liquid molecules and the molecules that make up the surface of the tube. This attraction tends to pull the liquid molecules upward along the surface against the pull of gravity. This process continues until the weight of the liquid balances the gravitational force. Capillary action can occur between water molecules and paper fibers, as shown in Figure 12-4. Capillary action is at least partly responsible for the transportation of water from the roots of a plant to its leaves. The same process is responsible for the concave liquid surface, called a *meniscus*, that forms in a test tube or graduated cylinder.

## Evaporation and Boiling

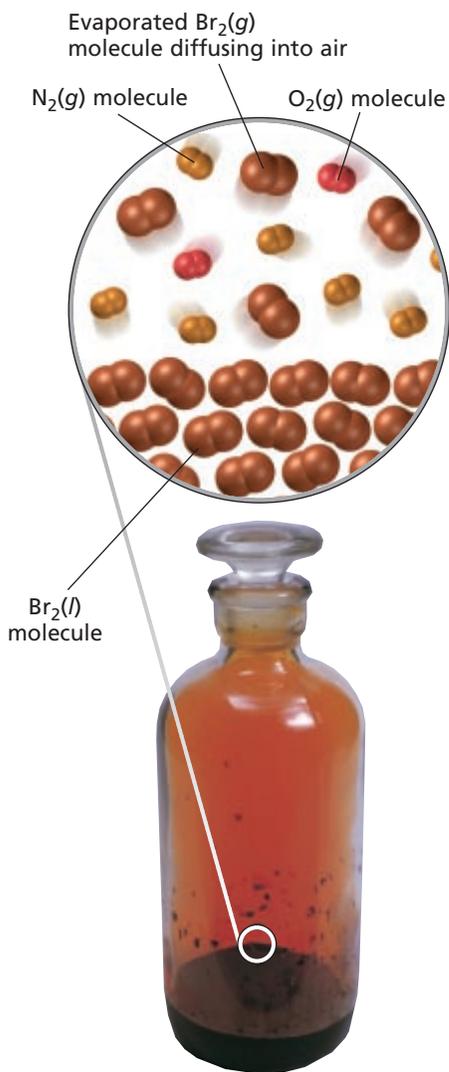
The process by which a liquid or solid changes to a gas is **vaporization**. Evaporation is a form of vaporization. **Evaporation** is the process by which particles escape from the surface of a nonboiling liquid and enter the gas state.



**FIGURE 12-3** As a result of surface tension, liquids form roughly spherical drops. The net attractive forces between the particles pull the molecules on the surface inward and closer together than those farther down in the liquid, minimizing the surface area.



**FIGURE 12-4** The attraction between polar water molecules and polar cellulose molecules in paper fibers causes the water to move up in the paper. The water-soluble ink placed near the bottom of the paper in (a) rises up the paper along with the water, as seen in (b). As the ink moves up the paper, it is separated into its various components, producing the different bands of color. This separation occurs because the water and the paper attract the molecules of the ink components differently. These phenomena are used in the separation process of paper chromatography seen here.



**FIGURE 12-5** Liquid bromine,  $\text{Br}_2$ , evaporates near room temperature. The resulting brownish red gas diffuses into the air above the surface of the liquid.

A small amount of liquid bromine was added to the bottle shown in Figure 12-5. Within a few minutes, the air above the liquid bromine turned brownish-red. That is because some bromine molecules escaped from the surface of the liquid. They have changed into the gas state, becoming bromine vapor, which mixed with the air. A similar phenomenon occurs if you apply perfume to your wrist. Within seconds, you become aware of the perfume's fragrance. Scent molecules evaporate from your skin and diffuse through the air, to be detected by your nose.

Evaporation occurs because the particles of a liquid have different kinetic energies. Particles with higher-than-average energies move faster. Some surface particles with higher-than-average energies can overcome the intermolecular forces that bind them to the liquid. They can then escape into the gas state.

Evaporation is a crucial process in nature. Evaporation removes fresh water from the surface of the ocean, leaving behind a higher concentration of salts. In subtropical areas, evaporation occurs at a higher rate, causing the surface water to be saltier. All water that falls to Earth in the form of rain and snow previously evaporated from oceans, lakes, and rivers. Evaporation of perspiration plays an important role in keeping you cool. Perspiration, which is mostly water, cools you by absorbing body heat when it evaporates. Heat energy is absorbed from the skin, causing the cooling effect.

*Boiling* is the change of a liquid to bubbles of vapor that appear throughout the liquid. Boiling differs from evaporation, as you will see in Section 12-3.

### Formation of Solids

When a liquid is cooled, the average energy of its particles decreases. If the energy is low enough, attractive forces pull the particles into an even more orderly arrangement. The substance then becomes a solid. *The physical change of a liquid to a solid by removal of heat is called freezing or solidification.* Perhaps the best-known example of freezing is the change of liquid water to solid water, or ice, at  $0^\circ\text{C}$ . Another familiar example is the solidification of paraffin at room temperature. All liquids freeze, although not necessarily at temperatures you normally encounter. Ethanol, for example, freezes near  $-115^\circ\text{C}$ .

## SECTION REVIEW

- Describe the liquid state according to the kinetic-molecular theory.
- List the properties of liquids.
- How does the kinetic-molecular theory explain the following properties of liquids? (a) their relatively high density, (b) their ability to diffuse, and (c) their ability to evaporate
- Explain why liquids in a test tube form a meniscus.
- Compare vaporization and evaporation.

# Solids

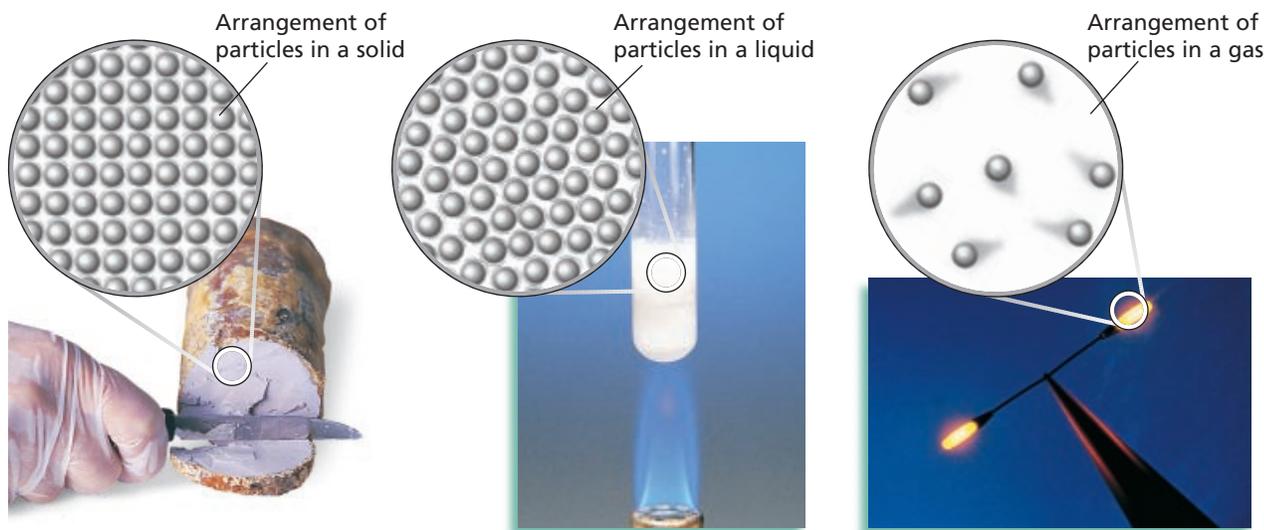
## SECTION 12-2

### OBJECTIVES

- Describe the motion of particles in solids and the properties of solids according to the kinetic-molecular theory.
- Distinguish between the two types of solids.
- Describe the different types of crystal symmetry. Define *crystal structure* and *unit cell*.

### Properties of Solids and the Kinetic-Molecular Theory

The particles of a solid are more closely packed than those of a liquid or gas. Intermolecular forces between particles are therefore much more effective in solids. Dipole-dipole attractions, London dispersion forces, and hydrogen bonding exert stronger effects in solids than in the corresponding liquids or gases. These forces tend to hold the particles of a solid in relatively fixed positions, with only vibrational movement around fixed points. Because the motions of the particles are restricted in this way, solids are more ordered than liquids and are much more ordered than gases. The importance of order and disorder in physical and chemical changes will be discussed in Chapter 17. Compare the physical appearance and molecular arrangement of the element in Figure 12-6 in solid, liquid, and gas form.



**FIGURE 12-6** Particles of sodium metal in three different states are shown. Sodium exists in a gaseous state in a sodium-vapor lamp.



**Module 1:** States of Matter/Classes of Matter

There are two types of solids: crystalline solids and amorphous solids. *Most solids are **crystalline solids**—they consist of crystals. A **crystal** is a substance in which the particles are arranged in an orderly, geometric, repeating pattern.* Noncrystalline solids, including glass and plastics, are called amorphous solids. *An **amorphous solid** is one in which the particles are arranged randomly.* The two types of solids will be discussed in more detail later in this section.

## Definite Shape and Volume

Unlike liquids and gases, solids can maintain a definite shape without a container. In addition, crystalline solids are geometrically regular. Even the fragments of a shattered crystalline solid have distinct geometric shapes that reflect their internal structure. Amorphous solids maintain a definite shape, but they do not have the distinct geometric shapes of crystalline solids. For example, glass can be molded into any shape. If it is shattered, glass fragments can have a wide variety of irregular shapes.

The volume of a solid changes only slightly with a change in temperature or pressure. Solids have definite volume because their particles are packed closely together. There is very little empty space into which the particles can be compressed. Crystalline solids generally do not flow because their particles are held in relatively fixed positions.

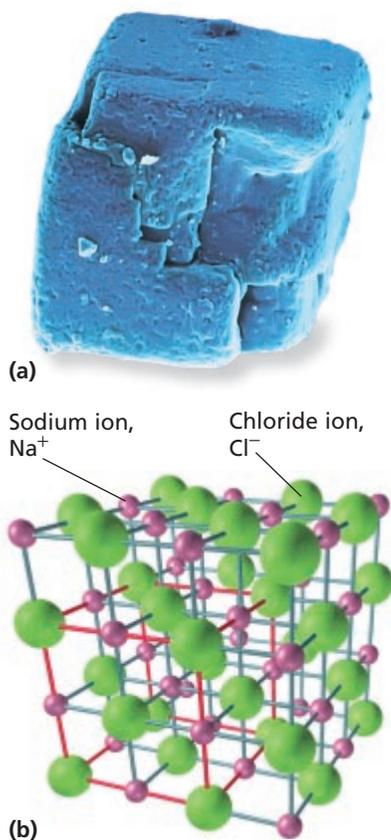
## Definite Melting Point

**Melting** is the physical change of a solid to a liquid by the addition of heat. The temperature at which a solid becomes a liquid is its **melting point**. At this temperature, the kinetic energies of the particles within the solid overcome the attractive forces holding them together. The particles can then break out of their positions in crystalline solids, which have definite melting points. In contrast, amorphous solids, such as glass and plastics, have no definite melting point. They have the ability to flow over a range of temperatures. Therefore, amorphous solids are sometimes classified as **supercooled liquids**, which are substances that retain certain liquid properties even at temperatures at which they appear to be solid. These properties exist because the particles in amorphous solids are arranged randomly, much like the particles in a liquid. Unlike the particles in a true liquid, however, the particles in amorphous solids are not constantly changing their positions.

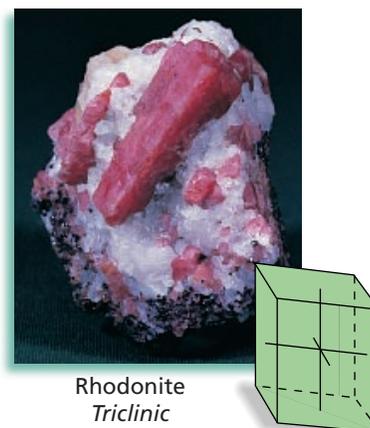
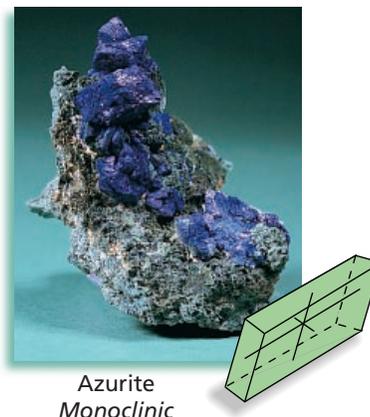
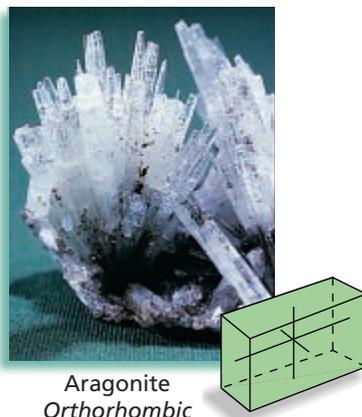
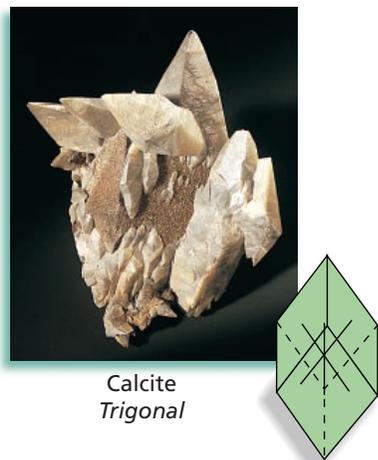
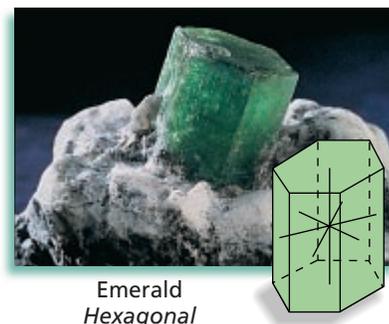
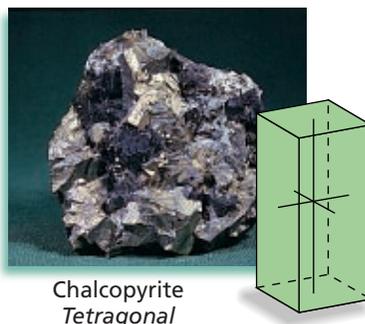
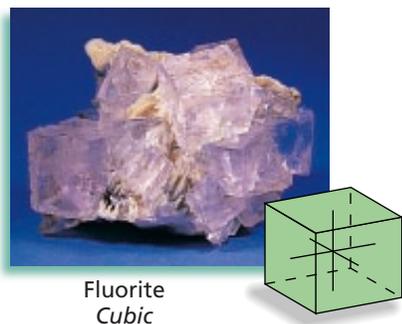
## High Density and Incompressibility

In general, substances are most dense in the solid state. Solids tend to be slightly denser than liquids and much denser than gases. The higher density results from the fact that the particles of a solid are more closely packed than those of a liquid or a gas. Solid hydrogen is the least dense solid; it has a density of about 1/320 of the densest element, osmium, Os.

Solids are generally less compressible than liquids. For practical purposes, solids can be considered incompressible. Some solids, such as wood and cork, may *seem* compressible, but they are not. They contain pores that are filled with air. When subjected to intense pressure, the pores are compressed, not the wood or cork itself.



**FIGURE 12-7** (a) This is a scanning electron micrograph (SEM) of a sodium chloride crystal. A sodium chloride crystal can be represented by its crystal structure (b), which is made up of individual unit cells represented regularly in three dimensions. Here, one unit cell is outlined in red.



### Low Rate of Diffusion

If a zinc plate and a copper plate are clamped together for a long time, a few atoms of each metal will diffuse into the other. This observation shows that diffusion does occur in solids. The rate of diffusion is millions of times slower in solids than in liquids, however.

## Crystalline Solids

Crystalline solids exist either as single crystals or as groups of crystals fused together. *The total three-dimensional arrangement of particles of a crystal is called a **crystal structure**.* The arrangement of particles in the crystal can be represented by a coordinate system called a lattice. *The smallest portion of a crystal lattice that shows the three-dimensional pattern of the entire lattice is called a **unit cell**.* Each crystal lattice contains many unit cells packed together. Figure 12-7 shows the relationship between a crystal lattice and its unit cell. A crystal and its unit cells can have any one of seven types of symmetry. This fact enables scientists to classify crystals by their shape. Diagrams and examples of each type of crystal symmetry are shown in Figure 12-8.

### Binding Forces in Crystals

Crystal structures can also be described in terms of the types of particles in them and the types of chemical bonding between the particles.

**FIGURE 12-8** Shown are the seven basic crystalline systems and representative minerals of each.

**TABLE 12-1** Melting and Boiling Points of Representative Crystalline Solids

Type of substance	Formula	Melting point (°C)	Boiling point at 1 atm (°C)
Ionic	NaCl	801	1413
	MgF <sub>2</sub>	1266	2239
Covalent network	(SiO <sub>2</sub> ) <sub>x</sub>	1610	2230
	C <sub>x</sub> (diamond)	3500	3930
Metallic	Hg	-39	357
	Cu	1083	2567
	Fe	1535	2750
	W	3410	5660
Covalent molecular (nonpolar)	H <sub>2</sub>	-259	-253
	O <sub>2</sub>	-218	-183
	CH <sub>4</sub>	-182	-164
	CCl <sub>4</sub>	-23	77
	C <sub>6</sub> H <sub>6</sub>	6	80
Covalent molecular (polar)	NH <sub>3</sub>	-78	-33
	H <sub>2</sub> O	0	100

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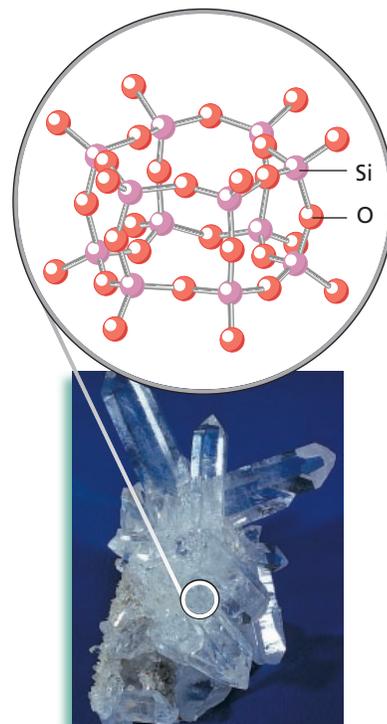
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According to this method of classification, there are four types of crystals. These types are listed in Table 12-1. Refer to this table as you read the following discussion.

- 1. Ionic crystals.** As discussed in Chapter 6, the ionic crystal structure consists of positive and negative ions arranged in a regular pattern. The ions can be monatomic or polyatomic. Generally, ionic crystals form when Group-1 or Group-2 metals combine with Group-16 or Group-17 nonmetals or nonmetallic polyatomic ions. The strong binding forces between the positive and negative ions in the crystal structure give the ionic crystals certain properties. For example, these crystals are hard and brittle, have high melting points, and are good insulators.
- 2. Covalent network crystals.** In covalent network crystals, the sites contain single atoms. Each atom is covalently bonded to its nearest neighboring atoms. The covalent bonding extends throughout a network that includes a very large number of atoms. Three-dimensional covalent network solids include diamond, C<sub>x</sub>, quartz, (SiO<sub>2</sub>)<sub>x</sub>—shown in Figure 12-9—silicon carbide, (SiC)<sub>x</sub>, and many oxides of transition metals. Such solids are essentially giant molecules. The subscript *x* in these formulas indicates that the component within the parentheses extends indefinitely. The network solids are nearly always very hard and brittle. They have rather high melting points and are usually nonconductors or semiconductors.
- 3. Metallic crystals.** As discussed in Chapter 6, the metallic crystal structure consists of metal atoms surrounded by a sea of valence electrons. The electrons are donated by the metal atoms and belong to

the crystal as a whole. The freedom of the outer-structure electrons to move throughout the crystal explains the high electric conductivity of metals. As you can see from Table 12-1, the melting points of different metallic crystals vary greatly.

4. **Covalent molecular crystals.** The crystal structure of a covalent molecular substance consists of covalently bonded molecules held together by intermolecular forces. If the molecules are nonpolar—for example, hydrogen,  $H_2$ , methane,  $CH_4$ , and benzene,  $C_6H_6$ —then there are only weak London dispersion forces between molecules. In a polar covalent molecular crystal—for example, water,  $H_2O$ , and ammonia,  $NH_3$ —molecules are held together by dispersion forces, by somewhat stronger dipole-dipole forces, and sometimes by even stronger hydrogen bonding. The forces that hold polar or nonpolar molecules together in the structure are much weaker than the covalent chemical bonds between the atoms within each molecule. Covalent molecular crystals thus have low melting points. They are easily vaporized, are relatively soft, and are good insulators. Ice crystals, the most familiar molecular crystals, are discussed in Section 12-4.



**FIGURE 12-9** Covalent network crystals include three-dimensional network solids, such as this quartz,  $(SiO_2)_x$ , shown here with its three-dimensional atomic structure.

## Amorphous Solids

The word *amorphous* comes from the Greek for “without shape.” Unlike crystals, amorphous solids do not have a regular, natural shape.

Amorphous solids tend to hold their shape for a long time. However, some amorphous solids do flow, although usually very slowly. Some samples of very old window glass are thicker at the bottom than at the top suggesting that the glass has flowed downward over the years. Glasses make up a distinctive group of amorphous solids. They are made by cooling certain molten materials in such a way that they do not crystallize but remain amorphous.

There are hundreds of types of plastic and glass, all of which have thousands of important applications. Glass is used for everything from fiberglass automobile bodies to optical fibers that use light to transmit telephone conversations.

## SECTION REVIEW

1. Describe the solid state according to the kinetic-molecular theory.
2. What is the difference between an amorphous solid and a crystalline solid?
3. Account for each of the following properties of solids: (a) the definite volume, (b) the relatively high density of solids, (c) the extremely low rate of diffusion.
4. Compare and contrast the four types of crystals.

## SECTION 12-3

## OBJECTIVES

- Explain the relationship between equilibrium and changes of state.
- Predict changes in equilibrium using Le Châtelier's principle.
- Explain what is meant by equilibrium vapor pressure.
- Describe the processes of boiling, freezing, melting, and sublimation.
- Interpret phase diagrams.



**Module 1:** States of Matter/  
Classes of Matter  
**Module 7:** Equilibrium

# Changes of State

Matter on Earth can exist in any of these states—gas, liquid, or solid—and can change from one state to another. Table 12-2 lists the possible changes of state. In this section, you will examine these changes of state and the factors that determine them.

## Equilibrium

**Equilibrium** is a dynamic condition in which two opposing changes occur at equal rates in a closed system. In a closed system, matter cannot enter or leave, but energy can. Both matter and energy can escape or enter an open system. For example, sunlight, heat from a burner, or cooling by ice can cause energy to enter or leave a system.

For an analogy of equilibrium, think of a public swimming pool on a summer day. In the morning, more people enter the pool than leave to go home. The pool gets more and more crowded. This system is not in equilibrium. Later in the day, the number of people entering and leaving will be the same. While the total number of people in the pool stays the same for a long time, individuals are constantly coming and going. The system is in equilibrium.

Equilibrium is a very important chemical concept. Here you will learn about it in relation to changes of state. In Chapter 18, you will study equilibrium in terms of chemical reactions.

## Equilibrium and Changes of State

Consider the evaporation of water in a closed container in which there is initially a vacuum over the liquid, as illustrated in Figure 12-10.

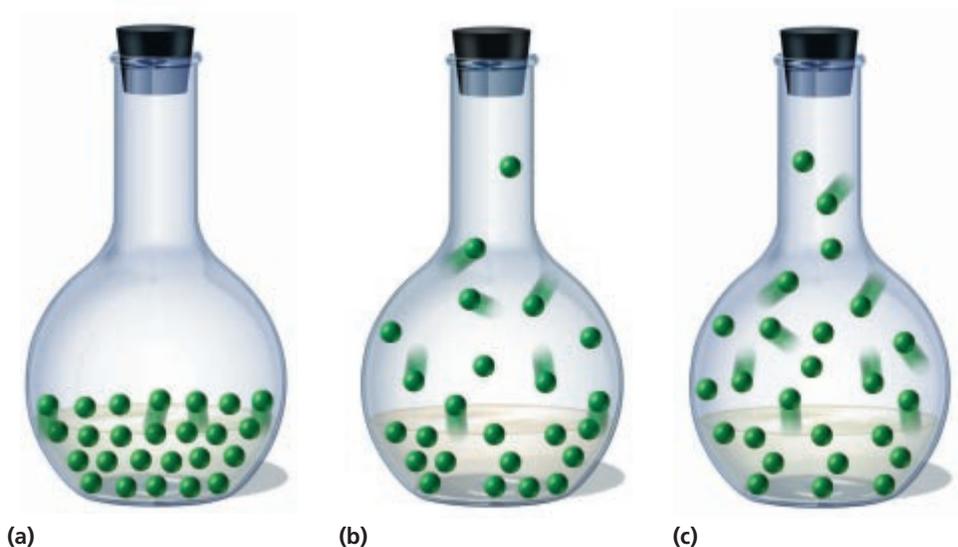
**TABLE 12-2** Possible Changes of State

Change of state	Process	Example
Solid → liquid	melting	ice → water
Solid → gas	sublimation	dry ice → CO <sub>2</sub> gas
Liquid → solid	freezing	water → ice
Liquid → gas	vaporization	liquid bromine → bromine vapor
Gas → liquid	condensation	water vapor → water
Gas → solid	deposition	water vapor → ice

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**FIGURE 12-10** A liquid-vapor equilibrium develops in a closed system. (a) At first there is only liquid present, but molecules are beginning to evaporate. (b) Evaporation continues at a constant rate. Some vapor molecules are beginning to condense to liquid. (c) Equilibrium has been reached between the rate of condensation and the rate of evaporation.

Assume that the contents of the container maintain the same temperature as the surroundings, approximately  $25^{\circ}\text{C}$ . The water and the container are the system. Initially, there is a single phase inside this system—the liquid phase. A **phase** is any part of a system that has uniform composition and properties.

If the energy of a water molecule at the upper surface of the liquid is high enough, the molecule can overcome the attraction of neighboring molecules, leave the liquid phase, and evaporate. Water molecules that have entered the vapor phase behave as typical gas molecules. Some of these vapor molecules move down toward the liquid surface and condense. That is, they reenter the liquid phase. **Condensation** is the process by which a gas changes to a liquid.

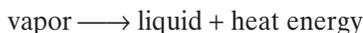
If the temperature and surface area of the liquid remain constant, the rate at which its molecules enter the vapor phase remains constant. The rate at which the water molecules pass from the vapor phase to the liquid phase depends on the concentration of molecules in the vapor phase. The concentration of vapor molecules, and therefore the rate of condensation, is initially zero, as shown in Figure 12-10(a). As time passes and evaporation continues, the concentration of vapor molecules increases. This increase in concentration results in an increase in the condensation rate. However, the rate of condensation is still lower than the rate of evaporation, as shown in Figure 12-10(b). Eventually, the concentration of vapor increases to the point at which the rate of condensation becomes equal to the rate of evaporation, as shown in Figure 12-10(c). In other words, equilibrium is reached and the amounts of liquid and of vapor now remain constant.

## An Equilibrium Equation

Whenever a liquid changes to a vapor, it absorbs heat energy from its surroundings. Evaporation can therefore be represented by the following equation.



Whenever a vapor condenses, it gives off heat energy to its surroundings. Condensation can therefore be represented by the following equation.



The liquid-vapor equilibrium can be represented by the following equation.



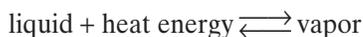
The “double-yields” sign in the equation above represents a reversible reaction. It means that the reaction can proceed in either direction. The forward reaction is represented when the equation is read from left to right (liquid + heat energy  $\longrightarrow$  vapor). The reverse reaction is represented when the equation is read from right to left (vapor  $\longrightarrow$  liquid + heat energy).

## Le Châtelier’s Principle

A system will remain at equilibrium until something occurs to change this condition. It is important to understand the factors that can be used to control the equilibrium of a system. In 1888, the French chemist Henri Louis Le Châtelier developed a principle that enables us to predict how a change in conditions will affect a system at equilibrium. **Le Châtelier’s principle** can be stated as follows: *When a system at equilibrium is disturbed by application of a stress, it attains a new equilibrium position that minimizes the stress.* A stress is typically a change in concentration, pressure, or temperature.

## Equilibrium and Temperature

You can use Le Châtelier’s principle to predict how the liquid-vapor equilibrium changes when a stress is applied in the closed container of liquid discussed earlier. For example, suppose the temperature of the system is increased from 25°C to 50°C. The equilibrium of the system can be represented by the following reversible reaction.



According to Le Châtelier’s principle, the system will respond to an increase in temperature. In this case, the forward reaction is endothermic; that is, it absorbs heat energy. The forward reaction is favored to counteract a rise in temperature and to minimize the stress applied to it (in



Module 7: Equilibrium

this case, the change in temperature). The forward reaction proceeds at a higher rate than the reverse reaction until a new equilibrium is reached. At 50°C, the concentration of vapor is higher than it was at 25°C. However, at equilibrium, the reverse reaction, condensation, also occurs at a higher rate than it did at the lower temperature.

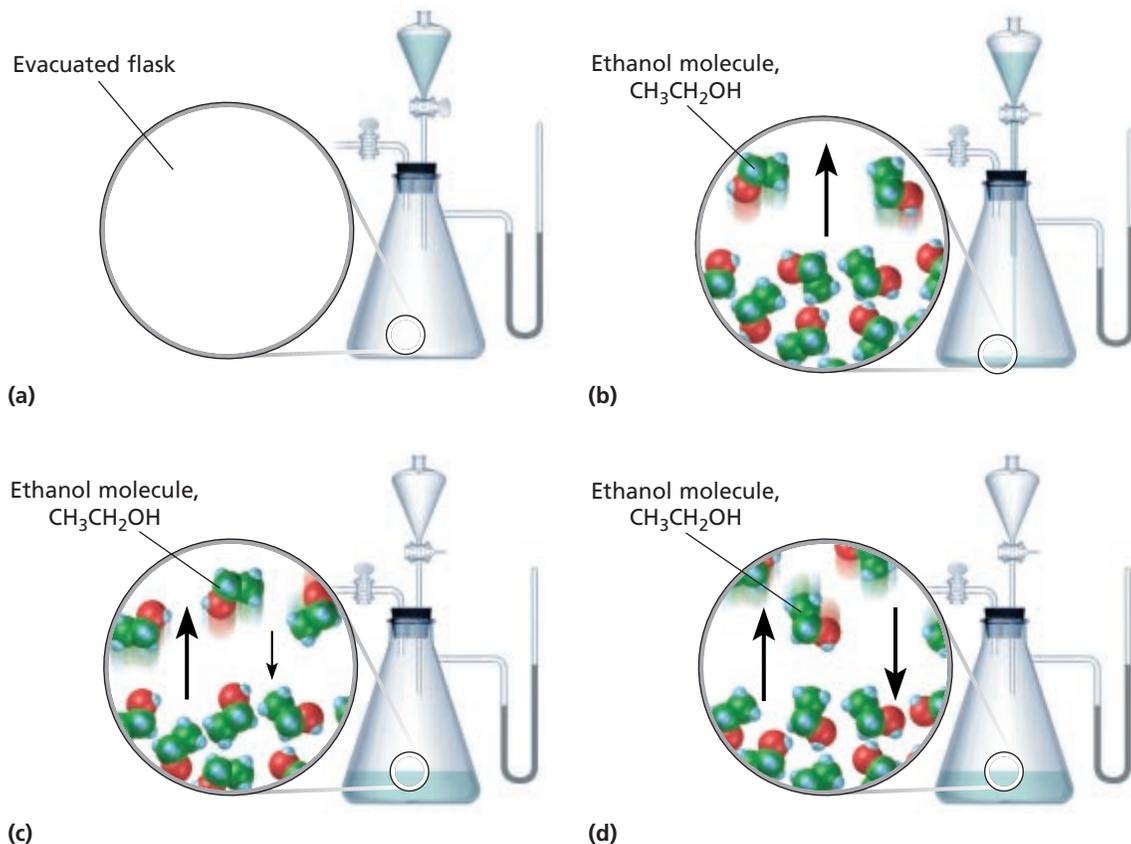
Suppose, on the other hand, that the temperature of the system in equilibrium at 25°C is lowered to 5°C. According to Le Châtelier's principle, the system will adjust to counteract the temperature decrease. Now the reverse reaction is favored because it is exothermic; that is, it releases heat energy. Equilibrium is shifted to the left and reestablished at 5°C. The vapor concentration is now lower than it originally was at 25°C.

## Equilibrium and Concentration

Suppose the mass and temperature of this equilibrium system remain the same, but the volume suddenly increases. What happens to the equilibrium? Initially, the concentration of molecules in the vapor phase decreases because the same number of vapor-phase molecules now occupies a larger volume. Because the concentration of vapor molecules decreases, fewer vapor molecules strike the liquid surface per second and return to the liquid phase. Therefore, the rate of condensation decreases. The rate of evaporation, however, has remained the same and is therefore higher now than the rate of condensation. As a result, an additional net evaporation of liquid occurs. When a new equilibrium is finally reestablished, the concentration of molecules in the vapor phase is the same as in the lower-volume system. Because there was a net movement of molecules from the liquid phase to the vapor phase, the number of liquid molecules has decreased. The equilibrium has therefore shifted to the right. Table 12-3 summarizes the effects on the equilibrium of this liquid-vapor system caused by certain changes.

**TABLE 12-3** Shifts in the Equilibrium for the Reaction  
*Liquid + Heat Energy*  $\rightleftharpoons$  *Vapor*

Change	Shift
Addition of liquid	right
Removal of liquid	left
Addition of vapor	left
Removal of vapor	right
Decrease in container volume	left
Increase in container volume	right
Decrease in temperature	left
Increase in temperature	right



**FIGURE 12-11** (a) The vapor pressure of ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$ , can be measured by dispensing liquid ethanol into an evacuated flask that is part of a closed system. (b) Ethanol molecules leave the liquid surface to form vapor. (c) Molecules continue to vaporize and condense until equilibrium is reached. (d) At equilibrium, the pressure exerted by the vapor is recorded by noting the mercury levels in the side arm.

## Equilibrium Vapor Pressure of a Liquid

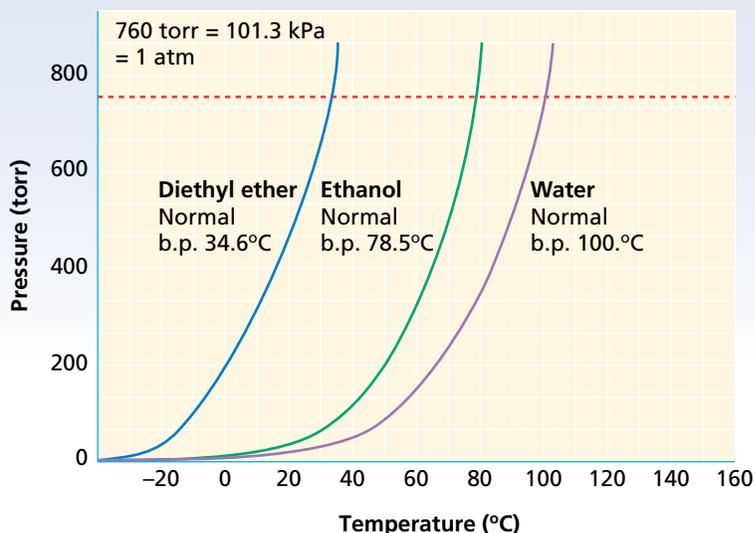
Vapor molecules in equilibrium with a liquid in a closed system exert a pressure proportional to the vapor concentration. *The pressure exerted by a vapor in equilibrium with its corresponding liquid at a given temperature is called the **equilibrium vapor pressure** of the liquid.* Figure 12-11 shows the apparatus and method used to measure the equilibrium vapor pressure of a liquid.

Figure 12-12 is a graph of the equilibrium vapor pressures of water, diethyl ether, and ethanol. The curve shows that at any given temperature, vapor in equilibrium with liquid exerts a specific vapor pressure. The equilibrium vapor pressure of the liquid increases as temperature increases (although not in direct proportion).

## Equilibrium Vapor Pressure and the Kinetic-Molecular Theory

The increase in equilibrium vapor pressure with increasing temperature can be explained in terms of the kinetic-molecular theory for the liquid and gaseous states. Increasing the temperature of a liquid

### Vapor Pressures of Diethyl Ether, Ethanol, and Water at Various Temperatures



**FIGURE 12-12** The vapor pressure of liquids increases as their temperature increases. A liquid boils when its vapor pressure equals the pressure of the atmosphere.

increases its average kinetic energy. That, in turn, increases the number of molecules that have enough energy to escape from the liquid phase into the vapor phase. The resulting increased evaporation rate increases the concentration of molecules in the vapor phase, which in turn increases the equilibrium vapor pressure. The liquid-vapor equilibrium is thus disturbed. However, the increase in concentration of vapor molecules then increases the rate at which molecules condense to liquid. Equilibrium is soon reestablished, but at a higher equilibrium vapor pressure.

### Volatile and Nonvolatile Liquids

Because all liquids have characteristic forces of attraction between their particles, every liquid has a specific equilibrium vapor pressure at a given temperature. The stronger these attractive forces are, the smaller is the percentage of liquid particles that can evaporate at any given temperature. A low percentage of evaporation results in a low equilibrium vapor pressure. **Volatile liquids**, which are liquids that evaporate readily, have relatively weak forces of attraction between particles. Ether is a typical volatile liquid. Nonvolatile liquids, which evaporate slowly, have relatively strong attractive forces between particles. Molten ionic compounds are examples of nonvolatile liquids.

It is important not to confuse the equilibrium vapor pressure of a liquid with the pressure of a vapor not in equilibrium with its corresponding liquid. The equilibrium vapor pressure of a liquid depends only on temperature. The pressure of a vapor not in equilibrium with the corresponding liquid follows the gas laws, like any other gas. Its pressure is inversely proportional to its volume at constant temperature, according to Boyle's law.

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## Boiling

Equilibrium vapor pressures can be used to explain and define the concept of boiling, which you read about in Section 12-1. **Boiling** is the conversion of a liquid to a vapor within the liquid as well as at its surface. It occurs when the equilibrium vapor pressure of the liquid equals the atmospheric pressure.

If the temperature of the liquid is increased, the equilibrium vapor pressure also increases. Finally, the boiling point is reached. *The boiling point of a liquid is the temperature at which the equilibrium vapor pressure of the liquid equals the atmospheric pressure.* The lower the atmospheric pressure is, the lower the boiling point is. Therefore, at high elevations, where atmospheric pressures are lower than at sea level, a cooking liquid boils at a lower temperature and foods take longer to cook.

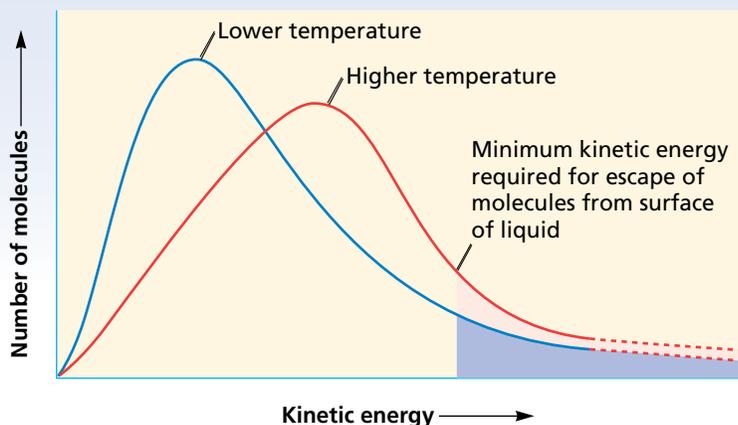
At the boiling point, all of the heat absorbed goes to evaporate the liquid, and the temperature remains constant as long as the pressure does not change. If the pressure above the liquid being heated is increased, the temperature of the liquid will rise until the vapor pressure equals the new pressure and the liquid boils once again. This is the principle behind the operation of a pressure cooker. The cooker is sealed so that steam pressure builds up over the surface of the boiling water inside. The pressure increases the boiling temperature of the water, resulting in shorter cooking times. Conversely, a device called a vacuum evaporator causes boiling at lower-than-normal temperatures. Vacuum evaporators are used to remove water from milk and sugar solutions. Under reduced pressure, the water boils away at a temperature low enough to avoid scorching the milk or sugar. This process is used to prepare evaporated milk and sweetened condensed milk.

At normal atmospheric pressure (1 atm, 760. torr, or 101.3 kPa), the boiling point of water is exactly 100.°C. This temperature is known as the *normal* boiling point of water. The normal boiling points of water and other liquids are shown in Figure 12-12. Note that the normal boiling point of each liquid is the temperature at which the liquid's equilibrium vapor pressure equals 760 torr.

### Energy and Boiling

As you know from experience, heat must be added continuously in order to keep a liquid boiling. A pot of boiling water stops boiling almost immediately after it is removed from the stove. Suppose you were to carefully measure the temperature of a boiling liquid and its vapor. You might be surprised to find that they are at the same constant temperature. The temperature, or average kinetic energy of the particles, at the boiling point remains constant despite the continuous addition of heat. Where does the added heat energy go? It is used to overcome the attractive forces between molecules of the liquid during the liquid-to-gas change. The energy is stored in the vapor as potential energy.

### Energy Distribution of Molecules in a Liquid at Different Temperatures



**FIGURE 12-13** The number of molecules in a liquid with various kinetic energies is represented at two different temperatures. Notice the shaded area, which shows the minimum amount of kinetic energy required for evaporation to take place.

## Molar Heat of Vaporization

The amount of heat energy needed to vaporize one mole of liquid at its boiling point is called the liquid's **molar heat of vaporization**. The magnitude of the molar heat of vaporization is a measure of the attraction between particles of the liquid. The stronger this attraction is, the more energy that is required to overcome it, which results in a higher molar heat of vaporization. Each liquid has a characteristic molar heat of vaporization. Compared with other liquids, water has an unusually high molar heat of vaporization due to the extensive hydrogen bonding in liquid water. This property makes water a very effective cooling agent. When water evaporates from your skin, the escaping molecules carry a great deal of heat away with them. Figure 12-13 shows the distribution of the kinetic energies of molecules in a liquid at two different temperatures. You can see that at the higher temperature a greater portion of the molecules have the kinetic energy required to escape from the liquid surface and become vapor.

## Freezing and Melting

As you learned in Section 12-1, the physical change of a liquid to a solid is called freezing. Freezing involves a loss of heat energy by the liquid and can be represented by the following reaction.



In the case of a pure crystalline substance, this change occurs at constant temperature. The **normal freezing point** is the temperature at which the solid and liquid are in equilibrium at 1 atm (760. torr, or 101.3 kPa) pressure. At the freezing point, particles of the liquid and the solid have the same average kinetic energy. Therefore, the energy loss during freezing is

a loss of potential energy that was present in the liquid. At the same time energy decreases, there is a significant increase in particle order because the solid state of a substance is much more ordered than the liquid state, even at the same temperature.

Melting, the reverse of freezing, also occurs at constant temperature. As a solid melts, it continuously absorbs heat, as represented by the following equation.



For pure crystalline solids, the melting point and freezing point are the same. At equilibrium, melting and freezing proceed at equal rates. The following general equilibrium equation can be used to represent these states.



At normal atmospheric pressure, the temperature of a system containing ice and liquid water will remain at  $0.^{\circ}\text{C}$  as long as both ice and water are present. That temperature will persist no matter what the surrounding temperature. As predicted by Le Châtelier's principle, adding heat to such a system shifts the equilibrium to the right. That shift increases the proportion of liquid water and decreases that of ice. Only after all the ice has melted will the addition of heat increase the temperature of the system.

## Molar Heat of Fusion

*The amount of heat energy required to melt one mole of solid at its melting point is its **molar heat of fusion**.* The heat absorbed increases the potential energy of the solid as its particles are pulled apart, overcoming the attractive forces holding them together. At the same time, there is a significant decrease in particle order as the substance makes the transformation from solid to liquid. Similar to the molar heat of vaporization, the magnitude of the molar heat of fusion depends on the attraction between the solid particles.

## Sublimation and Deposition

At sufficiently low temperature and pressure conditions, a liquid cannot exist. Under such conditions, a solid substance exists in equilibrium with its vapor instead of its liquid, as represented by the following equation.



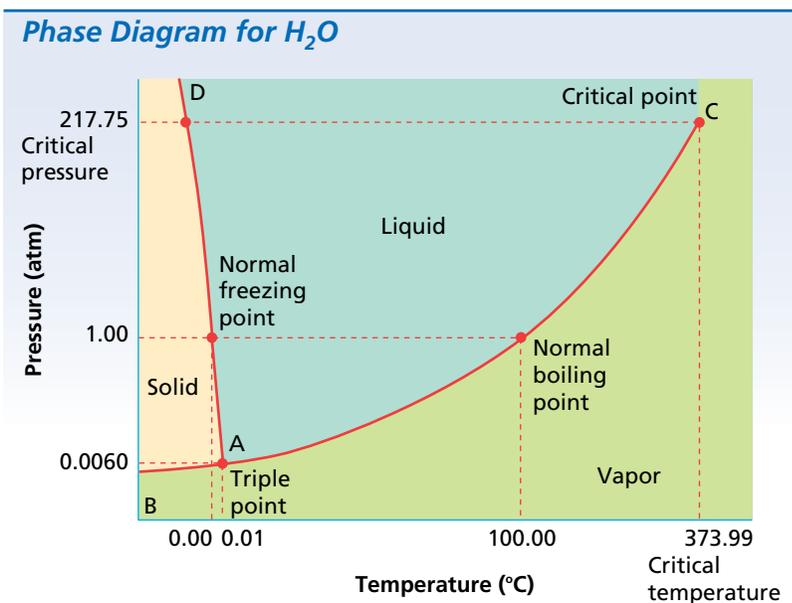
*The change of state from a solid directly to a gas is known as **sublimation**.* The reverse process is called **deposition**, *the change of state from a gas directly to a solid.* Among the common substances that sublime at ordinary temperatures are dry ice (solid  $\text{CO}_2$ ) and iodine. Ordinary ice sublimates slowly at temperatures lower than its melting point ( $0.^{\circ}\text{C}$ ). This explains how a thin layer of snow can eventually disappear, even if the temperature remains below  $0.^{\circ}\text{C}$ . Sublimation occurs in

frost-free refrigerators when the temperature in the freezer compartment is periodically raised to cause any ice that has formed to sublime. A blower then removes the water vapor that has formed. The formation of frost on a cold surface is a familiar example of deposition.

## Phase Diagrams

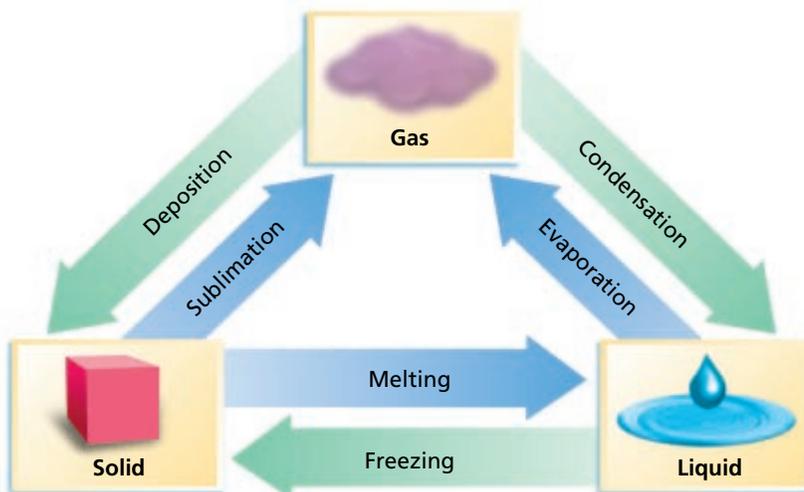
A **phase diagram** is a graph of pressure versus temperature that shows the conditions under which the phases of a substance exist. A phase diagram also reveals how the states of a system change with changing temperature or pressure.

Figure 12-14 shows the phase diagram for water over a range of temperatures and pressures. Note the three curves, AB, AC, and AD. Curve AB indicates the temperature and pressure conditions at which ice and water vapor can coexist at equilibrium. Curve AC indicates the temperature and pressure conditions at which liquid water and water vapor coexist at equilibrium. Similarly, curve AD indicates the temperature and pressure conditions at which ice and liquid water coexist at equilibrium. Because ice is less dense than liquid water, an increase in pressure lowers the melting point. (Most substances have a positive slope for this curve.) Point A is the triple point of water. The **triple point** of a substance indicates the temperature and pressure conditions at which the solid, liquid, and vapor of the substance can coexist at equilibrium. Point C is the critical point of water. The **critical point** of a substance indicates the critical temperature and critical pressure. The **critical temperature** ( $t_c$ ) is the temperature above which the substance cannot exist in the liquid state. The critical temperature of water is  $373.99^\circ\text{C}$ . Above this temperature, water cannot be liquefied, no matter how much pressure is



**FIGURE 12-14** This phase diagram shows the relationships between the physical states of water and its pressure and temperature.

**FIGURE 12-15** Solids, liquids, and gases can undergo various changes of state. The changes shown in green are exothermic, and those shown in blue are endothermic.

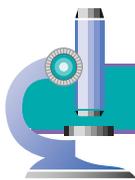


applied. The **critical pressure** ( $P_c$ ) is the lowest pressure at which the substance can exist as a liquid at the critical temperature. The critical pressure of water is 217.75 atm.

The phase diagram in Figure 12-14 indicates the normal boiling point and the normal freezing point of water. It also shows how boiling point and freezing point change with pressure. As shown by the slope of line AD, ice melts at a higher temperature with decreasing pressure. Below the triple point, the temperature of sublimation decreases with decreasing pressure. Foods are freeze-dried by freezing the food and then lowering the pressure to cause the ice in the food to sublime rather than melt. Figure 12-15 summarizes the changes of state of solids, liquids, and gases.

## SECTION REVIEW

1. What is equilibrium?
2. State Le Châtelier's principle.
3. What happens when a liquid-vapor system at equilibrium experiences an increase in temperature? What happens when it experiences a decrease in temperature?
4. What would be an example of deposition?
5. What is the equilibrium vapor pressure of a liquid?
6. What is the boiling point of a liquid?
7. In the phase diagram for water, what is meant by the triple point and the critical point?
8. Refer to the phase diagram for water on page 381 to answer the following questions.
  - a. Describe all the phase changes a sample of solid water would undergo when heated to its critical temperature at a pressure of 1.00 atm.
  - b. Describe all the phase changes a sample of water vapor would undergo when cooled to 5°C at a pressure of 1.00 atm.
  - c. At approximately what pressure will water be a vapor at 0°C?
  - d. Within what range of pressures will water be a liquid at temperatures above its normal boiling point?



# Phase-Change Materials

**T**he real estate ad of tomorrow could read like this: “Just listed! Perfect starter home! Two bedrooms, 2 1/2 baths, walk-in closets, heats and cools itself with minimal electricity or other power.” Ival Salyer, a senior research scientist at the University of Dayton Research Institute, says that homes like these may soon be commonplace. Phase-change technology will help control indoor temperature with walls that melt or freeze a bit as the weather changes.

When any material goes through a change in its physical form or state, it releases or absorbs heat. Salyer has designed walls that work on this principle. The wallboards are filled with a type of paraffin that melts or freezes above or below 75°F. When the temperature outside rises above 75°F, the paraffin melts and absorbs the heat inside the house. The opposite happens when the outdoor temperature drops. This change of state keeps the temperature of a house comfortably constant while using little power other than the heat of the sun.

By heating the material with electricity overnight, heat could be stored by changing the paraffin in the walls to a liquid state. When the heat is discontinued, the walls would freeze, radiating heat into the house and keeping it warm all day.

According to Salyer, because state change is an inherent



*Changes of state are physical changes that can be exothermic or endothermic, depending on the direction of energy flow between an object and its surroundings.*

property of matter, the walls heat and cool automatically, with no need for monitoring by people and no degradation from wear.

Another recent discovery that can dramatically reduce building, heating, and cooling costs is the use of molded inserts of phase-change materials in the hollow spaces of hollow-core concrete blocks. In the outside walls of buildings, this phase-change material can store warmth from the winter sun for heating and the coolness of a summer night for cooling.

Salyer foresees this technology being used in dozens of other applications. Phase-change material is already being marketed as a food warmer; after being microwaved for a few minutes, a pillow-like pad can release heat for hours. The same idea is being

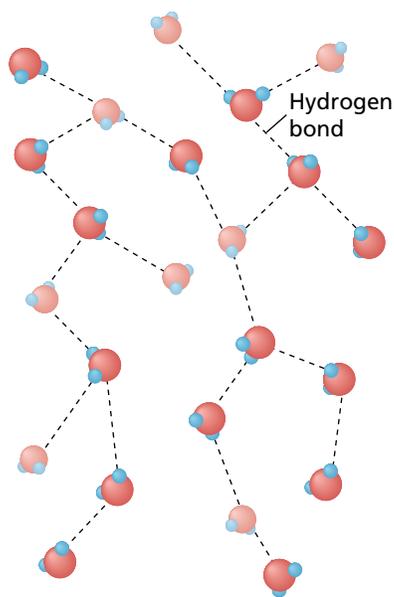
adapted for use with bowls and plates to keep food warm. Winter weather might not feel quite so harsh with phase-change material lining coats, hats, and gloves. Phase-change flowerpots could keep plants warm, and the asphalt of highway bridges and liners for car batteries could be protected from freezing with the use of phase-change materials. Phase-change uniforms for firefighters and soldiers could keep them comfortably cool, and the material could be used as a protective, heat-resistant coating around airplane flight-data recorders.

1. How does Ival Salyer think his research into phase-change materials will benefit society?
2. What benefits do you see for Mr. Salyer's research?

## SECTION 12-4

### OBJECTIVES

- Describe the structure of a water molecule.
- Discuss the physical properties of water. Explain how they are determined by the structure of water.
- Calculate the amount of heat energy absorbed or released when a quantity of water changes state.



Liquid water

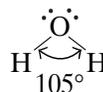
**FIGURE 12-16** The structure of liquid water shows that within the water molecule, oxygen and hydrogen are covalently bonded to each other, while the molecules are held together in groups by hydrogen bonds.

# Water

Water is a familiar substance in all three physical states: solid, liquid, and gas. On Earth, water is by far the most abundant liquid. Oceans, rivers, and lakes cover about 75% of Earth's surface. Significant quantities of water are also frozen in glaciers. Water is an essential component of all organisms; 70% to 90% of the mass of living things is water. The chemical reactions of most life processes take place in water, and water is frequently a reactant or product in such reactions. In order to better understand the importance of water, let us take a closer look at its structure and its properties.

## Structure of Water

As discussed in Chapter 6, water molecules consist of two atoms of hydrogen and one atom of oxygen united by polar-covalent bonds. Research shows that a water molecule is bent. The structure can be represented as follows.



The angle between the two hydrogen-oxygen bonds is about 105°. This is close to the angle expected for  $sp^3$  hybridization of the oxygen-atom orbitals.

The molecules in solid or liquid water are linked by hydrogen bonding. The number of linked molecules decreases with increasing temperature because increases in kinetic energy make hydrogen bond formation difficult. Nevertheless, there are usually from four to eight molecules per group in liquid water, as shown in Figure 12-16. If it were not for these molecular groups, water would be a gas at room temperature. Nonpolar molecules, such as methane,  $\text{CH}_4$ , that are similar in size and mass to water molecules, do not undergo hydrogen bonding. Such substances are gases at room temperature.

Ice consists of water molecules in the hexagonal arrangement shown in Figure 12-17. The empty spaces between molecules in this pattern account for the relatively low density of ice. As ice is heated, the increased energy of the molecules causes them to move and vibrate more vigorously. When the melting point is reached, the energy of the

molecules is so great that the rigid open structure of the ice crystals breaks down, and ice turns into liquid water.

Figures 12-16 and 12-17 also show that the hydrogen bonds between molecules of liquid water at  $0^{\circ}\text{C}$  are fewer and more disordered than those between molecules of ice at the same temperature. Because the rigid open structure of ice has broken down, water molecules can crowd closer together. Thus, liquid water is denser than ice.

As the liquid water is warmed from  $0^{\circ}\text{C}$ , the water molecules crowd still closer together. Water molecules are as tightly packed as possible at  $3.98^{\circ}\text{C}$ . At temperatures above  $3.98^{\circ}\text{C}$ , the increasing kinetic energy of the water molecules causes them to overcome molecular attractions. The molecules move farther apart as the temperature continues to rise. As the temperature approaches the boiling point, groups of liquid water molecules absorb enough energy to break up into separate molecules. Because of hydrogen bonding between water molecules, a high kinetic energy is needed, causing water's boiling point to be relatively high ( $100^{\circ}\text{C}$ ) compared to other liquids that have similar molar masses.

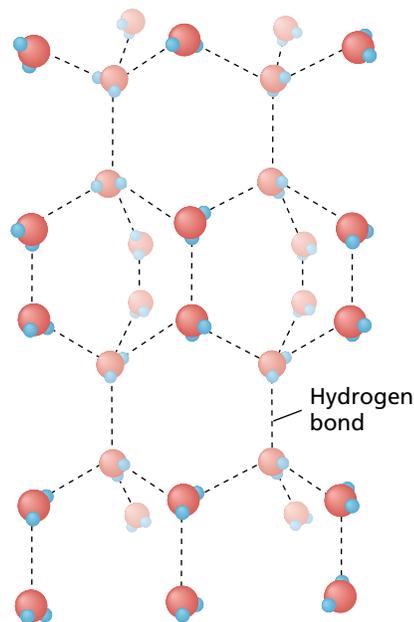
## Physical Properties of Water

At room temperature, pure liquid water is transparent, odorless, tasteless, and almost colorless. Any observable odor or taste is caused by impurities such as dissolved minerals, liquids, or gases.

As shown by its phase diagram in Figure 12-14 on page 381, water freezes at a pressure of 1 atm (101.3 kPa) and melts at  $0^{\circ}\text{C}$ . The molar heat of fusion of ice is 6.009 kJ/mol. That value is relatively large compared with the molar heats of fusion of other solids. As you have read, water has the unusual property of expanding in volume as it freezes because its molecules form an open rigid structure. As a result, ice at  $0^{\circ}\text{C}$  has a density of only about  $0.917\text{ g/cm}^3$ , compared with a density of  $0.99984\text{ g/cm}^3$  for liquid water at  $0^{\circ}\text{C}$ .

This lower density explains why ice floats in liquid water. The insulating effect of floating ice is particularly important in the case of large bodies of water. If ice were more dense than liquid water, it would sink to the bottom of lakes and ponds, where it would be less likely to melt completely. The water of such bodies of water in temperate climates would eventually freeze solid, killing nearly all the living things in it.

Under a pressure of 1 atm (101.3 kPa), water boils at  $100^{\circ}\text{C}$ . At this temperature, water's molar heat of vaporization is 40.79 kJ/mol. Both the boiling point and the molar heat of vaporization of water are quite high compared with those of nonpolar substances of comparable molecular mass, such as methane. The values are high because of the strong hydrogen bonding that must be overcome for boiling to occur. The high molar heat of vaporization makes water useful for household steam-heating systems. The steam (vaporized water) stores a great deal of heat. When the steam condenses in radiators, great quantities of heat are released.



Ice

**FIGURE 12-17** Ice contains the same types of bonding as liquid water. However, the structure of the hydrogen bonding is much more rigid and open than it is in liquid water.

## SAMPLE PROBLEM 12-1

**How much heat energy is absorbed when 47.0 g of ice melts at STP? How much heat energy is absorbed when this same mass of liquid water boils?**

### SOLUTION

#### 1 ANALYZE

**Given:** mass of  $\text{H}_2\text{O}(s) = 47.0 \text{ g}$   
mass of  $\text{H}_2\text{O}(l) = 47.0 \text{ g}$   
molar heat of fusion of ice =  $6.009 \text{ kJ/mol}$  (given on page 385)  
molar heat of vaporization =  $40.79 \text{ kJ/mol}$  (given on page 385)

**Unknown:** heat energy absorbed when ice melts  
heat energy absorbed when liquid water boils

#### 2 PLAN

First, convert the mass of water in grams to moles.

$$\text{g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = \text{mol H}_2\text{O}$$

Then, use the molar heat of fusion of a solid to calculate the amount of heat absorbed when the solid melts. Multiply the number of moles by the amount of energy needed to melt one mole of ice at its melting point (the molar heat of fusion of ice). Using the same method, calculate the amount of heat absorbed when water boils by using the molar heat of vaporization.

amount of substance (mol)  $\times$  molar heat of fusion or vaporization (kJ/mol) = heat energy (kJ)

#### 3 COMPUTE

$$47.0 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 2.61 \text{ mol H}_2\text{O}$$

$$2.61 \text{ mol} \times 6.009 \text{ kJ/mol} = 15.7 \text{ kJ (on melting)}$$

$$2.61 \text{ mol} \times 40.79 \text{ kJ/mol} = 106 \text{ kJ (on vaporizing or boiling)}$$

#### 4 EVALUATE

Units have canceled correctly. The answers have the proper number of significant digits and are reasonably close to estimated values of  $18 (3 \times 6)$  and  $120 (3 \times 40)$ , respectively.

### PRACTICE

1. What quantity of heat energy is released when 506 g of liquid water freezes? *Answer*  
169 kJ
2. What mass of steam is required to release  $4.97 \times 10^5 \text{ kJ}$  of heat energy on condensation? *Answer*  
 $2.19 \times 10^5 \text{ g}$

## SECTION REVIEW

1. Why is a water molecule polar?
2. How is the structure of water responsible for some of water's unique characteristics?
3. Describe the arrangement of molecules in liquid water and in ice.
4. Why does ice float? Why is this phenomenon important?

# CHAPTER 12 REVIEW

## CHAPTER SUMMARY

- 12-1**
- The particles of a liquid are closer together and more ordered than those of a gas and less ordered than those of a solid.
  - Liquids have a definite volume and a fairly high density, and they are relatively incompressible. Like gases, liquids can flow and are thus consid-

### Vocabulary

capillary action (365)

fluid (363)

evaporation (365)

freezing (366)

ered to be fluids. Liquids can dissolve other substances.

- Liquids have the ability to diffuse. They exhibit surface tension, and they can evaporate or boil. A liquid is said to freeze when it becomes a solid.

surface tension (365)

vaporization (365)

- 12-2**
- The particles of a solid are not nearly so free to move about as are those of a liquid or a gas. They can only vibrate about definite, fixed positions.
  - Solids have a definite shape and may be crystalline or amorphous. They have a definite volume and are generally nonfluid. Additional characteristics of solids are high density, incompressibility, extremely low rates of diffusion, and definite melting points (for crystals).
  - A crystal structure is the total three-dimensional

### Vocabulary

amorphous solids (368)

crystal structure (369)

crystal (368)

crystalline solids (368)

array of points that describes the arrangement of the particles of a crystal. A crystal can be classified into one of seven crystalline systems on the basis of the three-dimensional shape of its unit cell. A crystal can also be described as one of four types, based on the kind of particles it contains and the type of chemical bonding between its particles.

- Amorphous solids do not have a regular shape. Instead, they take on whatever shape is imposed on them.

melting (368)

supercooled liquids (368)

melting point (368)

unit cell (369)

- 12-3**
- A liquid in a closed system will gradually reach a liquid-vapor equilibrium as the rate at which molecules condense equals the rate at which they evaporate.
  - When two opposing changes occur at equal rates in the same closed system, the system is said to be in dynamic equilibrium. Le Châtelier's principle states that if any factor determining an equilibrium is changed, the system will adjust itself in a way that tends to minimize that change.
  - The pressure exerted by a vapor in equilibrium with its corresponding liquid at a given tempera-

### Vocabulary

boiling (378)

critical temperature (381)

boiling point (378)

deposition (380)

condensation (373)

equilibrium (372)

critical point (381)

equilibrium vapor pressure (376)

critical pressure (382)

ture is the liquid's equilibrium vapor pressure. A liquid boils when the equilibrium vapor pressure of the liquid is equal to the atmospheric pressure. The amount of heat energy required to vaporize one mole of liquid at its boiling point is called the molar heat of vaporization.

- Freezing involves a loss of energy, in the form of heat, by a liquid. Melting is the physical change of a solid to a liquid by the addition of heat. The amount of heat required to melt one mole of solid at its melting point is its molar heat of fusion.

freezing point (379)

phase (373)

Le Châtelier's principle (374)

phase diagram (381)

molar heat of fusion (380)

sublimation (380)

molar heat of vaporization (379)

triple point (381)

volatile liquids (377)

CHAPTER SUMMARY *continued*

- 12-4** • Water is a polar-covalent compound. A water molecule has a bent shape and a partial negative charge near its oxygen atom and a partial positive charge near each hydrogen atom.
- The structure and the types of bonds water is able to form are responsible for its relatively high melting point, molar heat of fusion, boiling point, and molar heat of vaporization.
  - The structure and bonding of water also explain why water expands upon freezing and why ice is able to float in liquid water.

## REVIEWING CONCEPTS

1. What is a fluid? (12-1)
2. What is surface tension? (12-1)
3. Give two reasons why evaporation is a crucial process in nature. (12-1)
4. List seven properties of solids, and explain each in terms of the kinetic-molecular theory of solids. (12-2)
5.
  - a. List four common examples of amorphous solids.
  - b. Why is glass sometimes classified as a supercooled liquid?
  - c. Name some uses of glass. (12-2)
6. Distinguish between a crystal structure, a lattice, and a unit cell. (12-2)
7.
  - a. List and describe the four types of crystals in terms of the nature of their component particles and the type of bonding between them.
  - b. What physical properties are associated with each type of crystal? (12-2)
8. Using Figure 12-12, estimate the approximate equilibrium vapor pressure of each of the following at the specified temperature.
  - a. water at 40°C
  - b. water at 80°C
  - c. diethyl ether at 20°C
  - d. ethanol at 60°C (12-3)
9.
  - a. What is sublimation?
  - b. Give two examples of common substances that sublime at ordinary temperatures. (12-3)
10. What is meant by the normal freezing point of a substance? (12-3)
11. Explain why the vapor pressure of a liquid increases with increasing temperature. (12-3)
12. Explain how the attractive forces between the particles in a liquid and the equilibrium vapor pressure of that liquid are related. (12-3)
13.
  - a. Explain the relationship between atmospheric pressure and the actual boiling point of a liquid.
  - b. During continual boiling at this pressure, what is the relationship between the temperature of the liquid and that of its vapor?
  - c. How can this phenomenon be explained? (12-3)
14. Explain the relationship between the magnitude of the molar heat of vaporization of a liquid and the strength of attraction between the particles of that liquid. (12-3)
15. Explain the relationship between the molar heat of fusion of a solid and the strength of attraction between its particles. (12-3)
16. Describe the structure of a water molecule. (12-4)
17. List at least eight physical properties of water. (12-4)

## PROBLEMS

## Molar Heat

18.
  - a. The molar heat of vaporization for water is 40.79 kJ/mol. Express this heat of vaporization in joules per gram.
  - b. The molar heat of fusion for water is 6.009 kJ/mol. Express this heat of fusion in joules per gram.
19. The standard molar heat of vaporization for water is 40.79 kJ/mol. How much energy would be required to vaporize each of the following?
  - a. 5.00 mol H<sub>2</sub>O
  - b. 45.0 g H<sub>2</sub>O
  - c. 8.45 × 10<sup>10</sup> molecules H<sub>2</sub>O

20. The molar heat of fusion for water is 6.009 kJ/mol. How much energy would be required to melt each of the following?  
 a. 12.75 mol ice                      b.  $6.48 \times 10^5$  kg ice
21. Calculate the molar heat of vaporization of a substance given that 0.433 mol of the substance absorbs 36.5 kJ of energy when it is vaporized.
22. Given that a substance has a molar mass of 259.0 g/mol and a 71.8 g sample of the substance absorbs 4.307 kJ when it melts,  
 a. calculate the number of moles in the sample.  
 b. calculate the molar heat of fusion.
23. a. Calculate the number of moles in a liquid sample of a substance that has a molar heat of fusion of 3.811 kJ/mol, given that the sample releases 83.2 kJ when it freezes.  
 b. Calculate the molar mass of this substance if the mass of the sample is 5519 g.

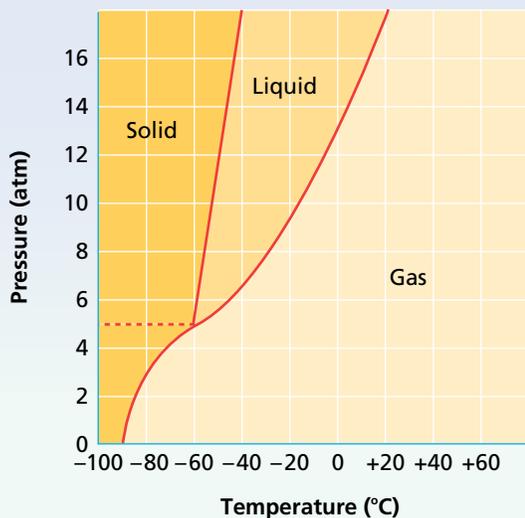
### Water

24. Which contains more molecules of water; 5.00 cm<sup>3</sup> of ice at 0°C or 5.00 cm<sup>3</sup> of liquid water at 0°C? How many more? What is the ratio of the numbers of molecules in these two samples?
25. Which contains more molecules of water (density =  $4.87 \times 10^{-6}$  g/cm<sup>3</sup>); 5.00 cm<sup>3</sup> of liquid water at 0°C or 5.00 cm<sup>3</sup> of water vapor at STP? How many more? What is the ratio of the numbers of molecules in these two samples?
26. a. What volume and mass of steam at 100.°C and 1.00 atm would, during condensation, release the same amount of heat as 100. cm<sup>3</sup> of liquid water during freezing?  
 b. What do you note, qualitatively, about the relative volumes and masses of steam and liquid water required to release the same amount of heat? (Hint: See Sample Problem 12-1.)

### MIXED REVIEW

27. Find the molar heat of vaporization for a substance, given that 3.21 mol of the substance absorbs 28.4 kJ of energy when it changes from a liquid to a gas.
28. Water's molar heat of fusion is 6.009 kJ/mol. Calculate the amount of energy required to melt  $7.95 \times 10^5$  g of ice.
29. A certain substance has a molar heat of vaporization of 31.6 kJ/mol. How much of the substance is in a sample that requires 57.0 kJ to vaporize?
30. Given that water has a molar heat of vaporization of 40.79 kJ/mol, how many grams of water could be vaporized by 0.545 kJ?
31. Calculate the amount of energy released by the freezing of 13.3 g of a liquid substance, given that the substance has a molar mass of 82.9 g/mol and a molar heat of fusion of 4.60 kJ/mol.
32. What volume and mass of steam at 100.°C and 760. torr would release the same amount of heat during condensation as 65.5 cm<sup>3</sup> of liquid water would release during freezing?
33. A substance has a molar heat of fusion of 3.43 kJ/mol. Calculate the molar mass of the substance, given that a 64.2 g sample of it absorbs 2.77 kJ on melting.
34. The following liquid-vapor system is at equilibrium at a given temperature in a closed system.
- $$\text{liquid} + \text{heat energy} \rightleftharpoons \text{vapor}$$
- Suppose the temperature is increased and equilibrium is established at the higher temperature. How does the final value of each of the following compare with its initial value? (In each case, answer either higher, lower, or the same.)  
 a. the rate of evaporation  
 b. the rate of condensation  
 c. the final concentration of vapor molecules  
 d. the final number of liquid molecules
35. Decide whether the temperature of a liquid-vapor equilibrium system should be increased or decreased to make each of the following changes in the system.  
 a. an increased final rate of evaporation  
 b. an increased final concentration of vapor  
 c. an increased final rate of condensation  
 d. an increased final number of liquid molecules.
36. Given a sample of water at any point on curve AB in Figure 12-14, what effect would each of the following changes have on that sample?  
 a. adding heat energy at constant pressure  
 b. decreasing the volume at constant temperature  
 c. removing heat energy at constant pressure  
 d. increasing the volume at constant temperature

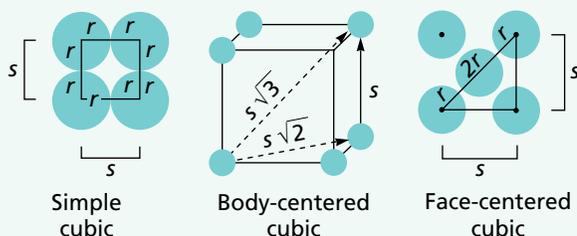
37. Using the phase diagram for  $\text{CO}_2$ , describe all the phase changes that would occur when  $\text{CO}_2$  is heated from  $-100^\circ\text{C}$  to  $-10^\circ\text{C}$  at a constant pressure of 6 atm.

 **$\text{CO}_2$  Phase Diagram****CRITICAL THINKING**

38. **Applying Ideas** Explain the role of humidity of the air in determining relative comfort on a hot day.
39. **Interpreting Concepts** During the freezing of a substance, energy is being removed from that substance. Yet the temperature of the liquid-solid system remains constant. Explain this phenomenon.
40. **Applying Models** At normal atmospheric pressure, the temperature of an ice-water system remains at  $0^\circ\text{C}$  as long as both ice and liquid water are present, regardless of the surrounding temperature. Explain this in terms of Le Châtelier's principle.
41. Describe the forces that must be overcome to explain why the heat of vaporization of a substance is always greater than its heat of fusion.
42. **Predicting Outcomes** Given a sample of water at any point on curve AD in Figure 12-14, how could more of the liquid water in that sample be converted into a solid without changing the temperature? Explain your reasoning.

43. **Interpreting Diagrams** Refer to the phase diagram in question 37.
- Explain what happens when solid  $\text{CO}_2$  ("dry ice") warms up to room temperature at normal atmospheric pressure.
  - Is there a pressure below which liquid  $\text{CO}_2$  cannot exist? Estimate that pressure from the graph.
44. **Interpreting Concepts** Methane,  $\text{CH}_4$ , which is similar to water in molecular size and mass, is a gas at room temperature. However, water is a liquid at that temperature. Explain why.
45. Three simple unit cells found in metals are shown below. The dimensions of each unit cell can be described mathematically using the following information.

$s$  = length of the edge  
 $r$  = atomic radius



Which of the following relationships applies to the simple cubic cell?

- $2r = s$
  - $8r = 2s$
  - $r = s$
  - $2s = r$
46. Which of the following relationships applies to the face-centered cubic cell?
- $2s = 4r$
  - $2r = s$
  - $4r = s\sqrt{2}$
  - $3r = s$

**TECHNOLOGY & LEARNING**

47. **Graphing Calculator** Calculating Vapor Pressure Using a Table

The graphing calculator can run a program that calculates a table for the vapor pressure in atmospheres at different temperatures (K) given the number of moles of a gas and its volume (V). Given a 0.50 mol gas sample with a volume of 10 L, you can calculate the pres-

sure at 290 K, using a table. Use this program to create the table. Next, use the table to perform the calculations.

Go to Appendix C. If you are using a TI 83 Plus, you can download the program and data and run the application as directed. If you are using another calculator, your teacher will provide you with keystrokes and data sets to use. Remember that you will need to name the program and check the display, as explained in Appendix C. You will then be ready to run the program. After you have graphed the data, answer these questions.

Note: All answers show five significant digits.

- What is the pressure for a gas with a mass of 1.3 mol, volume of 8.0 L, and temperature of 320° K?
- What is the pressure for a gas with a mass of 1.5 mol, volume of 10.0 L, and temperature of 340° K?
- Two gases are measured at 300° K. One has a mass of 1.3 mol and has a volume of 7.5 L, and the other has a mass of 0.5 mol and a volume of 10.0 L. Which gas has the lesser pressure?



## HANDBOOK SEARCH

- The *Elements Handbook* contains a table of properties for each group that includes information on the crystal structures of the elements. Most metals crystallize in one of three lattice arrangements: body-centered cubic, face-centered cubic, or hexagonal close-packed. Figure 12-7 shows a model of the face-centered cubic lattice for sodium chloride. Use this figure and the information in the *Elements Handbook* to answer the following.
  - What elements in Group 2 have the same lattice structure as sodium chloride?

- How would the model of an element in a face-centered cubic lattice differ from the compound shown in Figure 12-7?
- The body-centered cubic lattice is the least-efficient packing structure of the metals. What elements in Groups 1 and 2 show this arrangement?

## RESEARCH & WRITING

- Ceramics are formed from silicates found in the soil. Artists use them to create pottery, but engineers and scientists have created ceramics with superconductive properties. Investigate the growing field of superconductive ceramics.
- Liquid crystals are substances that possess the combined properties of both liquids and crystals. Write a report on these substances and the various uses we are finding for them.
- Consult reference materials at the library, and prepare a report on the process of freeze-drying, describing its history and applications.
- Prepare a report about the adjustments that must be made when cooking and baking at high elevations. Collect instructions for high-elevation adjustments from packages of prepared food mixes. Explain why changes must be made in recipes that will be prepared at high elevations. Check your library for cookbooks containing information about food preparation at high elevations.

## ALTERNATIVE ASSESSMENT

- Compile separate lists of crystalline and amorphous solids found in your home. Compare your lists with those of your classmates.
- Design an experiment to grow crystals of various safe, common household materials. Record the conditions under which each type of crystal is best grown.