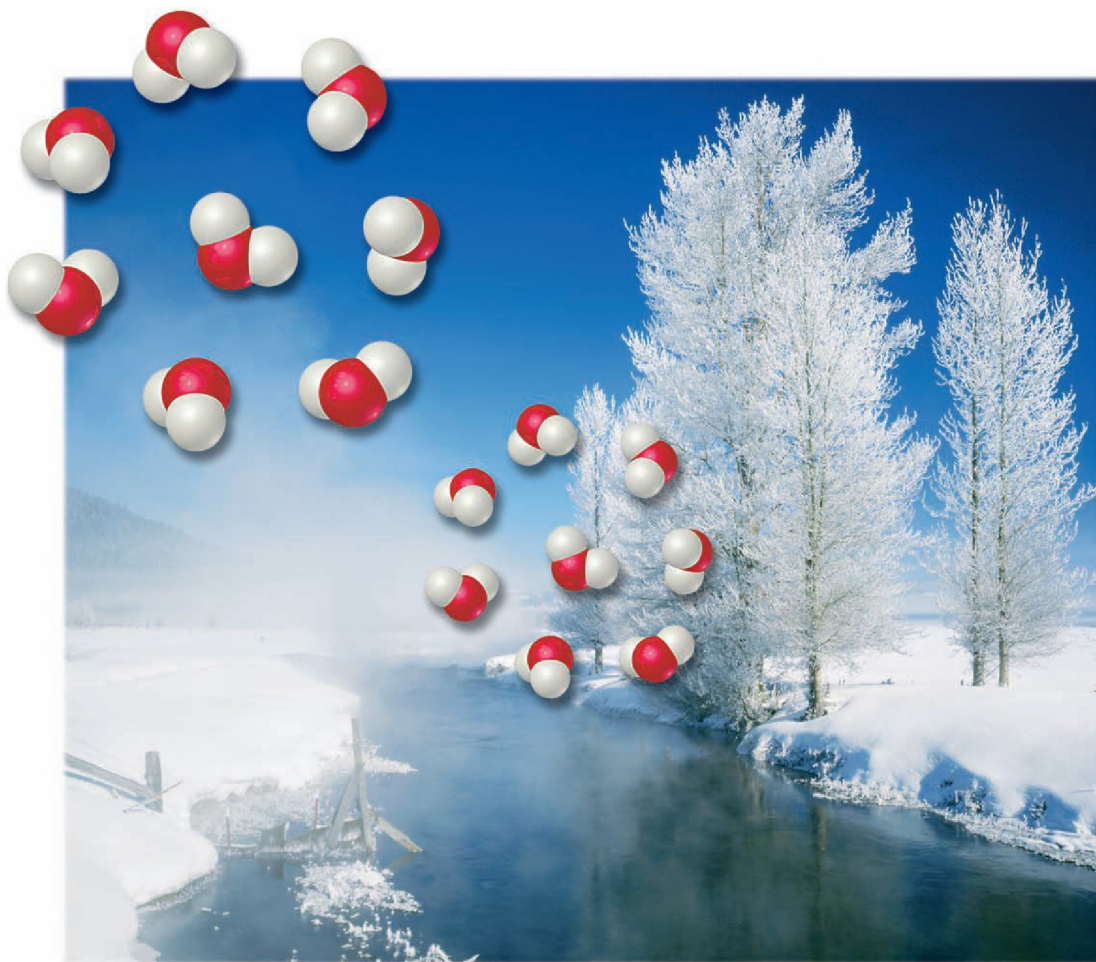


CHAPTER
11

INTERMOLECULAR FORCES, LIQUIDS, AND SOLIDS



THE WATER IN HOT SPRINGS is at least 5–10 °C warmer than the mean annual air temperature where they are located. There are over 1000 hot springs in the United States, the majority in the West. Some hot springs are popular for bathing, while others are far too hot for people to enter them safely.

11.1 A Molecular Comparison of Gases, Liquids, and Solids

We begin with a brief comparison of solids, liquids, and gases from a molecular perspective. This comparison reveals the important roles that temperature and *intermolecular forces* play in determining the physical state of a substance.

11.2 Intermolecular Forces

We then examine the main kinds of intermolecular forces that occur within and between substances: *ion-dipole forces*, *dipole-dipole forces*, *London dispersion forces*, and *hydrogen bonds*.

11.3 Some Properties of Liquids

We will learn that the nature and strength of the intermolecular forces between molecules are largely responsible for many properties of liquids, including their *viscosity*, which is a measure of a liquid's resistance to flow, and *surface tension*, which is a measure of a liquid's resistance to increasing its surface area.

11.4 Phase Changes

We will explore *phase changes*—the transitions of matter between the gaseous, liquid, and solid states—and their associated energies.

11.5 Vapor Pressure

We will examine the *dynamic equilibrium* that exists between a liquid and its gaseous state and introduce the idea of *vapor pressure*. A liquid boils when its vapor pressure equals the pressure acting on the surface of the liquid.

11.6 Phase Diagrams

We will recognize that in a *phase diagram* the equilibria among the gaseous, liquid, and solid phases are displayed graphically.

11.7 Structures of Solids

We then observe that the orderly arrangements of molecules or ions in three dimensions characterize *crystalline solids*. We also examine how the structure of a crystalline solid can be conveyed in terms of its *unit cell* and how simple molecules and ions are most efficiently arranged in three dimensions.

11.8 Bonding in Solids

We learn that solids can be characterized and classified according to the attractive forces between their component atoms, molecules, or ions. We examine four such classes: *molecular solids*, *covalent-network solids*, *ionic solids*, and *metallic solids*.

SITTING IN A HOT SPRING ON A SNOWY day is not something many of us have experienced. If we were in the hot spring shown in the chapter-opening photo, however, we would be surrounded simultaneously by all three phases of water—gas, liquid, and solid. The water vapor—

or humidity—in the air, the water in the hot spring, and the surrounding snow are all forms of the same substance, H_2O . They all have the same chemical properties. Their physical properties differ greatly, however, because the physical properties of a substance depend on its physical state. In Chapter 10 we discussed the gaseous state in some detail. In this chapter we turn our attention to the physical properties of liquids and solids and to the phase changes that occur between the three states of matter.

Many of the substances that we will consider in this chapter are molecular. In fact, virtually all substances that are liquids at room temperature are molecular substances. The intramolecular forces *within* molecules that give rise to covalent bonding influence molecular shape, bond energies, and many aspects of chemical behavior. The physical properties of molecular liquids and solids, however, are due largely to **intermolecular forces**, the forces that exist *between* molecules. We learned in Section 10.9 that attractions between gas molecules lead to deviations from ideal-gas behavior. But how do these intermolecular attractions arise? By understanding the nature and strength of intermolecular forces, we can begin to relate the composition and structure of molecules to their physical properties.

TABLE 11.1 ■ Some Characteristic Properties of the States of Matter

| | |
|--------|---|
| Gas | Assumes both the volume and shape of its container Is compressible Flows readily Diffusion within a gas occurs rapidly |
| Liquid | Assumes the shape of the portion of the container it occupies Does not expand to fill container Is virtually incompressible Flows readily Diffusion within a liquid occurs slowly |
| Solid | Retains its own shape and volume Is virtually incompressible Does not flow Diffusion within a solid occurs extremely slowly |

11.1 A MOLECULAR COMPARISON OF GASES, LIQUIDS, AND SOLIDS

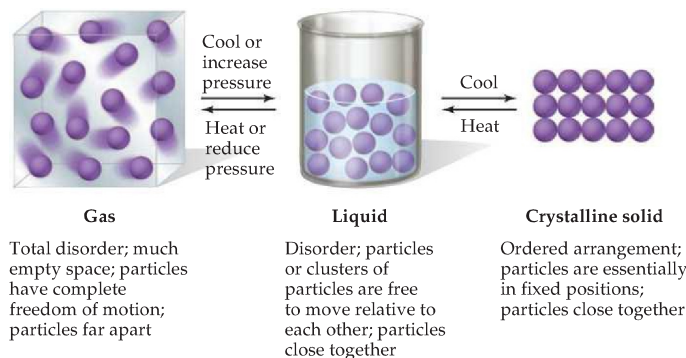
Some of the characteristic properties of gases, liquids, and solids are listed in Table 11.1. These properties can be understood in terms of the energy of motion (kinetic energy) of the particles (atoms, molecules, or ions) of each state, compared to the energy of the intermolecular interactions between those particles. As we learned from the kinetic-molecular theory of gases in Chapter 10, the average kinetic energy, which is related to the particle's average speed, is proportional to the absolute temperature.

Gases consist of a collection of widely separated particles in constant, chaotic motion. The average energy of the attractions between the particles is much smaller than their average kinetic energy. The lack of strong attractive forces between particles allows a gas to expand to fill its container.

In liquids the intermolecular attractive forces are stronger than in gases and are strong enough to hold particles close together. Thus, liquids are much denser and far less compressible than gases. Unlike gases, liquids have a definite volume, independent of the size and shape of their container. The attractive forces in liquids are not strong enough, however, to keep the particles from moving past one another. Thus, any liquid can be poured, and it assumes the shape of whatever portion of its container it occupies.

In solids the intermolecular attractive forces are strong enough to hold particles close together and to lock them virtually in place. Solids, like liquids, are not very compressible because the particles have little free space between them. Because the particles in a solid or liquid are fairly close together compared with those of a gas, we often refer to solids and liquids as *condensed phases*. Often the particles of a solid take up positions in a highly regular three-dimensional pattern. Solids that possess highly ordered three-dimensional structures are said to be *crystalline*. Because the particles of a solid are not free to undergo long-range movement, solids are rigid. Keep in mind, however, that the units that form the solid, whether ions or molecules, possess thermal energy and vibrate in place. This vibrational motion increases in amplitude as a solid is heated. In fact, the energy may increase to the point that the solid either melts or sublimates.

Figure 11.1 compares the three states of matter. The particles that compose the substance can be individual atoms, as in Ar; molecules, as in H₂O; or ions, as in NaCl. *The state of a substance depends largely on the balance between the kinetic energies of the particles and the interparticle energies of attraction.* The kinetic energies, which depend on temperature, tend to keep the particles apart and moving. The interparticle attractions tend to draw the particles together.



◀ **Figure 11.1 Molecular-level comparison of gases, liquids, and solids.** The particles can be atoms, ions, or molecules. The density of particles in the gas phase is exaggerated compared with most real situations.

Substances that are gases at room temperature have weaker interparticle attractions than those that are liquids; substances that are liquids have weaker interparticle attractions than those that are solids.

We can change a substance from one state to another by heating or cooling, which changes the average kinetic energy of the particles. NaCl, for example, which is a solid at room temperature, melts at 801 °C and boils at 1413 °C under 1 atm pressure. N₂O, on the other hand, which is a gas at room temperature, liquefies at -88.5 °C and solidifies at -90.8 °C under 1 atm pressure. As the temperature of a gas decreases, the average kinetic energy of its particles decreases, allowing the attractions between the particles to first draw the particles close together, forming a liquid, and then virtually locking them in place, forming a solid.

Increasing the pressure on a gas forces the molecules closer together, which in turn increases the strength of the intermolecular forces of attraction. Propane (C₃H₈) is a gas at room temperature and 1 atm pressure, whereas liquefied propane (LP) gas is a liquid at room temperature because it is stored under much higher pressure.

GIVE IT SOME THOUGHT

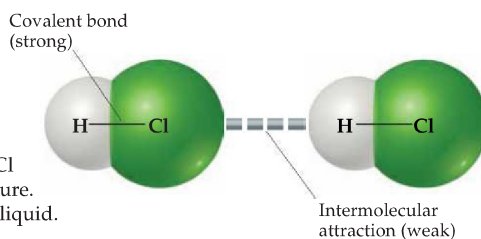
How does the energy of attraction between particles compare with their kinetic energies in (a) a gas, (b) a solid?

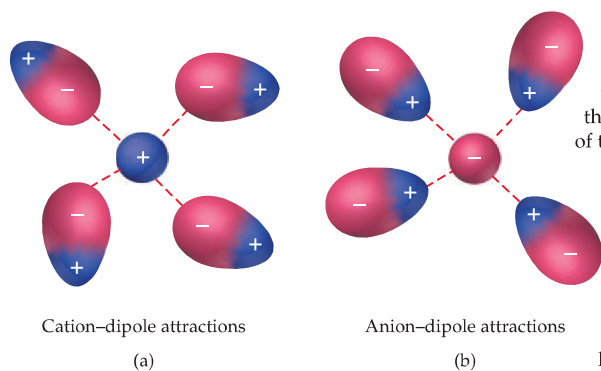
11.2 INTERMOLECULAR FORCES

The strengths of intermolecular forces of different substances vary over a wide range, but they are generally much weaker than ionic or covalent bonds (Figure 11.2▶). Less energy, therefore, is required to vaporize, or evaporate, a liquid or to melt a solid than to break covalent bonds in molecules. For example, only 16 kJ/mol is required to overcome the intermolecular attractions between HCl molecules in liquid HCl to vaporize it. In contrast, the energy required to break the covalent bond to dissociate HCl into H and Cl atoms is 431 kJ/mol. Thus, when a molecular substance such as HCl changes from solid to liquid to gas, the molecules themselves remain intact.

Many properties of liquids, including their *boiling points*, reflect the strengths of the intermolecular forces. For example, because the forces between HCl molecules are so weak, HCl boils at a very low temperature, -85 °C at atmospheric pressure. A liquid boils when bubbles of its vapor form within the liquid.

▼ **Figure 11.2 Intermolecular attraction.** Comparison of a covalent bond (an intramolecular force) and an intermolecular attraction. Because intermolecular attractions are weaker than covalent bonds, they are usually represented by dashes or dots.





▲ **Figure 11.3 Ion-dipole attractions.** Illustration of the preferred orientations of polar molecules toward ions. The negative end of the dipoles is oriented toward a cation (a), and the positive end of the dipoles is oriented toward an anion (b).

The molecules of a liquid must overcome their attractive forces to separate and form a vapor. The stronger the attractive forces are, the higher the temperature at which the liquid boils. Similarly, the *melting points* of solids increase as the strengths of the intermolecular forces increase.

Three types of intermolecular attractions exist between neutral molecules: dipole-dipole attractions, London dispersion forces, and hydrogen bonding. The first two forms of attraction are collectively called *van der Waals forces* after Johannes van der Waals, who developed the equation for predicting the deviation of gases from ideal behavior. ∞ (Section 10.9) Another kind of attractive force, the ion-dipole force, is important in solutions. All of these intermolecular

interactions are electrostatic in nature, involving attractions between positive and negative species. Even at their strongest, these interactions are much weaker than covalent or ionic bonds (<15% as strong).

Ion-Dipole Forces

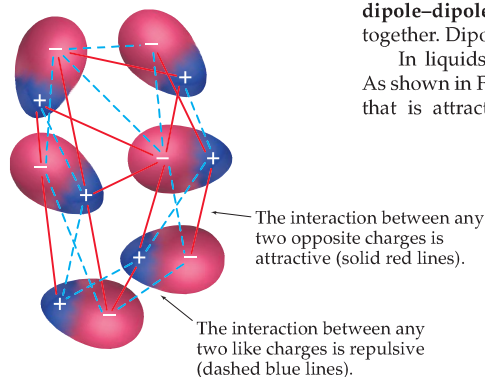
An **ion-dipole force** exists between an ion and the partial charge on the end of a polar molecule. Polar molecules are dipoles; they have a positive end and a negative end. ∞ (Section 9.3) HCl is a polar molecule, for example, because the electronegativities of the H and Cl atoms differ.

Positive ions are attracted to the negative end of a dipole, whereas negative ions are attracted to the positive end, as shown in Figure 11.3▲. The magnitude of the attraction increases as either the charge of the ion or the magnitude of the dipole moment increases. Ion-dipole forces are especially important for solutions of ionic substances in polar liquids, such as a solution of NaCl in water. ∞ (Section 4.1) We will discuss these solutions in more detail in Section 13.1.

GIVE IT SOME THOUGHT

In which of the following mixtures do you encounter ion-dipole forces: CH_3OH in water or $\text{Ca}(\text{NO}_3)_2$ in water?

▼ **Figure 11.4 Dipole-dipole attractions.** The interaction of many dipoles in a condensed state. There are both repulsive interactions between like charges and attractive interactions between unlike charges, but the attractive interactions predominate.



Dipole-Dipole Forces

Neutral polar molecules attract each other when the positive end of one molecule is near the negative end of another, as shown in Figure 11.4◀. These **dipole-dipole forces** are effective only when polar molecules are very close together. Dipole-dipole forces are generally weaker than ion-dipole forces.

In liquids polar molecules are free to move with respect to one another. As shown in Figure 11.4, the polar molecules will sometimes be in an orientation that is attractive (red solid lines) and sometimes in an orientation that is repulsive (blue dashed lines). Two molecules that are attracting each other spend more time near each other than do two that are repelling each other. Thus, the overall effect is a net attraction. When we examine various liquids, we find that *for molecules of approximately equal mass and size, the strengths of intermolecular attractions increase with increasing polarity*. We can see this trend in Table 11.2▶, which lists several substances with similar molecular weights but different dipole moments. Notice that the boiling point increases as the dipole moment increases. For dipole-dipole forces to operate, the molecules must be able to get close together in the correct orientation.

TABLE 11.2 Molecular Weights, Dipole Moments, and Boiling Points of Several Simple Organic Substances

| Substance | Molecular Weight (amu) | Dipole Moment μ (D) | Boiling Point (K) |
|--|------------------------|-------------------------|-------------------|
| Propane, $\text{CH}_3\text{CH}_2\text{CH}_3$ | 44 | 0.1 | 231 |
| Dimethyl ether, CH_3OCH_3 | 46 | 1.3 | 248 |
| Methyl chloride, CH_3Cl | 50 | 1.9 | 249 |
| Acetaldehyde, CH_3CHO | 44 | 2.7 | 294 |
| Acetonitrile, CH_3CN | 41 | 3.9 | 355 |

For molecules of comparable polarity, therefore, those with smaller molecular volumes generally experience higher dipole–dipole attractive forces.

GIVE IT SOME THOUGHT

For which of the substances in Table 11.2 are the dipole–dipole attractive forces greatest?

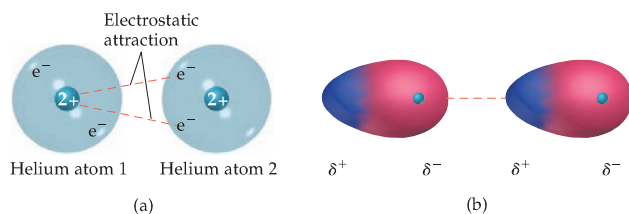
London Dispersion Forces

No dipole–dipole forces exist between nonpolar atoms and molecules, because nonpolar molecules (and atoms) do not have a dipole moment. Some kind of attractive interactions exist, however, because nonpolar gases such as helium and argon can be liquefied. Fritz London, a German-American physicist, first proposed the origin of this attraction in 1930. London recognized that the motion of electrons in an atom or molecule can create an *instantaneous*, or momentary, dipole moment.

In a collection of helium atoms, for example, the *average* distribution of the electrons about each nucleus is spherically symmetrical. The atoms are nonpolar and possess no permanent dipole moment. The *instantaneous* distribution of the electrons, however, can be different from the average distribution. If we could freeze the motion of the electrons in a helium atom at any given instant, both electrons could be on one side of the nucleus. At just that instant, then, the atom would have an instantaneous dipole moment.

The motions of electrons on one atom influence the motions of electrons on its neighbors. The temporary dipole on one atom can induce a similar temporary dipole on an adjacent atom, causing the atoms to be attracted to each other as shown in Figure 11.5. This attractive interaction is called the **London dispersion force** (or merely the *dispersion force*). The dispersion force, like dipole–dipole forces, is significant only when molecules are very close together.

The strength of the dispersion force depends on the ease with which the charge distribution in a molecule can be distorted to induce a momentary dipole. The ease with which the electron distribution in a molecule is distorted is called its **polarizability**. We can think of the polarizability of a molecule as a measure of the “squashiness” of its electron cloud; the greater the polarizability of the molecule, the more easily its electron cloud can be distorted to give a momentary dipole. Therefore, more polarizable molecules have larger dispersion forces.



◀ **Figure 11.5 Dispersion forces.** On the average, the charge distribution in the helium atoms is spherical, as represented by the spheres in (a). At a particular instant, however, there can be a nonspherical arrangement of the electrons, as indicated by the location of the electrons (e^-) in (a) and by the nonspherical shape of the electron cloud in (b). The nonspherical electron distributions produce momentary dipoles and allow momentary electrostatic attractions between atoms that are called London dispersion forces or merely dispersion forces.

TABLE 11.3 ■ Boiling Points of the Halogens and the Noble Gases

| Halogen | Molecular Weight (amu) | Boiling Point (K) | Noble Gas | Molecular Weight (amu) | Boiling Point (K) |
|-----------------|------------------------|-------------------|-----------|------------------------|-------------------|
| F ₂ | 38.0 | 85.1 | He | 4.0 | 4.6 |
| Cl ₂ | 71.0 | 238.6 | Ne | 20.2 | 27.3 |
| Br ₂ | 159.8 | 332.0 | Ar | 39.9 | 87.5 |
| I ₂ | 253.8 | 457.6 | Kr | 83.8 | 120.9 |
| | | | Xe | 131.3 | 166.1 |

In general, larger molecules tend to have greater polarizabilities because they have a greater number of electrons, and their electrons are farther from the nuclei. The strength of the dispersion forces, therefore, tends to increase with increasing atomic or molecular size. Because molecular size and mass generally parallel each other, *dispersion forces tend to increase in strength with increasing molecular weight*. Thus, the boiling points of the halogens and the noble gases increase with increasing molecular weight (Table 11.3▲).

GIVE IT SOME THOUGHT

List the substances CCl₄, CBr₄, and CH₄ in order of increasing (a) polarizability, (b) strength of dispersion forces, and (c) boiling point.

The shapes of molecules also influence the magnitudes of dispersion forces. For example, *n*-pentane* and neopentane, illustrated in Figure 11.6◀, have the same molecular formula (C₅H₁₂), yet the boiling point of *n*-pentane is 27 K higher than that of neopentane. The difference can be traced to the different shapes of the two molecules. The overall attraction between molecules is greater for *n*-pentane because the molecules can come in contact over the entire length of the long, somewhat cylindrically shaped molecule. Less contact is possible between the more compact and nearly spherical molecules of neopentane.

Dispersion forces operate between all molecules, whether they are polar or nonpolar. Polar molecules experience dipole–dipole interactions, but they also experience dispersion forces at the same time. In fact, dispersion forces between polar molecules commonly contribute more to intermolecular attractions than do dipole–dipole forces. In liquid HCl, for example, dispersion forces are estimated to account for more than 80% of the total attraction between molecules; dipole–dipole attractions account for the rest.

When comparing the relative strengths of intermolecular attractions in two substances, consider the following generalizations:

1. When the molecules of two substances have comparable molecular weights and shapes, dispersion forces are approximately equal in the two substances. In this case, differences in the magnitudes of the attractive forces are due to differences in the strengths of dipole–dipole attractions, with the more polar molecules having the stronger attractions.
2. When the molecules of two substances differ widely in molecular weights, dispersion forces tend to be decisive in determining which substance has the stronger intermolecular attractions. In this case differences in the magnitudes of the attractive forces can usually be associated with differences in molecular weights, with the substance made up of the more massive molecule having the strongest attractions (assuming similar dipole moments).

*The *n* in *n*-pentane is an abbreviation for the word *normal*. A *normal hydrocarbon* is one in which the carbon atoms are arranged in a straight chain. ∞∞ (Section 2.9)



n-Pentane
(bp = 309.4 K)



Neopentane
(bp = 282.7 K)

▲ **Figure 11.6 Molecular shape affects intermolecular attraction.** The *n*-pentane molecules make more contact with each other than do the neopentane molecules. Thus, *n*-pentane has the greater intermolecular attractive forces and therefore has the higher boiling point (bp).

The hydrogen bond, which we consider after Sample Exercise 11.1, is a special type of dipole–dipole attraction that is typically stronger than dispersion forces.

SAMPLE EXERCISE 11.1 | Comparing Intermolecular Forces

The dipole moments of acetonitrile, CH_3CN , and methyl iodide, CH_3I , are 3.9 D and 1.62 D, respectively. (a) Which of these substances has greater dipole–dipole attractions among its molecules? (b) Which of these substances has greater London dispersion attractions? (c) The boiling points of CH_3CN and CH_3I are 354.8 K and 315.6 K, respectively. Which substance has the greater overall attractive forces?

SOLUTION

(a) Dipole–dipole attractions increase in magnitude as the dipole moment of the molecule increases. Thus, CH_3CN molecules attract each other by stronger dipole–dipole forces than CH_3I molecules do. (b) When molecules differ in their molecular weights, the more massive molecule generally has the stronger dispersion attractions. In this case CH_3I (142.0 g/mol) is much more massive than CH_3CN (41.0 g/mol), so the dispersion forces will be stronger for CH_3I . (c) Because CH_3CN has the higher boiling point, we can conclude that more energy is required to overcome attractive interactions between CH_3CN molecules. Thus, the total intermolecular attractions are stronger for CH_3CN , suggesting that the energies resulting from dipole–dipole forces are decisive when comparing these two substances. Nevertheless, the attractive interactions due to dispersion forces play an important role in determining the properties of CH_3I .

PRACTICE EXERCISE

Of Br_2 , Ne, HCl, HBr, and N_2 , which is likely to have (a) the largest intermolecular dispersion forces, (b) the largest dipole–dipole attractive forces?

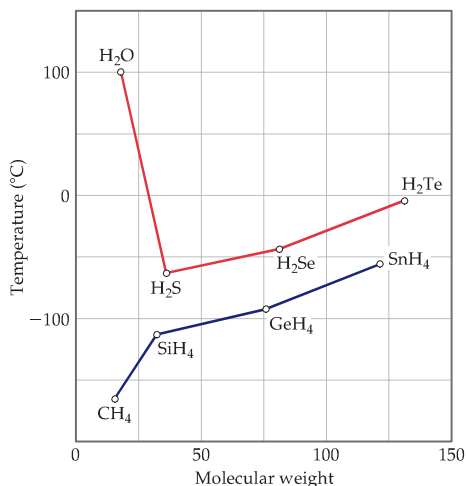
Answers: (a) Br_2 (largest molecular weight), (b) HCl (largest polarity)

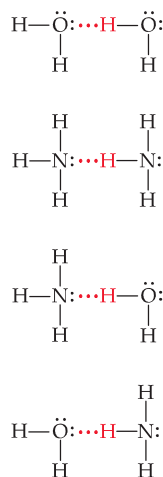
Hydrogen Bonding

Figure 11.7 shows the boiling points of the simple hydrogen compounds of group 4A and 6A elements. In general, the boiling point increases with increasing molecular weight, owing to increased dispersion forces. The notable exception to this trend is H_2O , whose boiling point is much higher than we would expect because of its molecular weight. This observation indicates that there are stronger intermolecular attractions between H_2O molecules than there are between other molecules in the same group. The compounds NH_3 and HF likewise have abnormally high boiling points. In fact, these compounds have many characteristics that distinguish them from other substances of similar molecular weight and polarity. For example, water has a high melting point, a high specific heat, and a high heat of vaporization. Each of these properties indicates that the intermolecular forces between H_2O molecules are abnormally strong.

The strong intermolecular attractions in H_2O result from hydrogen bonding. **Hydrogen bonding** is a special type of intermolecular attraction between the hydrogen atom in a polar bond (particularly an $\text{H}-\text{F}$, $\text{H}-\text{O}$, or $\text{H}-\text{N}$ bond) and nonbonding electron pair on a nearby small electronegative ion or atom (usually an F, O, or N atom in another molecule). For example, a hydrogen bond exists between the H atom in an HF molecule and the F atom of an adjacent HF molecule, $\text{F}-\text{H}\cdots\text{F}-\text{H}$ (where the

▼ **Figure 11.7 Boiling point as a function of molecular weight.** The boiling points of the group 4A (bottom) and 6A (top) hydrides are shown as a function of molecular weight. In general, the boiling points increase with increasing molecular weight, because of the increasing strength of dispersion forces. The very strong hydrogen-bonding forces between H_2O molecules, however, cause water to have an unusually high boiling point.

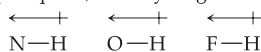




▲ **Figure 11.8** Examples of hydrogen bonding. The solid lines represent covalent bonds; the red dotted lines represent hydrogen bonds.

dots represent the hydrogen bond between the molecules). Several additional examples are shown in Figure 11.8 ◀.

Hydrogen bonds can be considered unique dipole–dipole attractions. Because F, N, and O are so electronegative, a bond between hydrogen and any of these three elements is quite polar, with hydrogen at the positive end:



The hydrogen atom has no inner core of electrons. Thus, the positive side of the bond dipole has the concentrated charge of the partially exposed, nearly bare proton of the hydrogen nucleus. This positive charge is attracted to the negative charge of an electronegative atom in a nearby molecule. Because the electron-poor hydrogen is so small, it can approach an electronegative atom very closely and thus interact strongly with it.

■ SAMPLE EXERCISE 11.2 Identifying Substances that Can Form Hydrogen Bonds

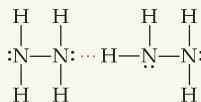
In which of the following substances is hydrogen bonding likely to play an important role in determining physical properties: methane (CH_4), hydrazine (H_2NNH_2), methyl fluoride (CH_3F), or hydrogen sulfide (H_2S)?

SOLUTION

Analyze: We are given the chemical formulas of four substances and asked to predict whether they can participate in hydrogen bonding. All of these compounds contain H, but hydrogen bonding usually occurs only when the hydrogen is covalently bonded to N, O, or F.

Plan: We can analyze each formula to see if it contains N, O, or F directly bonded to H. There also needs to be a nonbonding pair of electrons on an electronegative atom (usually N, O, or F) in a nearby molecule, which can be revealed by drawing the Lewis structure for the molecule.

Solve: The criteria listed above eliminate CH_4 and H_2S , which do not contain H bonded to N, O, or F. They also eliminate CH_3F , whose Lewis structure shows a central C atom surrounded by three H atoms and an F atom. (Carbon always forms four bonds, whereas hydrogen and fluorine form one each.) Because the molecule contains a C—F bond and not a H—F bond, it does not form hydrogen bonds. In H_2NNH_2 , however, we find N—H bonds. If we draw the Lewis structure for the molecule, we see that there is a nonbonding pair of electrons on each N atom. Therefore, hydrogen bonds can exist between the molecules as depicted below.



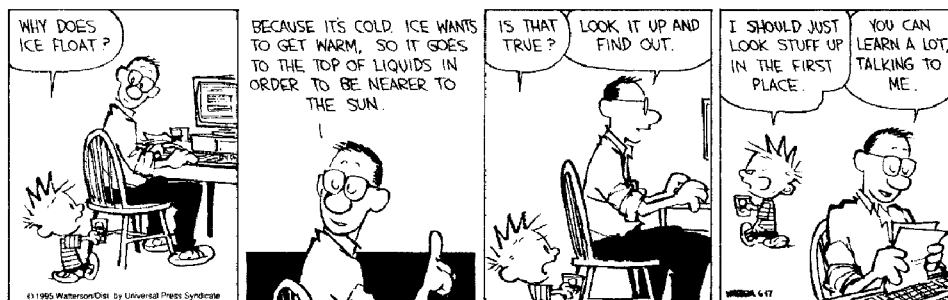
Check: While we can generally identify substances that participate in hydrogen bonding based on their containing N, O, or F covalently bonded to H, drawing the Lewis structure for the interaction, as shown above, provides a way to check the prediction.

■ PRACTICE EXERCISE

In which of the following substances is significant hydrogen bonding possible: methylene chloride (CH_2Cl_2), phosphine (PH_3), hydrogen peroxide (HOOH), or acetone (CH_3COCH_3)?

Answer: HOOH

The energies of hydrogen bonds vary from about 5 kJ/mol to 25 kJ/mol or so, although there are isolated examples of hydrogen bond energies that are close to 100 kJ/mol. Thus, hydrogen bonds are typically much weaker than ordinary chemical bonds, which have bond energies of 200–1100 kJ/mol (see Table 8.4). Nevertheless, because hydrogen bonds are generally stronger than dipole–dipole or dispersion forces, they play important roles in many chemical systems, including those of biological significance. For example, hydrogen bonds help stabilize the structures of proteins, which are key parts of skin, muscles, and other structural components of animal tissues. ∞ (Section 25.9) They are also responsible for the way that DNA is able to carry genetic information. ∞ (Section 25.11)



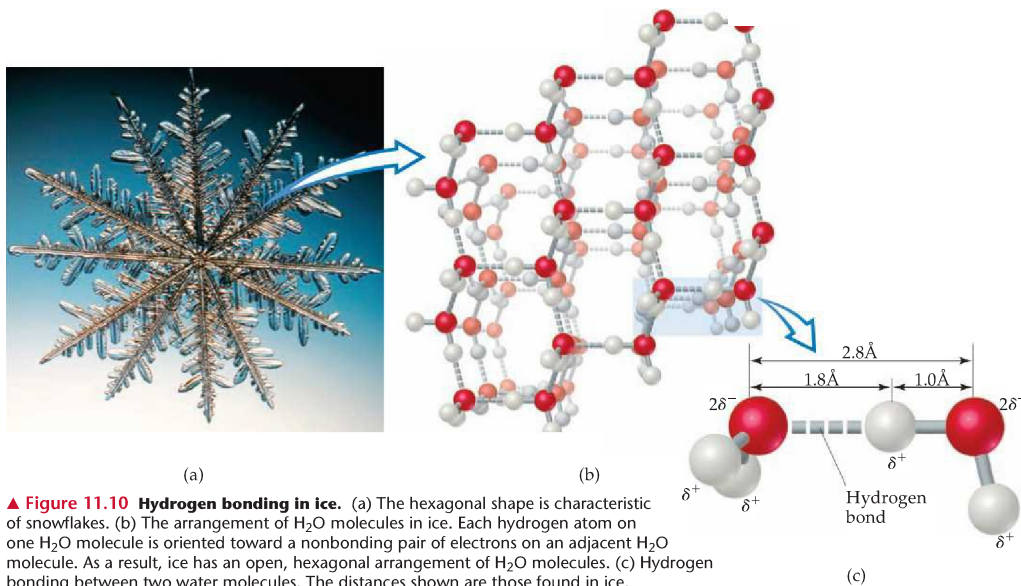
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One of the remarkable consequences of hydrogen bonding is found when the densities of ice and liquid water are compared. In most substances the molecules in the solid are more densely packed than in the liquid. Thus, the solid phase is denser than the liquid phase (Figure 11.9 ▶). By contrast, the density of ice at 0 °C (0.917 g/mL) is less than that of liquid water at 0 °C (1.00 g/mL), so ice floats on liquid water (Figure 11.9).

The lower density of ice compared to that of water can be understood in terms of hydrogen-bonding interactions between H₂O molecules. In ice, the H₂O molecules assume an ordered, open arrangement as shown in Figure 11.10 ▼. This arrangement optimizes the hydrogen bonding interactions between molecules, with each H₂O molecule forming hydrogen bonds to four other H₂O molecules. These hydrogen bonds, however, create the open cavities shown in the structure. When the ice melts, the motions of the molecules cause the structure to collapse. The hydrogen bonding in the liquid is more random than in ice, but it is strong enough to hold the molecules close together. Consequently, liquid water has a more dense structure than ice, meaning that a given mass of water occupies a smaller volume than the same mass of ice.



▲ **Figure 11.9 Comparing densities of liquid and solid phases.** As with most other substances, the solid phase of paraffin is denser than the liquid phase, and the solid therefore sinks below the surface of the liquid paraffin in the beaker on the left. In contrast, the solid phase of water, ice, is less dense than its liquid phase (right beaker), causing the ice to float on the water.



▲ **Figure 11.10 Hydrogen bonding in ice.** (a) The hexagonal shape is characteristic of snowflakes. (b) The arrangement of H₂O molecules in ice. Each hydrogen atom on one H₂O molecule is oriented toward a nonbonding pair of electrons on an adjacent H₂O molecule. As a result, ice has an open, hexagonal arrangement of H₂O molecules. (c) Hydrogen bonding between two water molecules. The distances shown are those found in ice.



▲ **Figure 11.11 Expansion of water upon freezing.** Water is one of the few substances that expand upon freezing. The expansion is due to the open structure of ice relative to that of liquid water.

The lower density of ice compared to liquid water profoundly affects life on Earth. Because ice floats (Figure 11.9), it covers the top of the water when a lake freezes in cold weather, thereby insulating the water below. If ice were more dense than water, ice forming at the top of a lake would sink to the bottom, and the lake could freeze solid. Most aquatic life could not survive under these conditions. The expansion of water upon freezing (Figure 11.11 ◀) is also what causes water pipes to break in freezing weather.

GIVE IT SOME THOUGHT

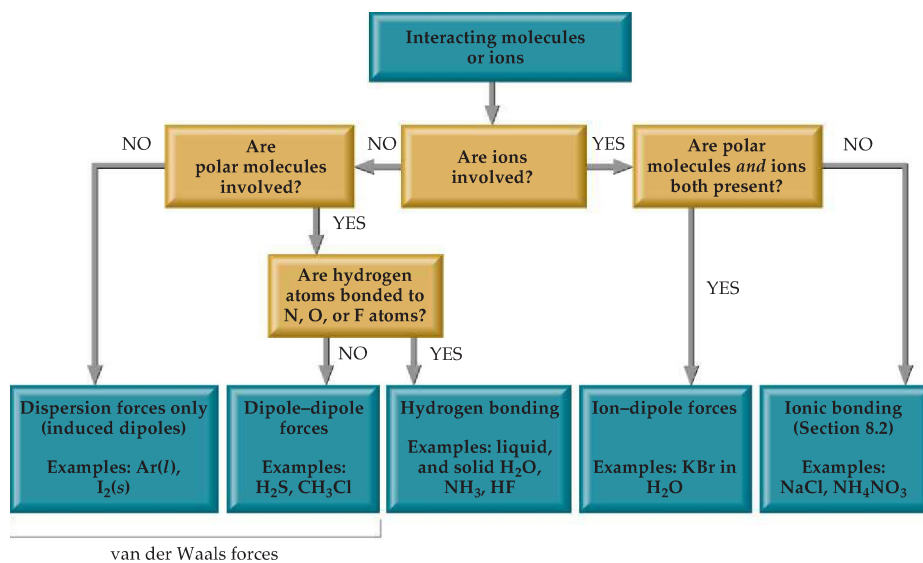
What is unusual about the relative densities of liquid water and ice?

Comparing Intermolecular Forces

We can identify the intermolecular forces that are operative in a substance by considering its composition and structure. *Dispersion forces are found in all substances.* The strengths of these attractions increase with increasing molecular weight and depend on molecular shapes. Dipole–dipole forces add to the effect of dispersion forces and are found in polar molecules. Hydrogen bonds, which require H atoms bonded to F, O, or N, also add to the effect of dispersion forces. Hydrogen bonds tend to be the strongest type of intermolecular attraction. None of these intermolecular attractions, however, is as strong as ordinary ionic or covalent bonds. In general, the energies associated with the dispersion forces and dipole–dipole forces are in the range of 2–10 kJ/mol, while the energies of hydrogen bonds are in the range 5–25 kJ/mol. Ion–dipole attractions lead to energies of approximately 15 kJ/mol.

It is important to realize that the effects of all these attractions are additive. For example, if a pair of molecules can make one hydrogen bond between them but a second pair can make three equivalent hydrogen bonds between them, the second pair of molecules will be held together with triple the energy of the first pair. Likewise, very large polar molecules such as proteins, which have multiple dipoles over their surfaces, can be held together in solution to a surprisingly high degree by multiple dipole–dipole attractions. Figure 11.12 ▼ presents a systematic way of identifying the kinds of intermolecular forces in a particular system, including ion–dipole and ion–ion forces.

▼ **Figure 11.12 Flowchart for determining intermolecular forces.** London dispersion forces occur in all instances. The strengths of the other forces generally increase proceeding from left to right across the chart.



SAMPLE EXERCISE 11.3 Predicting the Types and Relative Strengths of Intermolecular Attractions

List the substances BaCl_2 , H_2 , CO , HF , and Ne in order of increasing boiling points.

SOLUTION

Analyze: We need to relate the properties of the listed substances to boiling point.

Plan: The boiling point depends in part on the attractive forces in the liquid. We need to order these according to the relative strengths of the different kinds of intermolecular attractions.

Solve: The attractive forces are stronger for ionic substances than for molecular ones, so BaCl_2 should have the highest boiling point. The intermolecular forces of the remaining substances depend on molecular weight, polarity, and hydrogen bonding. The molecular weights are H_2 (2), CO (28), HF (20), and Ne (20). The boiling point of H_2 should be the lowest because it is nonpolar and has the lowest molecular weight. The molecular weights of CO , HF , and Ne are roughly the same. Because HF can hydrogen bond, however, it should have the highest boiling point of the three. Next is CO , which is slightly polar and has the highest molecular weight. Finally, Ne , which is nonpolar, should have the lowest boiling point of these three. The predicted order of boiling points is therefore



Check: The actual normal boiling points are H_2 (20 K), Ne (27 K), CO (83 K), HF (293 K), and BaCl_2 (1813 K)—in agreement with our predictions.

PRACTICE EXERCISE

(a) Identify the intermolecular attractions present in the following substances, and (b) select the substance with the highest boiling point: CH_3CH_3 , CH_3OH , and $\text{CH}_3\text{CH}_2\text{OH}$.

Answers: (a) CH_3CH_3 has only dispersion forces, whereas the other two substances have both dispersion forces and hydrogen bonds; (b) $\text{CH}_3\text{CH}_2\text{OH}$

11.3 SOME PROPERTIES OF LIQUIDS

The intermolecular attractions we have just discussed can help us understand many familiar properties of liquids and solids. In this section we examine two important properties of liquids: viscosity and surface tension.

Viscosity

Some liquids, such as molasses and motor oil, flow very slowly; others, such as water and gasoline, flow easily. The resistance of a liquid to flow is called its **viscosity**. The greater a liquid's viscosity, the more slowly it flows. Viscosity can be measured by timing how long it takes a certain amount of the liquid to flow through a thin tube under gravitational force. More viscous liquids take longer (Figure 11.13). Viscosity can also be determined by measuring the rate at which steel balls fall through the liquid. The balls fall more slowly as the viscosity increases.

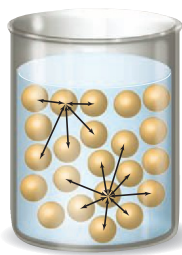
Viscosity is related to the ease with which individual molecules of the liquid can move with respect to one another. It thus depends on the attractive forces between molecules, and on whether structural features exist that cause the molecules to become entangled (for example, long molecules might become tangled like spaghetti). For a series of related compounds, therefore, viscosity increases with molecular weight, as illustrated in Table 11.4. The SI units for viscosity are $\text{kg}/\text{m}\cdot\text{s}$. For any given substance, viscosity decreases with increasing temperature. Octane, for example, has a viscosity of $7.06 \times 10^{-4} \text{ kg}/\text{m}\cdot\text{s}$ at 0°C , and of $4.33 \times 10^{-4} \text{ kg}/\text{m}\cdot\text{s}$ at 40°C . At higher temperatures the greater average kinetic energy of the molecules more easily overcomes the attractive forces between molecules.



▲ Figure 11.13 Comparing viscosities. The Society of Automotive Engineers (SAE) has established numbers to indicate the viscosity of motor oils. The higher the number, the greater the viscosity is at any given temperature. The SAE 40 motor oil on the left is more viscous and flows more slowly than the less viscous SAE 10 oil on the right.



▲ **Figure 11.14 Surface tension.** Surface tension permits an insect such as the water strider to “walk” on water.



▲ **Figure 11.15 Molecular-level view of surface and interior intermolecular forces in a liquid.** Molecules at the surface are attracted only by other surface molecules and by molecules below the surface. The result is a net downward attraction into the interior of the liquid. Molecules in the interior experience attractions in all directions, resulting in no net attraction in any direction.



▲ **Figure 11.16 Two meniscus shapes.** The water meniscus in a glass tube compared with the mercury meniscus in a similar tube. Water wets the glass, and the bottom of the meniscus is below the level of the water–glass contact line, giving a U-shape to the water surface. Mercury does not wet glass and the meniscus is above the mercury–glass contact line, giving an inverted U-shape to the mercury surface.

TABLE 11.4 ■ Viscosities of a Series of Hydrocarbons at 20 °C

| Substance | Formula | Viscosity (kg/m·s) |
|-----------|---|-----------------------|
| Hexane | CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃ | 3.26×10^{-4} |
| Heptane | CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃ | 4.09×10^{-4} |
| Octane | CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃ | 5.42×10^{-4} |
| Nonane | CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃ | 7.11×10^{-4} |
| Decane | CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃ | 1.42×10^{-3} |

Surface Tension

The surface of water behaves almost as if it had an elastic skin, as evidenced by the ability of certain insects to “walk” on water (Figure 11.14 ◀). This behavior is due to an imbalance of intermolecular forces at the surface of the liquid, as shown in Figure 11.15 ◀. Notice that molecules in the interior are attracted equally in all directions, whereas those at the surface experience a net inward force. The resultant inward force pulls molecules from the surface into the interior, thereby reducing the surface area and making the molecules at the surface pack closely together. Because spheres have the smallest surface area for their volume, water droplets assume an almost spherical shape. Similarly, water tends to “bead up” on a newly waxed car because there is little or no attraction between the polar water molecules and the nonpolar wax molecules.

A measure of the inward forces that must be overcome to expand the surface area of a liquid is given by its surface tension. **Surface tension** is the energy required to increase the surface area of a liquid by a unit amount. For example, the surface tension of water at 20 °C is $7.29 \times 10^{-2} \text{ J/m}^2$, which means that an energy of $7.29 \times 10^{-2} \text{ J}$ must be supplied to increase the surface area of a given amount of water by 1 m^2 . Water has a high surface tension because of its strong hydrogen bonds. The surface tension of mercury is even higher ($4.6 \times 10^{-1} \text{ J/m}^2$) because of even stronger metallic bonds between the atoms of mercury. ∞ (Section 11.8)

GIVE IT SOME THOUGHT

How do viscosity and surface tension change (a) as temperature increases, (b) as intermolecular forces of attraction become stronger?

Intermolecular forces that bind similar molecules to one another, such as the hydrogen bonding in water, are also called *cohesive forces*. Intermolecular forces that bind a substance to a surface are called *adhesive forces*. Water placed in a glass tube adheres to the glass because the adhesive forces between the water and glass are even greater than the cohesive forces between water molecules. The curved upper surface, or *meniscus*, of the water is therefore U-shaped (Figure 11.16 ◀). For mercury, however, the meniscus is curved downward where the mercury contacts the glass. In this case the cohesive forces between the mercury atoms are much greater than the adhesive forces between the mercury atoms and the glass.

When a small-diameter glass tube, or capillary, is placed in water, water rises in the tube. The rise of liquids up very narrow tubes is called **capillary action**. The adhesive forces between the liquid and the walls of the tube tend to increase the surface area of the liquid. The surface tension of the liquid tends to reduce the area, thereby pulling the liquid up the tube. The liquid climbs until the force of gravity on the liquid balances the adhesive and cohesive forces. Capillary action helps water and dissolved nutrients move upward through plants.

GIVE IT SOME THOUGHT

If a liquid in a thin tube has no meniscus (in other words, the top of the liquid looks completely flat), what does that imply about the relative strengths of cohesive and adhesive forces?

11.4 PHASE CHANGES

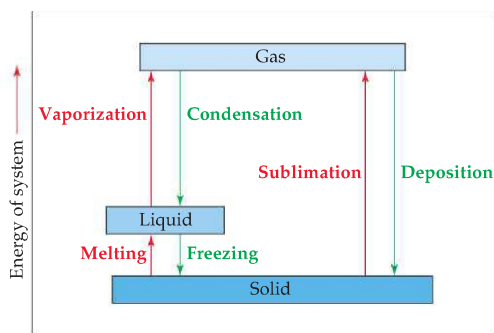
Water left uncovered in a glass for several days evaporates. An ice cube left in a warm room quickly melts. Solid CO_2 (sold as dry ice) *sublimes* at room temperature; that is, it changes directly from the solid to the vapor state. In general, each state of matter can change into either of the other two states. Figure 11.17 shows the name associated with each of these transformations. These transformations are called either **phase changes** or changes of state.

Energy Changes Accompanying Phase Changes

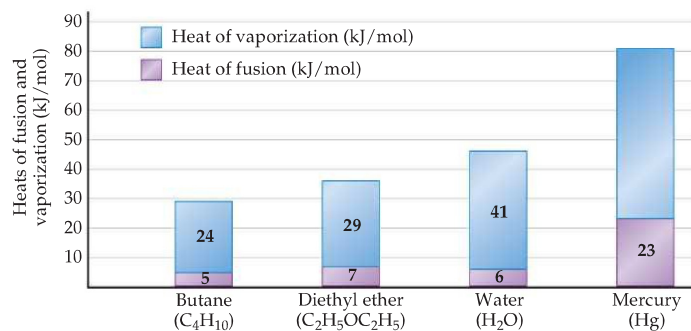
Every phase change is accompanied by a change in the energy of the system. In a solid, for example, the molecules or ions are in more or less fixed positions with respect to one another and closely arranged to minimize the energy of the system. As the temperature of the solid increases, the units of the solid vibrate about their equilibrium positions with increasingly energetic motion. When the solid melts, the units that made up the solid are freed to move with respect to one another, which ordinarily means that their average separations increase. This melting process is called (somewhat confusingly) *fusion*. The increased freedom of motion of the molecules or ions comes at a price, measured by the **heat of fusion**, or enthalpy of fusion, denoted ΔH_{fus} . The heat of fusion of ice, for example, is 6.01 kJ/mol.

As the temperature of the liquid phase increases, the molecules of the liquid move about with increasing energy. One measure of this increasing energy is that the concentration of gas-phase molecules over the liquid increases with temperature. These molecules exert a pressure called the vapor pressure. We will explore vapor pressure in Section 11.5. For now we just need to understand that the vapor pressure increases with increasing temperature until it equals the external pressure over the liquid, typically atmospheric pressure. At this point the liquid boils—the molecules of the liquid move into the gaseous state, where they are widely separated. The energy required to cause this transition is called the **heat of vaporization**, or enthalpy of vaporization, denoted ΔH_{vap} . For water, the heat of vaporization is 40.7 kJ/mol.

Figure 11.18 shows the comparative values of ΔH_{fus} and ΔH_{vap} for four substances. ΔH_{vap} values tend to be larger than ΔH_{fus} because in the transition from the liquid to the vapor state, the molecules must essentially sever all their intermolecular attractive interactions; whereas in melting, many of these attractive interactions remain.



▲ **Figure 11.17 Phase changes and the names associated with them.** Those changes indicated by red arrows and names are endothermic, whereas those in green are exothermic.



▲ **Figure 11.18 Comparing enthalpy changes for fusion and vaporization.** Heats of fusion (violet bars) and heats of vaporization (blue bars) for several substances. Notice that the heat of vaporization for a substance is always larger than its heat of fusion. The heat of sublimation is the sum of the heats of vaporization and fusion.

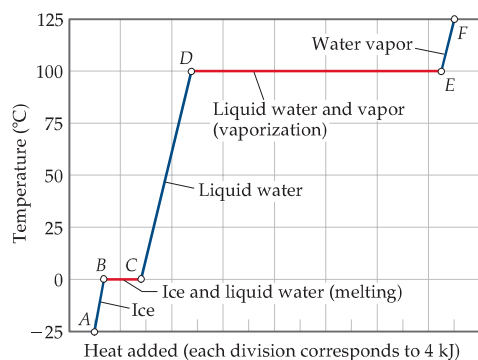
The molecules of a solid can be transformed directly into the gaseous state. The enthalpy change required for this transition is called the **heat of sublimation**, denoted ΔH_{sub} . For the substances shown in Figure 11.18, ΔH_{sub} is the sum of ΔH_{fus} and ΔH_{vap} . Thus, ΔH_{sub} for water is approximately 47 kJ/mol.

Phase changes of matter show up in important ways in our everyday experiences. We use ice cubes to cool our liquid drinks; the heat of fusion of ice cools the liquid in which the ice is immersed. We feel cool when we step out of a swimming pool or a warm shower because the heat of vaporization is drawn from our bodies as the water evaporates from our skin. Our bodies use the evaporation of water from skin to regulate body temperature, especially when we exercise vigorously in warm weather. A refrigerator also relies on the cooling effects of vaporization. Its mechanism contains an enclosed gas that can be liquefied under pressure. The liquid absorbs heat as it subsequently evaporates, thereby cooling the interior of the refrigerator. The vapor is then recycled through a compressor.

What happens to the heat absorbed when the liquid refrigerant vaporizes? According to the first law of thermodynamics (see Section 5.2), the heat absorbed by the liquid in vaporizing must be released when the reverse process, condensation of the vapor to form the liquid, occurs. As the refrigerator compresses the vapor to form a liquid, the heat released by the condensation process is dissipated through cooling coils in the back of the refrigerator. Just as the heat of condensation is equal in magnitude to the heat of vaporization and has the opposite sign, so also the *heat of deposition* is exothermic to the same degree that the heat of sublimation is endothermic; and the *heat of freezing* is exothermic to the same degree that the heat of fusion is endothermic. These relationships, shown in Figure 11.17, are consequences of the first law of thermodynamics.

GIVE IT SOME THOUGHT

What is the name of the phase change that occurs when ice left at room temperature changes to liquid water? Is this change exothermic or endothermic?



▲ Figure 11.19 Heating curve for water. This graph indicates the changes that occur when 1.00 mol of water is heated from -25°C to 125°C at a constant pressure of 1 atm. Blue lines show the heating of one phase from a lower temperature to a higher one. Red lines show the conversion of one phase to another at constant temperature.

Heating Curves

What happens when we heat an ice cube that is initially at -25°C and 1 atm pressure? The addition of heat causes the temperature of the ice to increase. As long as the temperature is below 0°C , the ice cube remains frozen. When the temperature reaches 0°C , the ice begins to melt. Because melting is an endothermic process, the heat we add at 0°C is used to convert ice to water; the temperature remains constant until all the ice has melted. Once we reach this point, the further addition of heat causes the temperature of the liquid water to increase.

A graph of the temperature of the system versus the amount of heat added is called a *heating curve*. Figure 11.19 shows a heating curve for transforming ice at -25°C to steam at 125°C under a constant pressure of 1 atm. Heating the ice from -25°C to 0°C is represented by the line segment *AB* in Figure 11.19, while converting the ice at 0°C to water at 0°C is the horizontal segment *BC*. Additional heat increases the temperature of the water until the temperature reaches 100°C (segment *CD*). The heat is then used to convert water to steam at a constant temperature of 100°C (segment *DE*). Once all the water has been converted to steam, the steam is heated to its final temperature of 125°C (segment *EF*).

We can calculate the enthalpy change of the system for each of the segments of the heating curve. In segments *AB*, *CD*, and *EF* we are heating a single phase from one temperature to another. As we saw in Section 5.5, the amount of heat needed to raise the temperature of a substance is given by the product of the specific heat, mass, and temperature change (Equation 5.22). The greater the specific heat of a substance, the more heat we must add to accomplish a certain temperature increase. Because the specific heat of water is greater than that of ice, the slope of segment *CD* is less than that of segment *AB*; we must add more heat to water to achieve a 1 °C temperature change than is needed to warm the same quantity of ice by 1 °C.

In segments *BC* and *DE* we are converting one phase to another at a constant temperature. The temperature remains constant during these phase changes because the added energy is used to overcome the attractive forces between molecules rather than to increase their average kinetic energy. For segment *BC*, in which ice is converted to water, the enthalpy change can be calculated by using ΔH_{fus} , while for segment *DE* we can use ΔH_{vap} . In Sample Exercise 11.4 we calculate the total enthalpy change for the heating curve in Figure 11.19.

■ SAMPLE EXERCISE 11.4 Calculating ΔH for Temperature and Phase Changes

Calculate the enthalpy change upon converting 1.00 mol of ice at $-25\text{ }^\circ\text{C}$ to water vapor (steam) at $125\text{ }^\circ\text{C}$ under a constant pressure of 1 atm. The specific heats of ice, water, and steam are $2.03\text{ J/g}\cdot\text{K}$, $4.18\text{ J/g}\cdot\text{K}$, and $1.84\text{ J/g}\cdot\text{K}$, respectively. For H_2O , $\Delta H_{\text{fus}} = 6.01\text{ kJ/mol}$ and $\Delta H_{\text{vap}} = 40.67\text{ kJ/mol}$.

SOLUTION

Analyze: Our goal is to calculate the total heat required to convert 1 mol of ice at $-25\text{ }^\circ\text{C}$ to steam at $125\text{ }^\circ\text{C}$.

Plan: We can calculate the enthalpy change for each segment and then sum them to get the total enthalpy change (Hess's law, Section 5.6).

Solve: For segment *AB* in Figure 11.19, we are adding enough heat to ice to increase its temperature by $25\text{ }^\circ\text{C}$. A temperature change of $25\text{ }^\circ\text{C}$ is the same as a temperature change of 25 K, so we can use the specific heat of ice to calculate the enthalpy change during this process:

$$AB: \Delta H = (1.00\text{ mol})(18.0\text{ g/mol})(2.03\text{ J/g}\cdot\text{K})(25\text{ K}) = 914\text{ J} = 0.91\text{ kJ}$$

For segment *BC* in Figure 11.19, in which we convert ice to water at $0\text{ }^\circ\text{C}$, we can use the molar enthalpy of fusion directly:

$$BC: \Delta H = (1.00\text{ mol})(6.01\text{ kJ/mol}) = 6.01\text{ kJ}$$

The enthalpy changes for segments *CD*, *DE*, and *EF* can be calculated in similar fashion:

$$CD: \Delta H = (1.00\text{ mol})(18.0\text{ g/mol})(4.18\text{ J/g}\cdot\text{K})(100\text{ K}) = 7520\text{ J} = 7.52\text{ kJ}$$

$$DE: \Delta H = (1.00\text{ mol})(40.67\text{ kJ/mol}) = 40.7\text{ kJ}$$

$$EF: \Delta H = (1.00\text{ mol})(18.0\text{ g/mol})(1.84\text{ J/g}\cdot\text{K})(25\text{ K}) = 830\text{ J} = 0.83\text{ kJ}$$

The total enthalpy change is the sum of the changes of the individual steps:

$$\Delta H = 0.91\text{ kJ} + 6.01\text{ kJ} + 7.52\text{ kJ} + 40.7\text{ kJ} + 0.83\text{ kJ} = 56.0\text{ kJ}$$

Check: The components of the total energy change are reasonable in comparison with the lengths of the horizontal segments of the lines in Figure 11.19. Notice that the largest component is the heat of vaporization.

■ PRACTICE EXERCISE

What is the enthalpy change during the process in which 100.0 g of water at $50.0\text{ }^\circ\text{C}$ is cooled to ice at $-30.0\text{ }^\circ\text{C}$? (Use the specific heats and enthalpies for phase changes given in Sample Exercise 11.4.)

Answer: $-20.9\text{ kJ} - 33.4\text{ kJ} - 6.09\text{ kJ} = -60.4\text{ kJ}$

Cooling a substance has the opposite effect of heating it. Thus, if we start with water vapor and begin to cool it, we would move right to left through the events shown in Figure 11.19. We would first lower the temperature of the

vapor ($F \rightarrow E$), then condense it ($E \rightarrow D$), and so forth. Sometimes as we remove heat from a liquid, we can temporarily cool it below its freezing point without forming a solid. This phenomenon is called *supercooling*. Supercooling occurs when heat is removed from a liquid so rapidly that the molecules literally have no time to assume the ordered structure of a solid. A supercooled liquid is unstable; particles of dust entering the solution or gentle stirring is often sufficient to cause the substance to solidify quickly.

Critical Temperature and Pressure

A gas normally liquefies at some point when pressure is applied to it. Suppose we have a cylinder with a piston, containing water vapor at 100 °C. If we increase the pressure on the water vapor, liquid water will form when the pressure is 760 torr. On the other hand, if the temperature is 110 °C, the liquid phase does not form until the pressure is 1075 torr. At 374 °C the liquid phase forms only at 1.655×10^5 torr (217.7 atm). Above this temperature no amount of pressure will cause a distinct liquid phase to form. Instead, as pressure increases, the gas merely becomes steadily more compressed. The highest temperature at which a distinct liquid phase can form is referred to as the **critical temperature**. The **critical pressure** is the pressure required to bring about liquefaction at this critical temperature.

The critical temperature is the highest temperature at which a liquid can exist. Above the critical temperature, the motional energies of the molecules are greater than the attractive forces that lead to the liquid state regardless of how much the substance is compressed to bring the molecules closer together. The greater the intermolecular forces, the greater the critical temperature of a substance.

The critical temperatures and pressures are listed for several substances in Table 11.5. Notice that nonpolar, low molecular weight substances, which have weak intermolecular attractions, have lower critical temperatures and pressures than those that are polar or of higher molecular weight. Notice also that water and ammonia have exceptionally high critical temperatures and pressures as a consequence of strong intermolecular hydrogen-bonding forces.

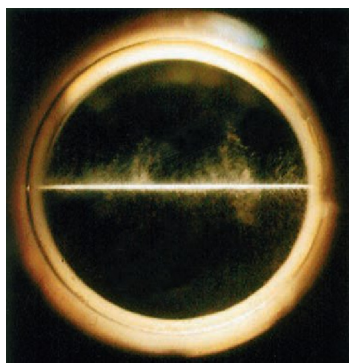
The critical temperatures and pressures of substances are often of considerable importance to engineers and other people working with gases, because they provide information about the conditions under which gases liquefy. Sometimes we want to liquefy a gas; other times we want to avoid liquefying it. It is useless to try to liquefy a gas by applying pressure if the gas is above its critical temperature. For example, O₂ has a critical temperature of 154.4 K. It must be cooled below this temperature before it can be liquefied by pressure. In contrast, ammonia has a critical temperature of 405.6 K. Thus, it can be liquefied at room temperature (approximately 295 K) by compressing the gas to a sufficient pressure.

TABLE 11.5 ■ Critical Temperatures and Pressures of Selected Substances

| Substance | Critical Temperature (K) | Critical Pressure (atm) |
|--|--------------------------|-------------------------|
| Ammonia, NH ₃ | 405.6 | 111.5 |
| Argon, Ar | 150.9 | 48 |
| Carbon dioxide, CO ₂ | 304.3 | 73.0 |
| Hydrogen sulfide, H ₂ S | 373.5 | 88.9 |
| Nitrogen, N ₂ | 126.1 | 33.5 |
| Oxygen, O ₂ | 154.4 | 49.7 |
| Phosphine, PH ₃ | 324.4 | 64.5 |
| Propane, CH ₃ CH ₂ CH ₃ | 370.0 | 42.0 |
| Water, H ₂ O | 647.6 | 217.7 |

At ordinary pressures, a substance above its critical temperature behaves as an ordinary gas. However, as pressure increases up to several hundred atmospheres, its character changes. Like a gas, the substance still expands to fill the confines of its container, but its density approaches that of a liquid. (For example, the critical temperature of water is 647.6 K, and its critical pressure is 217.7 atm. At this temperature and pressure, the density of water is 0.4 g/mL.) A substance at temperatures and pressures higher than its critical temperature and pressure is better considered a *supercritical fluid* rather than a gas.

Like liquids, supercritical fluids can behave as solvents, dissolving a wide range of substances. Using *supercritical fluid extraction*, the components of mixtures can be separated. The solvent power of a supercritical fluid increases as its density increases. Conversely, lowering its density (by either decreasing pressure or increasing temperature) causes the supercritical fluid and the dissolved material to separate. By appropriate manipulation of pressure, supercritical fluid extraction has been used successfully to separate complex mixtures in the chemical, food, pharmaceutical, and energy industries. Supercritical carbon dioxide, for example, is environmentally benign

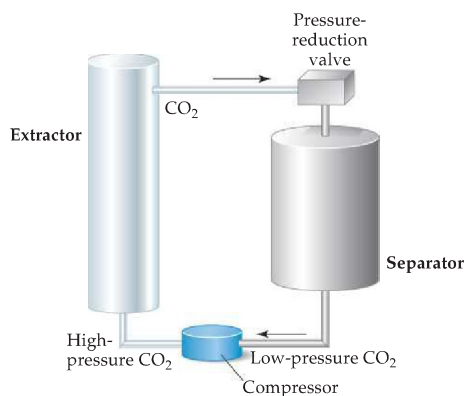


▲ **Figure 11.20** Photograph of carbon dioxide under temperature and pressure conditions so that it is a supercritical fluid.

because there are no problems disposing of solvent and there are no toxic residues resulting from the process. In addition, supercritical CO_2 is inexpensive compared to solvents other than water. Figure 11.20 ▼ shows what supercritical CO_2 looks like through a window in a high-pressure vessel.

A process for removing caffeine from green coffee beans by extraction with supercritical CO_2 , diagrammed in Figure 11.21 ▼, has been in commercial operation for several years. At the proper temperature and pressure the supercritical CO_2 removes caffeine from the beans by dissolution, but leaves the flavor and aroma components, producing decaffeinated coffee. Supercritical CO_2 is also now used as a solvent in dry cleaning. In 2007, the state of California banned the most common dry-cleaning solvent, perchloroethylene ($\text{Cl}_2\text{C}=\text{CCl}_2$), which is an environmental hazard and a suspected human carcinogen. Supercritical CO_2 is a more sustainable alternative.

Related Exercises: 11.41, 11.42, 11.87

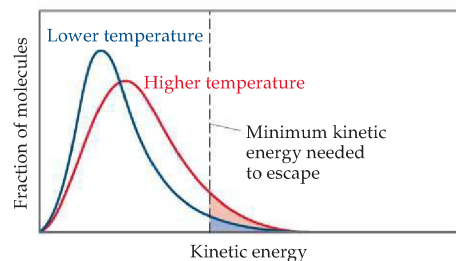
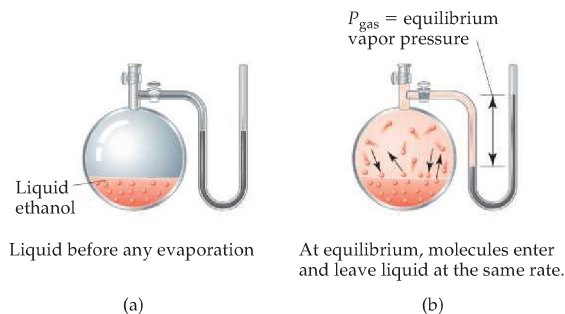


▲ **Figure 11.21** Diagram of a supercritical fluid extraction process. The material to be processed is placed in the extractor. The desired material dissolves in supercritical CO_2 at high pressure, then is precipitated in the separator when the CO_2 pressure is reduced. The carbon dioxide is then recycled through the compressor with a fresh batch of material in the extractor.

11.5 VAPOR PRESSURE

Molecules can escape from the surface of a liquid into the gas phase by evaporation. Suppose we conduct an experiment in which we place a quantity of ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) in an evacuated, closed container such as that in Figure 11.22 ▼. The ethanol will quickly begin to evaporate. As a result, the pressure exerted by the vapor in the space above the liquid will begin to increase. After a short time the pressure of the vapor will attain a constant value, which we call the **vapor pressure** of the substance.

► **Figure 11.22 Illustration of the equilibrium vapor pressure over a liquid.** In (a) we imagine that no molecules of the liquid are in the gas phase initially; there is zero vapor pressure in the vessel. In (b), after equilibrium is reached, the rate at which molecules leave the surface equals the rate at which gas molecules return to the liquid phase. These equal rates produce a stable vapor pressure that does not change as long as the temperature remains constant.



▲ **Figure 11.23 The effect of temperature on the distribution of kinetic energies in a liquid.** The distribution of kinetic energies of surface molecules of a hypothetical liquid are shown at two temperatures. Only the fastest molecules have sufficient kinetic energy to escape the liquid and enter the vapor, as shown by the shaded areas. The higher the temperature, the larger is the fraction of molecules with enough energy to escape from the liquid into the vapor phase.

Explaining Vapor Pressure on the Molecular Level

The molecules of a liquid move at various speeds. Figure 11.23 ◀ shows the distribution of kinetic energies of the particles at the surface of a liquid at two temperatures. The distribution curves are like those shown earlier for gases. ∞ (Section 10.7) At any instant some of the molecules on the surface of the liquid possess sufficient kinetic energy to overcome the attractive forces of their neighbors and escape into the gas phase. The weaker the attractive forces, the larger is the number of molecules that are able to escape and therefore the higher the vapor pressure.

At any particular temperature the movement of molecules from the liquid to the gas phase goes on continuously. As the number of gas-phase molecules increases, however, the probability increases that a molecule in the gas phase will strike the liquid surface and be recaptured by the liquid, as shown in Figure 11.22(b). Eventually, the rate at which molecules return to the liquid exactly equals the rate at which they escape. The number of molecules in the gas phase then reaches a steady value, and the pressure of the vapor at this stage becomes constant.

The condition in which two opposing processes are occurring simultaneously at equal rates is called a **dynamic equilibrium**, but is usually referred to merely as *equilibrium*. A liquid and its vapor are in dynamic equilibrium when evaporation and condensation occur at equal rates. It may appear that nothing is occurring at equilibrium because there is no net change in the system. In fact, a great deal is happening: molecules continuously pass from the liquid state to the gas state and from the gas state to the liquid state. All equilibria between different states of matter possess this dynamic character. *The vapor pressure of a liquid is the pressure exerted by its vapor when the liquid and vapor states are in dynamic equilibrium.*

Volatility, Vapor Pressure, and Temperature

When vaporization occurs in an open container, as when water evaporates from a bowl, the vapor spreads away from the liquid. Little, if any, is recaptured at the surface of the liquid. Equilibrium never occurs, and the vapor continues to form until the liquid evaporates to dryness. Substances with high vapor pressure (such as gasoline) evaporate more quickly than substances with low vapor pressure (such as motor oil). Liquids that evaporate readily are said to be **volatile**.

Hot water evaporates more quickly than cold water because vapor pressure increases with increasing temperature. We see this effect in Figure 11.23: As the temperature of a liquid is increased, the molecules move more energetically and a greater fraction can therefore escape more readily from their neighbors. Figure 11.24 depicts the variation in vapor pressure with temperature for four common substances that differ greatly in volatility. Note that the vapor pressure in all cases increases nonlinearly with increasing temperature.

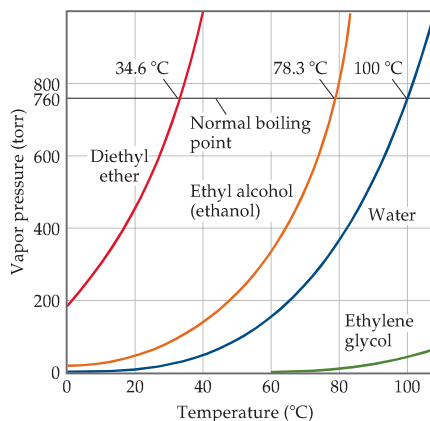
GIVE IT SOME THOUGHT

Which compound do you think would be more volatile at 25 °C, CCl_4 or CBr_4 ?

Vapor Pressure and Boiling Point

A liquid boils when its vapor pressure equals the external pressure acting on the surface of the liquid. At this point bubbles of vapor form within the liquid. The temperature at which a given liquid boils increases with increasing external pressure. The boiling point of a liquid at 1 atm (or 760 torr) pressure is called its **normal boiling point**. From Figure 11.24 we see that the normal boiling point of water is 100 °C.

The boiling point is important to many processes that involve heating liquids, including cooking. The time required to cook food depends on the temperature. As long as water is present, the maximum temperature of the food being cooked is the boiling point of water. Pressure cookers work by allowing steam to escape only when it exceeds a predetermined pressure; the pressure above the water can therefore increase above atmospheric pressure. The higher pressure causes the water to boil at a higher temperature, thereby allowing the food to get hotter and to cook more rapidly. The effect of pressure on boiling point also explains why it takes longer to cook food at higher elevations than at sea level. The atmospheric pressure is lower at higher altitudes, so water boils at a lower temperature and foods generally take longer to cook.



▲ **Figure 11.24 Vapor pressure for four common liquids as a function of temperature.** The temperature at which the vapor pressure is 760 torr is the normal boiling point of each liquid.

SAMPLE EXERCISE 11.5 | Relating Boiling Point to Vapor Pressure

Use Figure 11.24 to estimate the boiling point of diethyl ether under an external pressure of 0.80 atm.

SOLUTION

Analyze: We are asked to read a graph of vapor pressure versus temperature to determine the boiling point of a substance at a particular pressure. The boiling point is the temperature at which the vapor pressure is equal to the external pressure.

Plan: We need to convert 0.80 atm to torr because that is the pressure scale on the graph. We estimate the location of that pressure on the graph, move horizontally to the vapor pressure curve, and then drop vertically from the curve to estimate the temperature.

Solve: The pressure equals $(0.80 \text{ atm})(760 \text{ torr/atm}) = 610 \text{ torr}$. From Figure 11.24 we see that the boiling point at this pressure is about 27 °C, which is close to room temperature.

Comment: We can make a flask of diethyl ether boil at room temperature by using a vacuum pump to lower the pressure above the liquid to about 0.8 atm.

PRACTICE EXERCISE

At what external pressure will ethanol have a boiling point of 60 °C?

Answer: about 340 torr (0.45 atm)

A Closer Look THE CLAUSIUS–CLAPEYRON EQUATION

You might have noticed that the plots of the variation of vapor pressure with temperature shown in Figure 11.24 have a distinct shape: Each curves sharply upward to a higher vapor pressure with increasing temperature. The relationship between vapor pressure and temperature is given by an equation called the *Clausius–Clapeyron equation*:

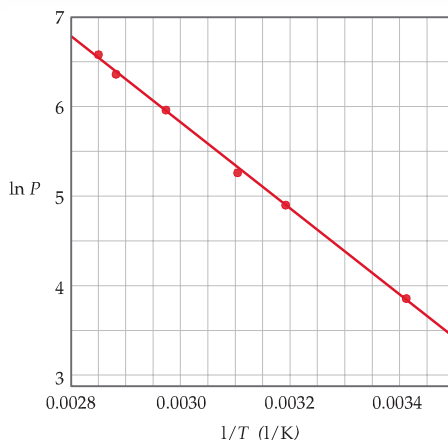
$$\ln P = \frac{-\Delta H_{\text{vap}}}{RT} + C \quad [11.1]$$

In this equation P is the vapor pressure, T is the absolute temperature, R is the gas constant (8.314 J/mol·K), ΔH_{vap} is the molar enthalpy of vaporization, and C is a constant. The Clausius–Clapeyron equation predicts that a graph of $\ln P$ versus $1/T$ should give a straight line with a slope equal to $-\Delta H_{\text{vap}}/R$. Thus, we can use such a plot to determine the enthalpy of vaporization of a substance as follows:

$$\Delta H_{\text{vap}} = -\text{slope} \times R$$

As an example of the application of the Clausius–Clapeyron equation, the vapor-pressure data for ethanol shown in Figure 11.24 are graphed as $\ln P$ versus $1/T$ in Figure 11.25. The data lie on a straight line with a negative slope. We can use the slope of the line to determine ΔH_{vap} for ethanol. We can also extrapolate the line to obtain values for the vapor pressure of ethanol at temperatures above and below the temperature range for which we have data.

Related Exercises: 11.89, 11.90, 11.91



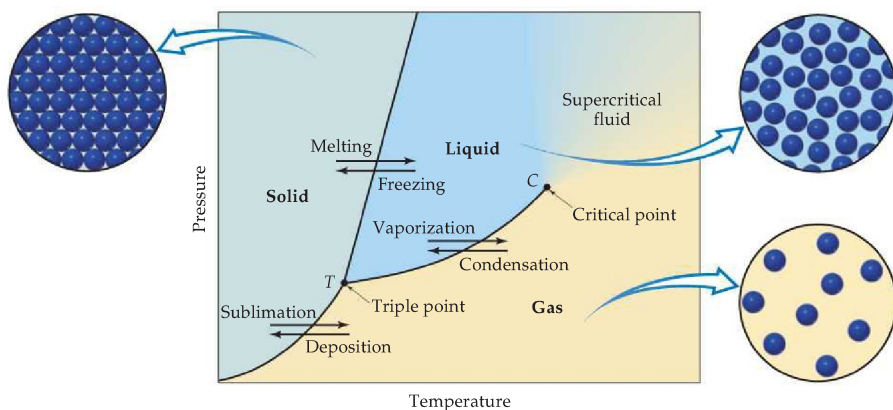
▲ **Figure 11.25** Linear graph of vapor pressure data for ethanol. The Clausius–Clapeyron equation, Equation 11.1, indicates that a graph of $\ln P$ versus $1/T$ gives a straight line whose slope equals $-\Delta H_{\text{vap}}/R$. The slope of this line gives $\Delta H_{\text{vap}} = 38.56$ kJ/mol.

11.6 PHASE DIAGRAMS

The equilibrium between a liquid and its vapor is not the only dynamic equilibrium that can exist between states of matter. Under appropriate conditions of temperature and pressure, a solid can be in equilibrium with its liquid state or even with its vapor state. A **phase diagram** is a graphic way to summarize the conditions under which equilibria exist between the different states of matter. Such a diagram also allows us to predict the phase of a substance that is stable at any given temperature and pressure.

The general form of a phase diagram for a substance that can exist in any one of the three phases of matter is shown in Figure 11.26. The diagram is a two-dimensional graph, with pressure and temperature as the axes. It contains three important curves, each of which represents the conditions of temperature and pressure at which the various phases can coexist at equilibrium. The only substance present in the system is the one whose phase diagram is under consideration. The pressure shown in the diagram is either the pressure applied to the system or the pressure generated by the substance itself. The curves may be described as follows:

1. The line from T to C is the vapor-pressure curve of the liquid. It represents the equilibrium between the liquid and gas phases. The point on this curve where the vapor pressure is 1 atm is the normal boiling point of the substance. The vapor-pressure curve ends at the *critical point* (C), which is at the critical temperature and critical pressure of the substance. Beyond the critical point the liquid and gas phases become indistinguishable from each other, and the state of the substance is a *supercritical fluid*.



▲ **Figure 11.26 Phase diagram for a three-phase system.** In this generic diagram, the substance being investigated can exist as a solid, a liquid, or a gas, depending on pressure and temperature. Beyond the critical point (C), the distinction between liquid and gas is lost, and the substance is a supercritical fluid.

- The line that separates the solid phase from the gas phase represents the change in the vapor pressure of the solid as it sublimates at different temperatures.
- The line that separates the solid phase from the liquid phase corresponds to the change in melting point of the solid with increasing pressure. This line usually slopes slightly to the right as pressure increases, because for most substances the solid form is denser than the liquid form. An increase in pressure usually favors the more compact solid phase; thus, higher temperatures are required to melt the solid at higher pressures. The *melting point* of a substance is identical to its *freezing point*. The two differ only in the direction from which the phase change is approached. The melting point at 1 atm is the **normal melting point**.

Point *T*, where the three curves intersect, is known as the **triple point**. All three phases are in equilibrium at this temperature and pressure. Any other point on the three curves represents equilibrium between two phases. Any point on the diagram that does not fall on a line corresponds to conditions under which only one phase is present. The gas phase, for example, is stable at low pressures and high temperatures, whereas the solid phase is stable at low temperatures and high pressures. Liquids are stable in the region between the other two.

GIVE IT SOME THOUGHT

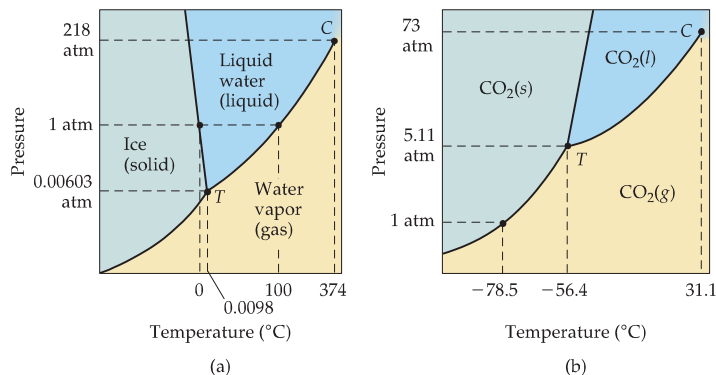
On a phase diagram, which way does the line representing boiling usually slope, and why?

The Phase Diagrams of H₂O and CO₂

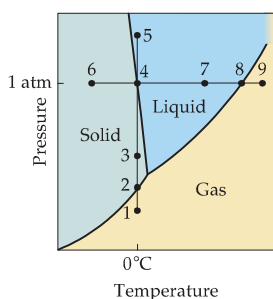
Figure 11.27 ▼ shows the phase diagrams of H₂O and CO₂. The solid–liquid equilibrium (melting point) line of CO₂ follows the typical behavior, slanting to the right with increasing pressure, telling you that its melting point increases with increasing pressure. In contrast, the melting point line of H₂O is atypical, slanting to the left with increasing pressure, indicating that for water the melting point *decreases* with increasing pressure. As seen in Figure 11.11, water is among the very few substances whose liquid form is more compact than its solid form. ∞ (Section 11.2)

The triple point of H₂O (0.0098 °C and 0.00603 atm) is at much lower pressure than that of CO₂ (−56.4 °C and 5.11 atm). For CO₂ to exist as a liquid, the pressure must exceed 5.11 atm. Consequently, solid CO₂ does not melt but

► **Figure 11.27 Phase diagrams of H₂O and CO₂.** The axes are not drawn to scale in either case. In (a), for water, note the triple point *T* at 0.0098 °C and 0.00603 atm, the normal melting (or freezing) point of 0 °C at 1 atm, the normal boiling point of 100 °C at 1 atm, and the critical point *C* (374.4 °C and 217.7 atm). In (b), for carbon dioxide, note the triple point *T* at -56.4 °C and 5.11 atm, the normal sublimation point of -78.5 °C at 1 atm, and the critical point *C* (31.1 °C and 73.0 atm).



sublimes when heated at 1 atm. Thus, CO₂ does not have a normal melting point; instead, it has a normal sublimation point, -78.5 °C. Because CO₂ sublimates rather than melts as it absorbs energy at ordinary pressures, solid CO₂ (dry ice) is a convenient coolant. For water (ice) to sublime, however, its vapor pressure must be below 0.00603 atm. Food is “freeze-dried” by placing frozen food in a low-pressure chamber (below 0.00603 atm) so that the ice in it sublimates.



▲ **Figure 11.28 Phase diagram of H₂O.**

SAMPLE EXERCISE 11.6 | Interpreting a Phase Diagram

Referring to Figure 11.28 ◀, describe any changes in the phases present when H₂O is (a) kept at 0 °C while the pressure is increased from that at point 1 to that at point 5 (vertical line), (b) kept at 1.00 atm while the temperature is increased from that at point 6 to that at point 9 (horizontal line).

SOLUTION

Analyze: We are asked to use the phase diagram provided to deduce what phase changes might occur when specific pressure and temperature changes are brought about.

Plan: Trace the path indicated on the phase diagram, and note what phases and phase changes occur.

Solve:

(a) At point 1, H₂O exists totally as a vapor. At point 2 a solid–vapor equilibrium exists. Above that pressure, at point 3, all the H₂O is converted to a solid. At point 4 some of the solid melts and equilibrium between solid and liquid is achieved. At still higher pressures all the H₂O melts, so only the liquid phase is present at point 5.

(b) At point 6 the H₂O exists entirely as a solid. When the temperature reaches point 4, the solid begins to melt and equilibrium exists between the solid and liquid phases. At an even higher temperature, point 7, the solid has been converted entirely to a liquid. A liquid–vapor equilibrium exists at point 8. Upon further heating to point 9, the H₂O is converted entirely to the vapor phase.

Check: The indicated phases and phase changes are consistent with our knowledge of the properties of water.

PRACTICE EXERCISE

Using Figure 11.27(b), describe what happens when the following changes are made to a CO₂ sample: (a) Pressure increases from 1 atm to 60 atm at a constant temperature of -60 °C. (b) Temperature increases from -60 °C to -20 °C at a constant pressure of 60 atm.

Answers: (a) CO₂(g) → CO₂(s); (b) CO₂(s) → CO₂(l)

11.7 STRUCTURES OF SOLIDS

Throughout the remainder of this chapter we will focus on how the properties of solids relate to their structures and bonding. Solids can be either crystalline or amorphous (noncrystalline). In a **crystalline solid** the atoms, ions, or molecules are ordered in well-defined three-dimensional arrangements.



(a) Pyrite (fool's gold)

(b) Fluorite

(c) Amethyst

These solids usually have flat surfaces, or *faces*, that make definite angles with one another. The orderly stacks of particles that produce these faces also cause the solids to have highly regular shapes (Figure 11.29 ▲). Quartz and diamond are crystalline solids.

An **amorphous solid** (from the Greek words for “without form”) is a solid in which particles have no orderly structure. These solids lack well-defined faces and shapes. Many amorphous solids are mixtures of particles that do not stack together well. Most others are composed of large, complicated molecules. Familiar amorphous solids include rubber and glass.

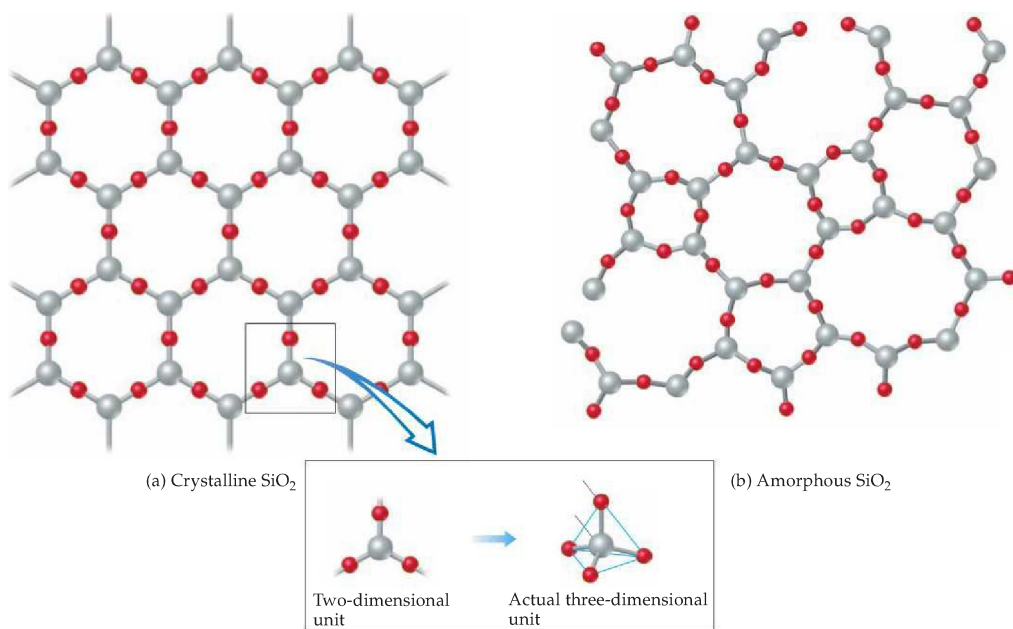
Quartz (SiO_2) is a crystalline solid with a three-dimensional structure like that shown in Figure 11.30(a) ▼. When quartz melts (at about 1600°C), it becomes a viscous, tacky liquid. Although the silicon–oxygen network remains largely intact, many $\text{Si}-\text{O}$ bonds are broken, and the rigid order of the quartz is lost. If the melt is rapidly cooled, the atoms are unable to return to an orderly arrangement. As a result, an amorphous solid known either as quartz glass or as silica glass results [Figure 11.30(b)].

▲ **Figure 11.29 Crystalline solids.**

Crystalline solids come in a variety of forms and colors: (a) pyrite (fool's gold), (b) fluorite, (c) amethyst.

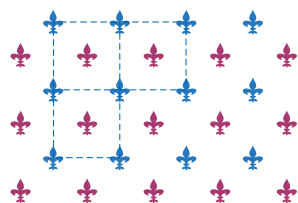
▼ **Figure 11.30 Schematic comparisons of (a) crystalline SiO_2 (quartz) and (b) amorphous SiO_2 (quartz glass).**

The structures are actually three-dimensional and not planar as drawn. The two-dimensional unit shown as the basic building block of the structure (silicon and three oxygens) actually has four oxygens, the fourth coming out of the plane of the paper and capable of bonding to other silicon atoms. The actual three-dimensional building block is shown.

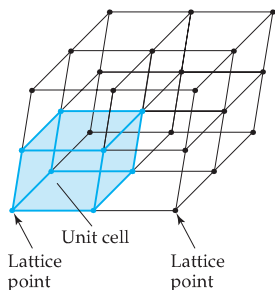
(a) Crystalline SiO_2 (b) Amorphous SiO_2

Two-dimensional unit

Actual three-dimensional unit



▲ **Figure 11.31** A two-dimensional analog of a lattice and its unit cell. The wallpaper design shows a characteristic repeat pattern. Each dashed blue square denotes a unit cell of the pattern. The unit cell could equally well be selected with red figures at the corners.



▲ **Figure 11.32** Part of a simple crystal lattice and its associated unit cell. A lattice is an array of points that define the positions of particles in a crystalline solid. Each lattice point represents an identical environment in the solid. The points here are shown connected by lines to help convey the three-dimensional character of the lattice and to help us see the unit cell.

Because the particles of an amorphous solid lack any long-range order, intermolecular forces vary in strength throughout a sample. Thus, amorphous solids do not melt at specific temperatures. Instead, they soften over a temperature range as intermolecular forces of various strengths are overcome. A crystalline solid, in contrast, melts at a specific temperature.

GIVE IT SOME THOUGHT

What is the general difference in the melting behaviors of crystalline and amorphous solids?

Unit Cells

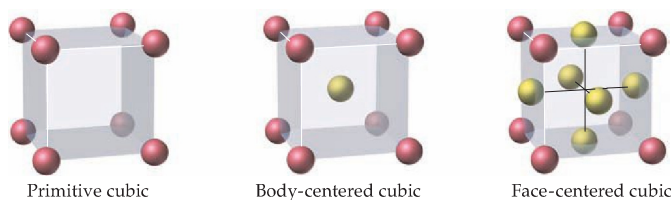
The characteristic order of crystalline solids allows us to convey a picture of an entire crystal by looking at only a small part of it. We can think of the solid as being built by stacking together identical building blocks, much as stacking rows of individual “identical” bricks forms a brick wall. The repeating unit of a solid, the crystalline “brick,” is known as the **unit cell**. A simple two-dimensional example appears in the sheet of wallpaper shown in Figure 11.31 ◀. There are several ways of choosing a unit cell, but the choice is usually the smallest unit cell that shows clearly the symmetry characteristic of the entire pattern.

A crystalline solid can be represented by a three-dimensional array of points called a **crystal lattice**. Each point in the lattice is called a *lattice point*, and it represents an identical environment within the solid. The crystal lattice is, in effect, an abstract scaffolding for the crystal structure. We can imagine forming the entire crystal structure by arranging the contents of the unit cell repeatedly on the crystal lattice. In the simplest case the crystal structure would consist of identical atoms, and each atom would be centered on a lattice point. This is the case for most metals.

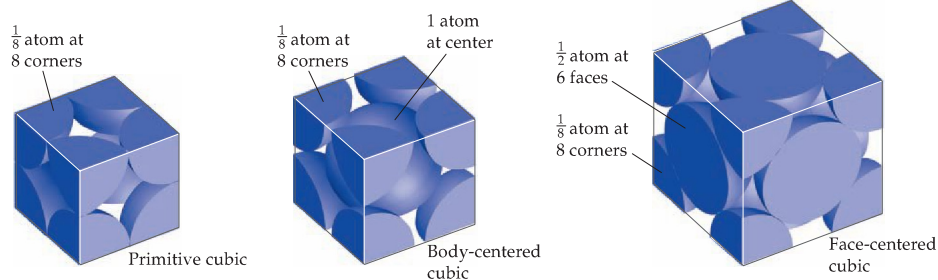
Figure 11.32 ◀ shows a crystal lattice and its associated unit cell. In general, unit cells are parallelepipeds (six-sided figures whose faces are parallelograms). Each unit cell can be described by the lengths of the edges of the cell and by the angles between these edges. Seven basic types of unit cells can describe the lattices of all crystalline compounds. The simplest of these is the cubic unit cell, in which all the sides are equal in length and all the angles are 90° .

Three kinds of cubic unit cells are illustrated in Figure 11.33 ▼. When lattice points are at the corners only, the unit cell is called **primitive cubic** (or *simple cubic*). When a lattice point also occurs at the center of the unit cell, the cell is **body-centered cubic**. When the cell has lattice points at the center of each face, as well as at each corner, it is **face-centered cubic**.

The simplest crystal structures are cubic unit cells with only one atom centered at each lattice point. Most metals have such structures. Nickel, for example, has a face-centered cubic unit cell, whereas sodium has a body-centered cubic one. Figure 11.34 ► shows how atoms fill the cubic unit cells. Notice that



▲ **Figure 11.33** The three types of unit cells found in cubic lattices. For clarity, the corner spheres are red and the body-centered and face-centered ones are yellow. Each sphere represents a lattice point (an identical environment in the solid).



▲ **Figure 11.34** Space-filling view of cubic unit cells. Only the portion of each atom that belongs to the unit cell is shown.

TABLE 11.6 Fraction of an Atom That Occupies a Unit Cell for Various Positions in the Unit Cell

| Position in Unit Cell | Fraction in Unit Cell |
|-----------------------|-----------------------|
| Center | 1 |
| Face | $\frac{1}{2}$ |
| Edge | $\frac{1}{4}$ |
| Corner | $\frac{1}{8}$ |

the atoms on the corners and faces do not lie wholly within the unit cell. Instead, these atoms are shared between unit cells. As an example, let's look at the primitive cubic structure in Figure 11.34. In an actual solid, this primitive cubic structure has other primitive cubic unit cells next to it in all directions, on top of it, and underneath it. If you look at any one corner of the primitive cubic unit cell, you will see that it is shared by 8 unit cells. Therefore, in an individual primitive cubic unit cell, each corner contains only one-eighth of an atom. Because a cube has eight corners, each primitive cubic unit cell has a total of $1/8 \times 8 = 1$ atom. Similarly, each body-centered cubic unit cell shown in Figure 11.34 contains two atoms ($1/8 \times 8 = 1$ from the corners, and 1 totally inside the cube). Two unit cells share equally atoms that are on the faces of a face-centered cubic unit cell so that only one-half of the atom belongs to each unit cell. Therefore, the total number of atoms in the face-centered cubic unit cell shown in Figure 11.34 is four (that is, $1/8 \times 8 = 1$ from the corners and $1/2 \times 6 = 3$ from the faces). Table 11.6 summarizes the fraction of an atom that occupies a unit cell when atoms are shared between unit cells.

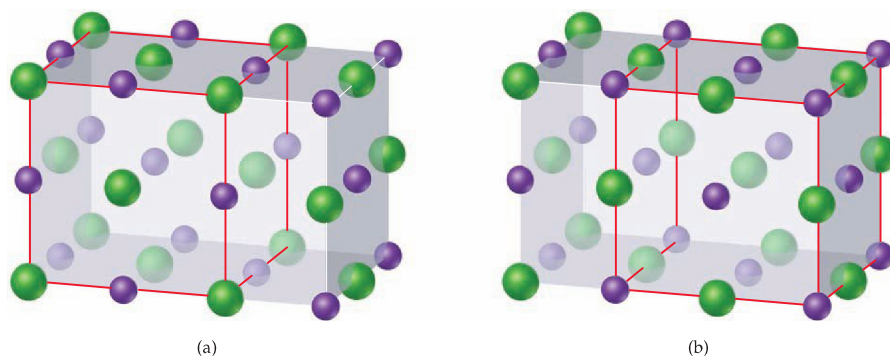
GIVE IT SOME THOUGHT

If you know the unit cell dimensions for a solid, the number of atoms per unit cell, and the mass of the atoms, show how you can calculate the density of the solid.

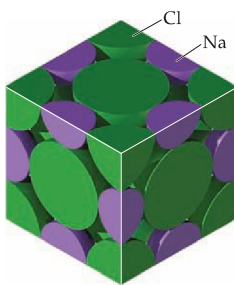
The Crystal Structure of Sodium Chloride

In the crystal structure of NaCl (Figure 11.35) we can center either the Na^+ ions or the Cl^- ions on the lattice points of a face-centered cubic unit cell. Thus, we can describe the structure as being face-centered cubic.

▼ **Figure 11.35** Two ways of defining the unit cell of NaCl. A representation of an NaCl crystal lattice can show either (a) Cl^- ions (green spheres) or (b) Na^+ ions (purple spheres) at the lattice points of the unit cell. In both cases, the red lines define the unit cell. Both of these choices for the unit cell are acceptable; both have the same volume, and in both cases identical points are arranged in a face-centered cubic fashion.



► **Figure 11.36**
Relative size of ions in an NaCl unit cell.
 As in Figure 11.35, purple represents Na^+ ions and green represents Cl^- ions. Only portions of most of the ions lie within the boundaries of the single unit cell.



In Figure 11.35 the Na^+ and Cl^- ions have been moved apart so the symmetry of the structure can be seen more clearly. In this representation no attention is paid to the relative sizes of the ions. The representation in Figure 11.36 ◀, on the other hand, shows the relative sizes of the ions and how they fill the unit cell. Notice that other unit cells share the particles at corners, edges, and faces.

The total cation-to-anion ratio of a unit cell must be the same as that for the entire crystal. Therefore, within the unit cell of NaCl there must be an equal number of Na^+ and Cl^- ions. Similarly, the unit cell for CaCl_2 would have one Ca^{2+} for every two Cl^- , and so forth.

■ SAMPLE EXERCISE 11.7 | Determining the Contents of a Unit Cell

Determine the net number of Na^+ and Cl^- ions in the NaCl unit cell (Figure 11.36).

SOLUTION

Analyze: We must sum the various contributing elements to determine the number of Na^+ and Cl^- ions within the unit cell.

Plan: To find the total number of ions of each type, we must identify the different locations within the unit cell and determine the fraction of the ion that lies within the unit cell boundaries.

Solve: There is one-fourth of an Na^+ on each edge, a whole Na^+ in the center of the cube (refer also to Figure 11.35), one-eighth of a Cl^- on each corner, and one-half of a Cl^- on each face. Thus, we have the following:

$$\begin{aligned} \text{Na}^+: & \left(\frac{1}{4} \text{Na}^+ \text{ per edge}\right)(12 \text{ edges}) = 3 \text{Na}^+ \\ & (1 \text{Na}^+ \text{ per center})(1 \text{ center}) = 1 \text{Na}^+ \\ \text{Cl}^-: & \left(\frac{1}{8} \text{Cl}^- \text{ per corner}\right)(8 \text{ corners}) = 1 \text{Cl}^- \\ & \left(\frac{1}{2} \text{Cl}^- \text{ per face}\right)(6 \text{ faces}) = 3 \text{Cl}^- \end{aligned}$$

Thus, the unit cell contains

$$4 \text{Na}^+ \text{ and } 4 \text{Cl}^-$$

Check: Since individually the Cl^- ions form a face-centered cubic lattice [see Figure 11.35(a)], as do the Na^+ ions [see Figure 11.35(b)], we would expect there to be four ions of each type in the unit cell. More important, the presence of equal amounts of the two ions agree with the compound's stoichiometry:

$$1 \text{Na}^+ \text{ for each } \text{Cl}^-$$

■ PRACTICE EXERCISE

The element iron crystallizes in a form called α -iron, which has a body-centered cubic unit cell. How many iron atoms are in the unit cell?

Answer: two

■ SAMPLE EXERCISE 11.8 | Using the Contents and Dimensions of a Unit Cell to Calculate Density

The geometric arrangement of ions in crystals of LiF is the same as that in NaCl. The unit cell of LiF is 4.02 \AA on an edge. Calculate the density of LiF.

SOLUTION

Analyze: We are asked to calculate the density of LiF from the size of the unit cell.

Plan: Density is mass per volume, and this is true at the unit cell level as well as the bulk level. We need to determine the number of formula units of LiF within the unit cell. From that, we can calculate the total mass within the unit cell. Because we know the mass and can calculate the volume of the unit cell, we can then calculate density.

Solve: The arrangement of ions in LiF is the same as that in NaCl (Sample Exercise 11.7), so a unit cell of LiF contains

$$4 \text{Li}^+ \text{ ions and } 4 \text{F}^- \text{ ions}$$

Density is mass per unit volume. Thus, we can calculate the density of LiF from the mass contained in a unit cell and the volume of the unit cell. The mass contained in one unit cell is

$$4(6.94 \text{ amu}) + 4(19.0 \text{ amu}) = 103.8 \text{ amu}$$

The volume of a cube of length a on an edge is a^3 , so the volume of the unit cell is $(4.02 \text{ \AA})^3$. We can now calculate the density, converting to the common units of g/cm^3 :

$$\text{Density} = \frac{(103.8 \text{ amu})}{(4.02 \text{ \AA})^3} \left(\frac{1 \text{ g}}{6.02 \times 10^{23} \text{ amu}} \right) \left(\frac{1 \text{ \AA}}{10^{-8} \text{ cm}} \right)^3 = 2.65 \text{ g}/\text{cm}^3$$

Check: This value agrees with that found by simple density measurements, $2.640 \text{ g}/\text{cm}^3$ at 20°C . The size and contents of the unit cell are therefore consistent with the macroscopic density of the substance.

■ PRACTICE EXERCISE

The body-centered cubic unit cell of a particular crystalline form of iron is 2.8664 \AA on each side. Calculate the density of this form of iron.

Answer: $7.8753 \text{ g}/\text{cm}^3$

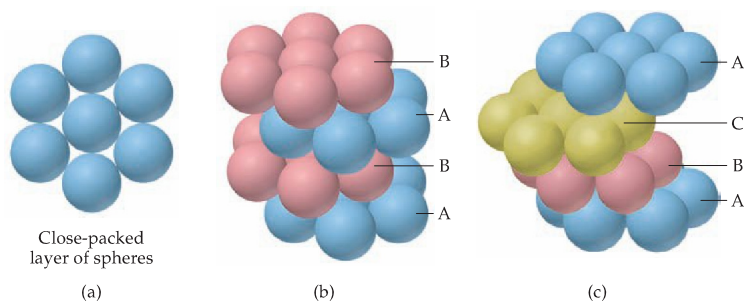
Close Packing of Spheres

The structures adopted by crystalline solids are those that bring particles in closest contact to maximize the attractive forces between them. In many cases the particles that make up the solids are spherical or approximately so. Such is the case for atoms in metallic solids. It is therefore instructive to consider how equal-sized spheres can pack most efficiently (that is, with the minimum amount of empty space).

The most efficient arrangement of a layer of equal-sized spheres is shown in Figure 11.37(a). Each sphere is surrounded by six others in the layer. A second layer of spheres can be placed in the depressions on top of the first layer. A third layer can then be added above the second with the spheres sitting in the depressions of the second layer. However, there are two types of depressions for this third layer, and they result in different structures, as shown in Figure 11.37(b) and (c).

If the spheres of the third layer are placed in line with those of the first layer, as shown in Figure 11.37(b), the structure is known as **hexagonal close packing**. The third layer repeats the first layer, the fourth layer repeats the second layer, and so forth, giving a layer sequence that we denote ABAB.

The spheres of the third layer, however, can be placed so they do not sit above the spheres in the first layer. The resulting structure, shown in Figure 11.37(c), is known as **cubic close packing**. In this case it is the fourth layer that repeats the first layer, and the layer sequence is ABCA. Although it cannot be seen in Figure 11.37(c), the unit cell of the cubic close-packed structure is face-centered cubic.



▲ Figure 11.37 Close packing of equal-sized spheres. (a) Close packing of a single layer of equal-sized spheres. (b) In the hexagonal close-packed structure the atoms in the third layer lie directly over those in the first layer. The order of layers is ABAB. (c) In the cubic close-packed structure the atoms in the third layer are not over those in the first layer. Instead, they are offset a bit, and it is the fourth layer that lies directly over the first. Thus, the order of layers is ABCA.

In both of the close-packed structures, each sphere has 12 equidistant nearest neighbors: six in one plane, three above that plane, and three below. We say that each sphere has a **coordination number** of 12. The coordination number is the number of particles immediately surrounding a particle in the crystal structure. In both types of close packing, spheres occupy 74% of the total volume of the structure; 26% is empty space between the spheres. By comparison, each sphere in the body-centered cubic structure has a coordination number of 8, and only 68% of the space is occupied. In the primitive cubic structure the coordination number is 6, and only 52% of the space is occupied.

When unequal-sized spheres are packed in a lattice, the larger particles sometimes assume one of the close-packed arrangements, with smaller particles occupying the holes between the large spheres. In Li_2O , for example, the larger oxide ions assume a cubic close-packed structure, and the smaller Li^+ ions occupy small cavities that exist between oxide ions.



GIVE IT SOME THOUGHT

Based on the information given above for close-packed structures and structures with cubic unit cells, what qualitative relationship exists between coordination numbers and packing efficiencies?

11.8 BONDING IN SOLIDS

The physical properties of crystalline solids, such as melting point and hardness, depend both on the arrangements of particles (atoms, ions, or molecules) and on the attractive forces between them. Table 11.7 ▼ classifies solids according to the types of forces between particles in solids.

Molecular Solids

Molecular solids consist of atoms or molecules held together by intermolecular forces (dipole–dipole forces, London dispersion forces, and hydrogen bonds). Because these forces are weak, molecular solids are soft. Furthermore, they normally have relatively low melting points (usually below 200 °C). Most substances that are gases or liquids at room temperature form molecular solids at low temperature. Examples include Ar, H_2O , and CO_2 .

TABLE 11.7 ■ Types of Crystalline Solids

| Type of Solid | Form of Unit Particles | Forces Between Particles | Properties | Examples |
|------------------|--|--|---|---|
| Molecular | Atoms or molecules | London dispersion forces, dipole–dipole forces, hydrogen bonds | Fairly soft, low to moderately high melting point, poor thermal and electrical conduction | Argon, Ar; methane, CH_4 ; sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$; Dry Ice, CO_2 |
| Covalent-network | Atoms connected in a network of covalent bonds | Covalent bonds | Very hard, very high melting point, variable thermal and electrical conduction | Diamond, C; quartz, SiO_2 |
| Ionic | Positive and negative ions | Electrostatic attractions | Hard and brittle, high melting point, poor thermal and electrical conduction | Typical salts—for example, NaCl, $\text{Ca}(\text{NO}_3)_2$ |
| Metallic | Atoms | Metallic bonds | Soft to very hard, low to very high melting point, excellent thermal and electrical conduction, malleable and ductile | All metallic elements—for example, Cu, Fe, Al, Pt |

A Closer Look X-RAY DIFFRACTION BY CRYSTALS

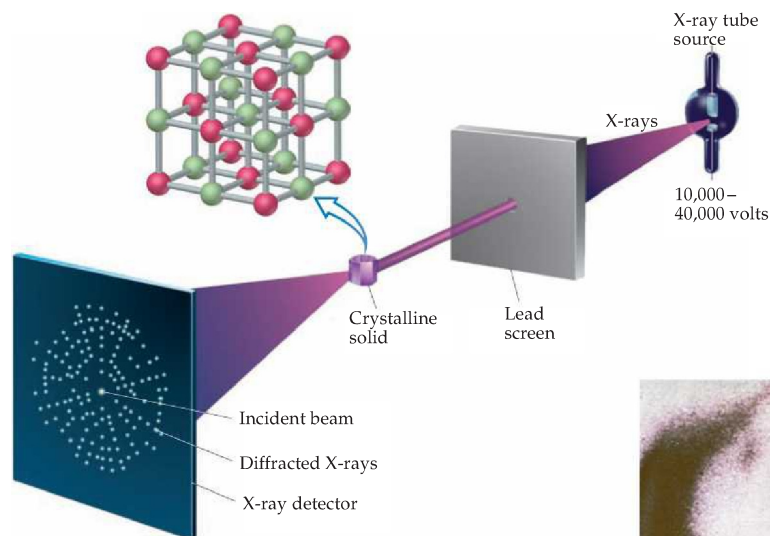
When light waves pass through a narrow slit, they are scattered in such a way that the wave seems to spread out. This physical phenomenon is called *diffraction*. When light passes through many evenly spaced narrow slits (a *diffraction grating*), the scattered waves interact to form a series of bright and dark bands, known as a diffraction pattern. The bright bands correspond to constructive overlapping of the light waves, and the dark bands correspond to destructive overlapping of the light waves (see Section 9.8, “A Closer Look: Phases in Atomic and Molecular Orbitals”). The most effective diffraction of light occurs when the wavelength of the light and the width of the slits are similar in magnitude.

The spacing of the layers of atoms in solid crystals is usually about 2–20 Å. The wavelengths of X-rays are also in this range. Thus, a crystal can serve as an effective diffraction grating for X-rays. X-ray diffraction results from the scattering of X-rays by a regular arrangement of atoms, molecules, or ions. Much of what we know about crystal structures has been obtained from studies of X-ray diffraction by crystals, a technique known as *X-ray crystallography*. Figure 11.38 depicts the diffraction of a beam of X-rays as it passes through a crystal. The diffracted X-rays were formerly detected by photographic film. Today, crystallographers use an *array detector*, a device analogous to that used in digital cameras, to capture and measure the intensities of the diffracted rays. The diffraction pattern of spots on the detector in Figure 11.38 depends on the particular arrangement of atoms in the crystal. Thus, different types of crystals give rise to different diffraction

patterns. In 1913 the English scientists William and Lawrence Bragg (father and son) determined for the first time how the spacing of layers in crystals leads to different X-ray diffraction patterns. By measuring the intensities of the diffracted beams and the angles at which they are diffracted, it is possible to reason backward to the structure that must have given rise to the pattern. One of the most famous X-ray diffraction patterns is the one for crystals of the genetic material DNA (Figure 11.39 ▼), first obtained in the early 1950s. Working from X-ray diffraction data obtained by Rosalind Franklin, Franklin, Maurice Wilkins, James Watson, and Francis Crick determined the double-helix structure of DNA, one of the most important discoveries in molecular biology. For this achievement, Watson, Crick, and Wilkins were awarded the Nobel Prize in Physiology or Medicine in 1962. Franklin died in 1958, at age 37, from cancer; Nobel Prizes are awarded only to the living (and can be shared by three people at the most).

Today X-ray crystallography is used extensively to determine the structures of molecules in crystals. The instruments used to measure X-ray diffraction, known as *X-ray diffractometers*, are now computer-controlled, making the collection of diffraction data highly automated. The diffraction pattern of a crystal can be determined very accurately and quickly (sometimes in a matter of hours), even though thousands of diffraction points are measured. Computer programs are then used to analyze the diffraction data and determine the arrangement and structure of the molecules in the crystal.

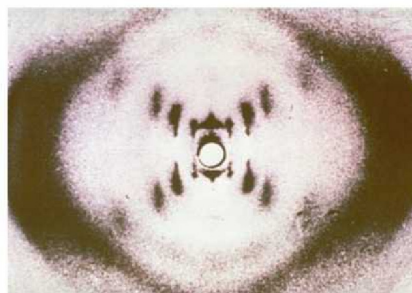
Related Exercises: 11.95, 11.96


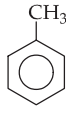
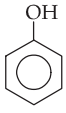


◀ **Figure 11.38 Diffraction of X-rays by a crystal.**

In X-ray crystallography, an X-ray beam is diffracted by a crystal. The diffraction pattern can be recorded as spots where the diffracted X-rays strike a detector, which records the positions and intensities of the spots.

▶ **Figure 11.39 The X-ray diffraction photograph of one form of crystalline DNA.** This photograph was taken in the early 1950s. From the pattern of dark spots, the double-helical shape of the DNA molecule was deduced.



| | | | |
|--------------------|---|---|---|
| |  |  |  |
| | Benzene | Toluene | Phenol |
| Melting point (°C) | 5 | -95 | 43 |
| Boiling point (°C) | 80 | 111 | 182 |

▲ **Figure 11.40** Comparative melting and boiling points for benzene, toluene, and phenol.

The properties of molecular solids depend on the strengths of the forces that exist between molecules and on the abilities of the molecules to pack efficiently in three dimensions. Benzene (C_6H_6), for example, is a highly symmetrical planar molecule. [∞∞ \(Section 8.6\)](#) It has a higher melting point than toluene, a compound in which one of the hydrogen atoms of benzene has been replaced by a CH_3 group (Figure 11.40 ◀). The lower symmetry of toluene molecules prevents them from packing as efficiently as benzene molecules. As a result, the intermolecular forces that depend on close contact are not as effective and the melting point is lower. In contrast, the boiling point of toluene is higher than that of benzene, indicating that the intermolecular attractive forces are larger in liquid toluene than in liquid benzene. Both the melting and boiling points of phenol, another substituted benzene shown in Figure 11.40, are higher than those of benzene because the OH group of phenol can form hydrogen bonds.

GIVE IT SOME THOUGHT

Which of the following substances would you expect to form molecular solids: Co, C_6H_6 , or K_2O ?

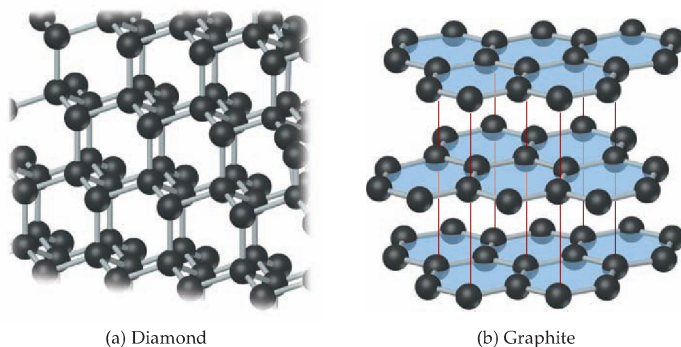
Covalent-Network Solids

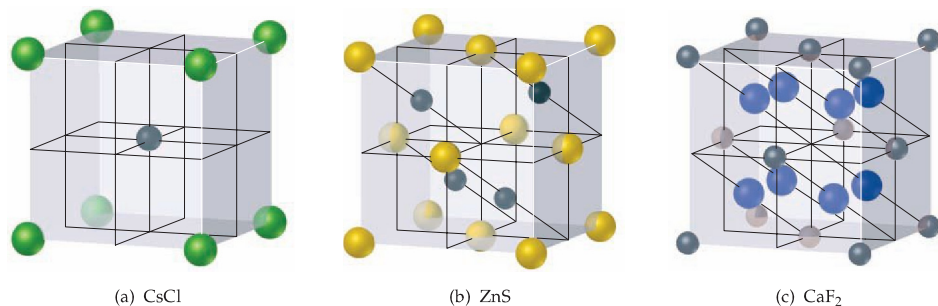
Covalent-network solids consist of atoms held together, throughout the entire sample of material, in large networks or chains by covalent bonds. Because covalent bonds are much stronger than intermolecular forces, these solids are much harder and have higher melting points than molecular solids. Diamond and graphite, two allotropes of carbon, are covalent-network solids. Other examples include silicon and germanium; quartz, SiO_2 ; silicon carbide, SiC ; and boron nitride, BN.

In diamond, each carbon atom is bonded tetrahedrally to four other carbon atoms, as shown in Figure 11.41(a) ▼. This interconnected three-dimensional array of strong carbon-carbon single bonds that are sp^3 hybridized contributes to diamond's unusual hardness. Industrial-grade diamonds are employed in the blades of saws for the most demanding cutting jobs. Diamond also has a high melting point, $3550\text{ }^\circ\text{C}$.

In graphite, the carbon atoms are bonded in trigonal planar geometries to three other carbons to form interconnected hexagonal rings, as shown in Figure 11.41(b). The distance between adjacent carbon atoms in the plane, 1.42 \AA , is very close to the C—C distance in benzene, 1.395 \AA . In fact, the bonding resembles that of benzene, with delocalized π bonds extending over the layers. [∞∞ \(Section 9.6\)](#) Electrons move freely through the delocalized orbitals,

► **Figure 11.41** Structures of (a) diamond and (b) graphite. The blue color in (b) is added to emphasize the planarity of the carbon layers.





▲ **Figure 11.42 Unit cells of some common ionic structures.** The ZnS shown in (b) is called zinc blende, and the CaF_2 of (c) is known as fluorite.

making graphite a good conductor of electricity along the layers. (In fact, graphite is used as a conducting electrode in batteries.) These sp^2 -hybridized sheets of carbon atoms are separated by 3.35 \AA from one another, and the sheets are held together only by weak dispersion forces. Thus, the layers readily slide past one another when rubbed, giving graphite a greasy feel. Graphite is used as a lubricant and in the “lead” in pencils. The enormous differences in physical properties of graphite and diamond—both of which are pure carbon—arise from their differences in their three-dimensional structure and bonding.

Ionic Solids

Ionic solids consist of ions held together by ionic bonds. ∞ (Section 8.2) The strength of an ionic bond depends greatly on the charges of the ions. Thus, NaCl, in which the ions have charges of $1+$ and $1-$, has a melting point of $801 \text{ }^\circ\text{C}$, whereas MgO, in which the charges are $2+$ and $2-$, melts at $2852 \text{ }^\circ\text{C}$.

The structures of simple ionic solids can be classified as a few basic types. The NaCl structure is a representative example of one type. Other compounds that possess this same structure include LiF, KCl, AgCl, and CaO. Three other common types of crystal structures are shown in Figure 11.42 ▲.

The structure adopted by an ionic solid depends largely on the charges and relative sizes of the ions. In the NaCl structure, for example, the Na^+ ions have a coordination number of 6 because each Na^+ ion is surrounded by six nearest neighbor Cl^- ions. In the CsCl structure [Figure 11.42(a)], by comparison, the Cl^- ions adopt a primitive cubic arrangement with each Cs^+ ion surrounded by eight Cl^- ions. The increase in the coordination number as the alkali metal ion changes from Na^+ to Cs^+ is a consequence of the larger size of Cs^+ compared to Na^+ .

In the zinc blende (ZnS) structure [Figure 11.42(b)], the S^{2-} ions adopt a face-centered cubic arrangement, with the smaller Zn^{2+} ions arranged so they are each surrounded tetrahedrally by four S^{2-} ions (compare with Figure 11.33). CuCl also adopts this structure.

In the fluorite (CaF_2) structure [Figure 11.42(c)], the Ca^{2+} ions are shown in a face-centered cubic arrangement. As required by the chemical formula of the substance, there are twice as many F^- ions (blue) in the unit cell as there are Ca^{2+} ions. Other compounds that have the fluorite structure include BaCl_2 and PbF_2 .

Metallic Solids

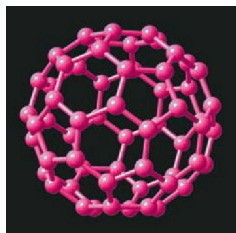
Metallic solids, also simply called metals, consist entirely of metal atoms. Metallic solids usually have hexagonal close-packed, cubic close-packed (face-centered cubic), or body-centered cubic structures. Thus, each atom typically is surrounded by eight or 12 adjacent atoms.

A Closer Look THE THIRD FORM OF CARBON

Until the mid-1980s pure solid carbon was thought to exist in only two forms: diamond and graphite, both of which are covalent-network solids. In 1985 a group of researchers led by Richard Smalley and Robert Curl of Rice University in Houston and Harry Kroto of the University of Sussex in England made a startling discovery. They vaporized a sample of graphite with an intense pulse of laser light and used a stream of helium gas to carry the vaporized carbon into a mass spectrometer (see Section 2.4, “A Closer Look: The Mass Spectrometer”). The mass spectrum showed peaks corresponding to clusters of carbon atoms, with a particularly strong peak corresponding to molecules composed of 60 carbon atoms, C_{60} .

Because C_{60} clusters were so preferentially formed, the group proposed a radically different form of carbon, namely, C_{60} molecules that were nearly spherical in shape. They proposed that the carbon atoms of C_{60} form a “ball” with 32 faces, 12 of which are pentagons and 20 are hexagons (Figure 11.43 ▼), exactly like a soccer ball. The shape of this molecule is reminiscent of the geodesic dome invented by the U.S. engineer and philosopher R. Buckminster Fuller, so C_{60} was whimsically named “buckminsterfullerene,” or “buckyball” for short. Since the discovery of C_{60} , other related molecules of carbon atoms have been discovered. These molecules are now known as fullerenes.

Appreciable amounts of buckyball can be prepared by electrically evaporating graphite in an atmosphere of helium gas. About 14% of the resulting soot consists of C_{60} and a related molecule, C_{70} , which has a more elongated structure.

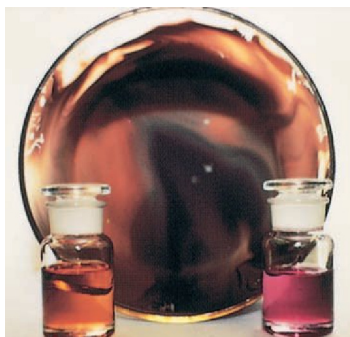


▲ **Figure 11.43** The buckminsterfullerene molecule, C_{60} . The molecule has a highly symmetric structure in which the 60 carbon atoms sit at the vertices of a truncated icosahedron—the same geometry as a soccer ball.

The carbon-rich gases from which C_{60} and C_{70} condense also contain other fullerenes, mostly with more carbon atoms such as C_{76} and C_{84} . The smallest possible fullerene, C_{20} , was first detected in 2000. This small, ball-shaped molecule is much more reactive than the larger fullerenes.

Because the fullerenes are composed of individual molecules, they dissolve in various organic solvents, whereas diamond and graphite do not (Figure 11.44 ▼). This solubility permits the fullerenes to be separated from the other components of soot and even from each other. It also allows the study of their reactions in solution. Study of these substances has led to the discovery of some very interesting chemistry. For example, it is possible to place a metal atom inside a buckyball, generating a molecule in which a metal atom is completely enclosed by the carbon sphere. The C_{60} molecules also react with potassium to give K_3C_{60} , which contains a face-centered cubic array of buckyballs with K^+ ions in the cavities between them. This compound is a superconductor at 18 K (to see Section 12.1), suggesting the possibility that other fullerenes may also have interesting electrical, magnetic, or optical properties. For their discovery and pioneering work with fullerenes, Professors Smalley, Curl, and Kroto were awarded the 1996 Nobel Prize in Chemistry.

Related Exercise: 11.97



▲ **Figure 11.44** Solutions of fullerenes. Unlike diamond and graphite, the new molecular forms of carbon can be dissolved in organic solvents. The orange solution on the left is a solution of C_{70} in *n*-hexane, which is a colorless liquid. The magenta solution on the right is a solution of buckyball, C_{60} , in *n*-hexane.

The bonding in metals is too strong to be due to London dispersion forces, and yet there are not enough valence electrons for ordinary covalent bonds between atoms. The bonding is due to valence electrons that are delocalized throughout the entire solid. In fact, we can visualize the metal as an array of positive ions immersed in a sea of delocalized valence electrons, as shown in Figure 11.45 ▶. This type of bonding is called *metallic bonding* and will be discussed in more detail in Section 23.5.

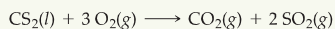
Metals vary greatly in the strength of their bonding, as shown by their wide range of physical properties such as hardness and melting point. In general, however, the strength of the bonding increases as the number of electrons available for bonding increases. Thus, sodium, which has only one valence electron per atom, melts at 97.5 °C, whereas chromium, with six electrons beyond the noble-gas core, melts at 1890 °C. The mobility of the electrons explains why metals are good conductors of heat and electricity. The bonding and properties of metals will be examined more closely in Chapter 23.

SAMPLE INTEGRATIVE EXERCISE | Putting Concepts Together

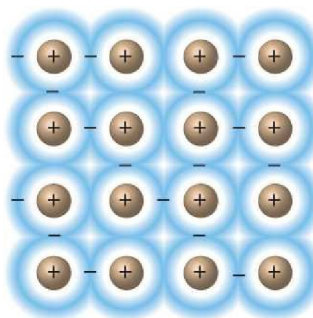
The substance CS_2 has a melting point of $-110.8\text{ }^\circ\text{C}$ and a boiling point of $46.3\text{ }^\circ\text{C}$. Its density at $20\text{ }^\circ\text{C}$ is 1.26 g/cm^3 . It is highly flammable. (a) What is the name of this compound? (b) List the intermolecular forces that CS_2 molecules would have with each other. (c) Predict what type of crystalline solid $\text{CS}_2(\text{s})$ would form. (d) Write a balanced equation for the combustion of this compound in air. (You will have to decide on the most likely oxidation products.) (e) The critical temperature and pressure for CS_2 are 552 K and 78 atm, respectively. Compare these values with those for CO_2 (Table 11.5), and discuss the possible origins of the differences. (f) Would you expect the density of CS_2 at $40\text{ }^\circ\text{C}$ to be greater or less than at $20\text{ }^\circ\text{C}$? What accounts for the difference?

SOLUTION

(a) The compound is named carbon disulfide, in analogy with the naming of other binary molecular compounds such as carbon dioxide. \leftrightarrow (Section 2.8)
 (b) Only London dispersion forces affect CS_2 ; it does not have a dipole moment, based upon its molecular shape, and obviously cannot undergo hydrogen bonding.
 (c) Because $\text{CS}_2(\text{s})$ consists of individual CS_2 molecules, it will be a molecular solid.
 (d) The most likely products of the combustion will be CO_2 and SO_2 . \leftrightarrow (Sections 3.2 and 7.8) Under some conditions SO_3 might be formed, but this would be the less likely outcome. Thus, we have the following equation for combustion:



(e) The critical temperature and pressure of CS_2 (552 K and 78 atm) are both higher than those given for CO_2 in Table 11.5 (304 K and 73 atm). The difference in critical temperatures is especially notable. The higher values for CS_2 arise from the greater London dispersion attractions between the CS_2 molecules compared with CO_2 . These greater attractions are due to the larger size of the sulfur compared to oxygen and therefore its greater polarizability.
 (f) The density would be lower at the higher temperature. Density decreases with increasing temperature because the molecules possess higher kinetic energies. Their more energetic movements result in larger average distances between molecules, which translate into lower densities.



▲ Figure 11.45 Representation of a cross section of a metal. Each sphere represents the nucleus and inner-core electrons of a metal atom. The surrounding blue “fog” represents the mobile sea of electrons that binds the atoms together.

CHAPTER REVIEW

SUMMARY AND KEY TERMS

Introduction and Section 11.1 Substances that are gases or liquids at room temperature are usually composed of molecules. In gases the intermolecular attractive forces are negligible compared to the kinetic energies of the molecules; thus, the molecules are widely separated and undergo constant, chaotic motion. In liquids the intermolecular forces are strong enough to keep the molecules in close proximity; nevertheless, the molecules are free to move with respect to one another. In solids the interparticle attractive forces are strong enough to restrain

molecular motion and to force the particles to occupy specific locations in a three-dimensional arrangement.

Section 11.2 Three types of intermolecular forces exist between neutral molecules: **dipole–dipole forces**, **London dispersion forces**, and **hydrogen bonding**. **Ion–dipole forces** are important in solutions in which ionic compounds are dissolved in polar solvents. London dispersion forces operate between all molecules (and atoms, for atomic substances such as He, Ne, Ar, and so forth). The relative

strengths of the dipole–dipole and dispersion forces depend on the polarity, **polarizability**, size, and shape of the molecule. Dipole–dipole forces increase in strength with increasing polarity. Dispersion forces increase in strength with increasing molecular weight, although molecular shape is also an important factor. Hydrogen bonding occurs in compounds containing O—H, N—H, and F—H bonds. Hydrogen bonds are generally stronger than dipole–dipole or dispersion forces.

Section 11.3 The stronger the intermolecular forces, the greater is the **viscosity**, or resistance to flow, of a liquid. The surface tension of a liquid also increases as intermolecular forces increase in strength. **Surface tension** is a measure of the tendency of a liquid to maintain a minimum surface area. The adhesion of a liquid to the walls of a narrow tube and the cohesion of the liquid account for **capillary action** and the formation of a meniscus at the surface of a liquid.

Section 11.4 A substance may exist in more than one state of matter, or phase. **Phase changes** are transformations from one phase to another. Changes of a solid to liquid (melting), solid to gas (sublimation), and liquid to gas (vaporization) are all endothermic processes. Thus, the **heat of fusion** (melting), the **heat of sublimation**, and the **heat of vaporization** are all positive quantities. The reverse processes are exothermic. A gas cannot be liquefied by application of pressure if the temperature is above its **critical temperature**. The pressure required to liquefy a gas at its critical temperature is called the **critical pressure**.

Section 11.5 The **vapor pressure** of a liquid indicates the tendency of the liquid to evaporate. The vapor pressure is the partial pressure of the vapor when it is in **dynamic equilibrium** with the liquid. At equilibrium the rate of transfer of molecules from the liquid to the vapor equals the rate of transfer from the vapor to the liquid. The higher the vapor pressure of a liquid, the more readily it evaporates and the more **volatile** it is. Vapor pressure increases nonlinearly with temperature. Boiling occurs when the vapor pressure equals the external pressure.

The **normal boiling point** is the temperature at which the vapor pressure equals 1 atm.

Section 11.6 The equilibria between the solid, liquid, and gas phases of a substance as a function of temperature and pressure are displayed on a **phase diagram**. A line indicates equilibria between any two phases. The line through the melting point usually slopes slightly to the right as pressure increases, because the solid is usually more dense than the liquid. The melting point at 1 atm is the **normal melting point**. The point on the diagram at which all three phases coexist in equilibrium is called the **triple point**.

Section 11.7 In a **crystalline solid**, particles are arranged in a regularly repeating pattern. An **amorphous solid** is one whose particles show no such order. The essential structural features of a crystalline solid can be represented by its **unit cell**, the smallest part of the crystal that can, by simple displacement, reproduce the three-dimensional structure. The three-dimensional structures of a crystal can also be represented by its **crystal lattice**. The points in a crystal lattice represent positions in the structure where there are identical environments. The simplest unit cells are cubic. There are three kinds of cubic unit cells: **primitive cubic**, **body-centered cubic**, and **face-centered cubic**. Many solids have a close-packed structure in which spherical particles are arranged so as to leave the minimal amount of empty space. Two closely related forms of close packing, **cubic close packing** and **hexagonal close packing**, are possible. In both, each sphere has a **coordination number** of 12.

Section 11.8 The properties of solids depend both on the arrangements of particles and on the attractive forces between them. **Molecular solids**, which consist of atoms or molecules held together by intermolecular forces, are soft and low melting. **Covalent-network solids**, which consist of atoms held together by covalent bonds that extend throughout the solid, are hard and high melting. **Ionic solids** are hard and brittle and have high melting points. **Metallic solids**, which consist of metal cations held together by a sea of electrons, exhibit a wide range of properties.

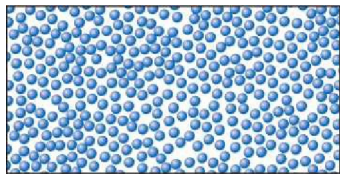
KEY SKILLS

- Understand and be able to describe the intermolecular attractive interactions (ion–dipole, dipole–dipole, London dispersion, hydrogen bonding) that exist between molecules or ions, and be able to compare the relative strengths of intermolecular attractions in substances based on their molecular structure, or physical properties.
- Understand the concept of polarizability.
- Understand the concepts of viscosity and surface tension in liquids.
- Know the names of the various phase changes for a pure substance.
- Interpret heating curves and be able to calculate quantities related to temperature and enthalpies of phase changes.
- Define critical pressure, critical temperature, vapor pressure, normal boiling point, normal melting point, critical point, triple point.
- Be able to interpret and sketch phase diagrams; know how water's phase diagram differs from most other substances, and why.

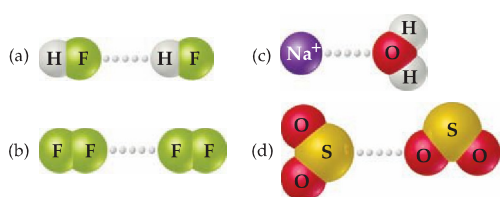
- Know the difference between crystalline and amorphous solids, and be able to explain the differences between primitive cubic, body-centered cubic, and face-centered cubic unit cells.
- Classify solids based on their bonding/intermolecular forces and understand how difference in bonding relates to physical properties.

VISUALIZING CONCEPTS

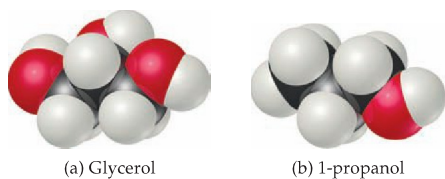
- 11.1 Does the following diagram best describe a crystalline solid, liquid, or gas? Explain. [Section 11.1]



- 11.2 (a) What kind of intermolecular attractive force is shown in each of the following cases? (b) Predict which two interactions are stronger than the other two. [Section 11.2]

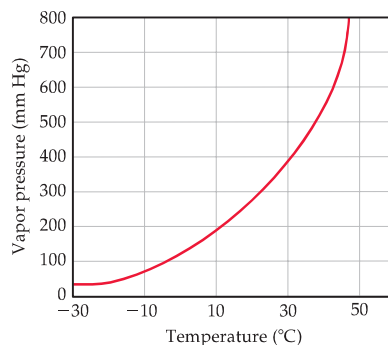


- 11.3 The molecular models of glycerol and 1-propanol are given here.

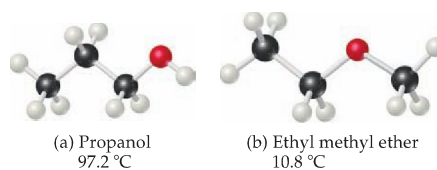


Do you expect the viscosity of glycerol to be larger or smaller than that of 1-propanol? Explain. [Section 11.3]

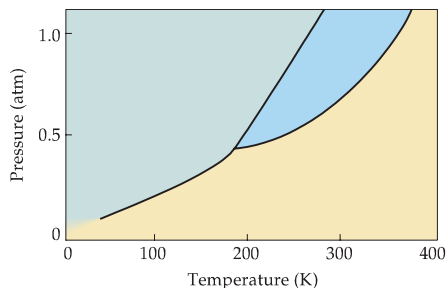
- 11.4 Using the following graph of CS_2 data, determine (a) the approximate vapor pressure of CS_2 at 30°C , (b) the temperature at which the vapor pressure equals 300 torr, (c) the normal boiling point of CS_2 . [Section 11.5]



- 11.5 The following molecules have the same molecular formula ($\text{C}_3\text{H}_8\text{O}$), yet they have different normal boiling points, as shown. Rationalize the difference in boiling points. [Sections 11.2 and 11.5]

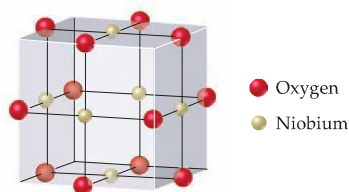


- 11.6 The phase diagram of a hypothetical substance is shown below.



- (a) Estimate the normal boiling point and freezing point of the substance.
- (b) What is the physical state of the substance under the following conditions?
- $T = 150\text{ K}, P = 0.2\text{ atm}$
 - $T = 100\text{ K}, P = 0.8\text{ atm}$
 - $T = 300\text{ K}, P = 1.0\text{ atm}$
- (c) What is the triple point of the substance? [Section 11.6]

- 11.7 Niobium(II) oxide crystallizes in the following cubic unit cell.



- (a) How many niobium atoms and how many oxygen atoms are within the unit cell?
 (b) What is the empirical formula of niobium oxide?
 (c) Is this a molecular, covalent-network, or ionic solid? [Sections 11.7 and 11.8]

- 11.8 (a) What kind of packing arrangement is seen in the accompanying photo? (b) What is the coordination number of each orange in the interior of the stack? (c) If each orange represents an argon atom, what category of solid is represented? [Sections 11.7 and 11.8]



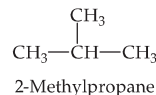
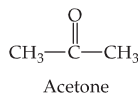
EXERCISES

Molecular Comparisons of Gases, Liquids, and Solids

- 11.9 List the three states of matter in order of (a) increasing molecular disorder and (b) increasing intermolecular attractions. (c) Which state of matter is most easily compressed?
- 11.10 (a) How does the average kinetic energy of molecules compare with the average energy of attraction between molecules in solids, liquids, and gases? (b) Why does increasing the temperature cause a solid substance to change in succession from a solid to a liquid to a gas? (c) What happens to a gas if you put it under extremely high pressure?
- 11.11 If you mix olive oil with water, the olive oil will float on top of the water. The density of water is 1.00 g/cm^3 at room temperature. (a) Is the density of olive oil more or less than 1.00 g/cm^3 ? (b) The density of olive oil in its liquid phase does vary with temperature. Do you think olive oil would be more dense or less dense at higher temperatures? Explain.
- 11.12 Benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, melts at 122°C . The density in the liquid state at 130°C is 1.08 g/cm^3 . The density of solid benzoic acid at 15°C is 1.266 g/cm^3 . (a) In which of these two states is the average distance between molecules greater? (b) Explain the difference in densities at the two temperatures in terms of the relative kinetic energies of the molecules.

Intermolecular Forces

- 11.13 Which type of intermolecular attractive force operates between (a) all molecules, (b) polar molecules, (c) the hydrogen atom of a polar bond and a nearby small electronegative atom?
- 11.14 Based on what you have learned about intermolecular forces, would you say that matter is fundamentally attracted or repulsed by other matter?
- 11.15 Describe the intermolecular forces that must be overcome to convert each of the following from a liquid or solid to a gas: (a) I_2 , (b) $\text{CH}_3\text{CH}_2\text{OH}$, (c) H_2Se .
- 11.16 What type of intermolecular force accounts for the following differences in each case? (a) CH_3OH boils at 65°C , CH_3SH boils at 6°C . (b) Xe is liquid at atmospheric pressure and 120 K , whereas Ar is a gas. (c) Kr, atomic weight 84, boils at 120.9 K , whereas Cl_2 , molecular weight about 71, boils at 238 K . (d) Acetone boils at 56°C , whereas 2-methylpropane boils at -12°C .



- 11.17 (a) What is meant by the term *polarizability*? (b) Which of the following atoms would you expect to be most polarizable: N, P, As, Sb? Explain. (c) Put the following molecules in order of increasing polarizability: GeCl_4 , CH_4 , SiCl_4 , SiH_4 , and GeBr_4 . (d) Predict the order of boiling points of the substances in part (c).

- 11.18 True or false:
- The more polarizable the molecules, the stronger the dispersion forces between them.
 - The boiling points of the noble gases decrease as you go down the column in the periodic table.
 - In general, the smaller the molecule, the stronger the dispersion forces.
 - All other factors being the same, dispersion forces between molecules increase with the number of electrons in the molecules.
- 11.19 Which member of the following pairs has the larger London dispersion forces: (a) H_2O or H_2S , (b) CO_2 or CO , (c) SiH_4 or GeH_4 ?
- 11.20 Which member of the following pairs has the stronger intermolecular dispersion forces: (a) Br_2 or O_2 , (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$ or $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$, (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ or $(\text{CH}_3)_2\text{CHCl}$?
- 11.21 Butane and 2-methylpropane, whose space-filling models are shown, are both nonpolar and have the same molecular formula, yet butane has the higher boiling point (-0.5°C compared to -11.7°C). Explain.



(a) Butane (b) 2-Methylpropane

- 11.22 Propyl alcohol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$) and isopropyl alcohol [$(\text{CH}_3)_2\text{CHOH}$], whose space-filling models are shown, have boiling points of 97.2°C and 82.5°C , respectively. Explain why the boiling point of propyl alcohol is higher, even though both have the molecular formula of $\text{C}_3\text{H}_8\text{O}$.



(a) Propyl alcohol (b) Isopropyl alcohol

- 11.23 (a) What atoms must a molecule contain to participate in hydrogen bonding with other molecules of the same kind? (b) Which of the following molecules can form hydrogen bonds with other molecules of the same kind: CH_3F , CH_3NH_2 , CH_3OH , CH_3Br ?
- 11.24 Rationalize the difference in boiling points between the members of the following pairs of substances: (a) HF (20°C) and HCl (-85°C), (b) CHCl_3 (61°C) and CHBr_3 (150°C), (c) Br_2 (59°C) and ICl (97°C).
- 11.25 Ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$), the major substance in antifreeze, has a normal boiling point of 198°C . By comparison, ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$) boils at 78°C at atmospheric pressure. Ethylene glycol dimethyl ether ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$) has a normal boiling point of 83°C , and ethyl methyl ether ($\text{CH}_3\text{CH}_2\text{OCH}_3$) has a normal boiling point of 11°C . (a) Explain why replacement of a hydrogen on the oxygen by CH_3 generally results in a lower boiling point. (b) What are the major factors responsible for the difference in boiling points of the two ethers?
- 11.26 Identify the types of intermolecular forces present in each of the following substances, and select the substance in each pair that has the higher boiling point: (a) C_6H_{14} or C_8H_{18} , (b) C_3H_8 or CH_3OCH_3 , (c) HOOH or HSSH , (d) NH_2NH_2 or CH_3CH_3 .
- 11.27 Look up and compare the normal boiling points and normal melting points of H_2O and H_2S . (a) Based on these physical properties, which substance has stronger intermolecular forces? What kind of intermolecular forces exist for each molecule? (b) Predict whether solid H_2S is more or less dense than liquid H_2S . How does this compare to H_2O ? Explain. (c) Water has an unusually high specific heat. Is this related to its intermolecular forces? Explain.
- 11.28 The following quote about ammonia (NH_3) is from a textbook of inorganic chemistry: "It is estimated that 26% of the hydrogen bonding in NH_3 breaks down on melting, 7% on warming from the melting to the boiling point, and the final 67% on transfer to the gas phase at the boiling point." From the standpoint of the kinetic energy of the molecules, explain (a) why there is a decrease of hydrogen-bonding energy on melting and (b) why most of the loss in hydrogen bonding occurs in the transition from the liquid to the vapor state.

Viscosity and Surface Tension

- 11.29 (a) Explain why surface tension and viscosity decrease with increasing temperature. (b) Why do substances with high surface tensions also tend to have high viscosities?
- 11.30 (a) Distinguish between adhesive forces and cohesive forces. (b) What adhesive and cohesive forces are involved when a paper towel absorbs water? (c) Explain the cause for the U-shaped meniscus formed when water is in a glass tube.
- 11.31 Explain the following observations: (a) The surface tension of CHBr_3 is greater than that of CHCl_3 . (b) As temperature increases, oil flows faster through a narrow tube. (c) Raindrops that collect on a waxed automobile hood take on a nearly spherical shape. (d) Oil droplets that collect on a waxed automobile hood take on a flat shape.
- 11.32 Hydrazine (H_2NNH_2), hydrogen peroxide (HOOH), and water (H_2O) all have exceptionally high surface tensions compared with other substances of comparable molecular weights. (a) Draw the Lewis structures for these three compounds. (b) What structural property do these substances have in common, and how might that account for the high surface tensions?

Phase Changes

- 11.33** Name the phase transition in each of the following situations, and indicate whether it is exothermic or endothermic: (a) When ice is heated, it turns to water. (b) Wet clothes dry on a warm summer day. (c) Frost appears on a window on a cold winter day. (d) Droplets of water appear on a cold glass of beer.
- 11.34** Name the phase transition in each of the following situations, and indicate whether it is exothermic or endothermic: (a) Bromine vapor turns to bromine liquid as it is cooled. (b) Crystals of iodine disappear from an evaporating dish as they stand in a fume hood. (c) Rubbing alcohol in an open container slowly disappears. (d) Molten lava from a volcano turns into solid rock.
- 11.35** Explain why the heat of fusion of any substance is generally lower than its heat of vaporization.
- 11.36** Ethyl chloride (C_2H_5Cl) boils at $12^\circ C$. When liquid C_2H_5Cl under pressure is sprayed on a room-temperature ($25^\circ C$) surface in air, the surface is cooled considerably. (a) What does this observation tell us about the specific heat of $C_2H_5Cl(g)$ as compared with $C_2H_5Cl(l)$? (b) Assume that the heat lost by the surface is gained by ethyl chloride. What enthalpies must you consider if you were to calculate the final temperature of the surface?
- 11.37** For many years drinking water has been cooled in hot climates by evaporating it from the surfaces of canvas bags or porous clay pots. How many grams of water can be cooled from $35^\circ C$ to $20^\circ C$ by the evaporation of 60 g of water? (The heat of vaporization of water in this temperature range is 2.4 kJ/g . The specific heat of water is $4.18 \text{ J/g}\cdot K$.)
- 11.38** Compounds like CCl_2F_2 are known as chlorofluorocarbons, or CFCs. These compounds were once widely used as refrigerants but are now being replaced by compounds that are believed to be less harmful to the environment. The heat of vaporization of CCl_2F_2 is 289 J/g . What mass of this substance must evaporate to freeze 200 g of water initially at $15^\circ C$? (The heat of fusion of water is 334 J/g ; the specific heat of water is $4.18 \text{ J/g}\cdot K$.)
- 11.39** Ethanol (C_2H_5OH) melts at $-114^\circ C$ and boils at $78^\circ C$. Its density is 0.789 g/mL . The enthalpy of fusion of ethanol is 5.02 kJ/mol , and its enthalpy of vaporization is 38.56 kJ/mol . The specific heats of solid and liquid ethanol are $0.97 \text{ J/g}\cdot K$ and $2.3 \text{ J/g}\cdot K$, respectively. (a) How much heat is required to convert 25.0 g of ethanol at $25^\circ C$ to the vapor phase at $78^\circ C$? (b) How much heat is required to convert 5.00 L of ethanol at $-140^\circ C$ to the vapor phase at $78^\circ C$?
- 11.40** The fluorocarbon compound $C_2Cl_3F_3$ has a normal boiling point of $47.6^\circ C$. The specific heats of $C_2Cl_3F_3(l)$ and $C_2Cl_3F_3(g)$ are $0.91 \text{ J/g}\cdot K$ and $0.67 \text{ J/g}\cdot K$, respectively. The heat of vaporization for the compound is 27.49 kJ/mol . Calculate the heat required to convert 50.0 g of $C_2Cl_3F_3$ from a liquid at $10.00^\circ C$ to a gas at $85.00^\circ C$.
- 11.41** (a) What is the significance of the critical pressure of a substance? (b) What happens to the critical temperature of a series of compounds as the force of attraction between molecules increases? (c) Which of the substances listed in Table 11.5 can be liquefied at the temperature of liquid nitrogen ($-196^\circ C$)?
- 11.42** The critical temperatures (K) and pressures (atm) of a series of halogenated methanes are as follows:

| Compound | CCl_3F | CCl_2F_2 | $CClF_3$ | CF_4 |
|----------------------|----------|------------|----------|--------|
| Critical Temperature | 471 | 385 | 302 | 227 |
| Critical Pressure | 43.5 | 40.6 | 38.2 | 37.0 |

- (a) List the intermolecular forces that occur for each compound. (b) Predict the order of increasing intermolecular attraction, from least to most, for this series of compounds. (c) Predict the critical temperature and pressure for CCl_4 based on the trends in this table. Look up the experimentally determined critical temperatures and pressures for CCl_4 , using a source such as the *CRC Handbook of Chemistry and Physics*, and suggest a reason for any discrepancies.

Vapor Pressure and Boiling Point

- 11.43** Explain how each of the following affects the vapor pressure of a liquid: (a) volume of the liquid, (b) surface area, (c) intermolecular attractive forces, (d) temperature, (e) density of the liquid.
- 11.44** A liquid that has an equilibrium vapor pressure of 130 torr at $25^\circ C$ is placed into a 1-L vessel like that shown in Figure 11.22. What is the pressure difference shown on the manometer, and what is the composition of the gas in the vessel, under each of the following conditions: (a) Two hundred mL of the liquid is introduced into the vessel and frozen at the bottom. The vessel is evacuated and sealed, and the liquid is allowed to warm to $25^\circ C$. (b) Two hundred milliliters of the liquid is added to the vessel at $25^\circ C$ under atmospheric pressure, and after a few minutes the vessel is closed off. (c) A few mL of the liquid is introduced into the vessel at $25^\circ C$ while it has a pressure of 1 atm of air in it, without allowing any of the air to escape. After a few minutes a few drops of liquid remain in the vessel.
- 11.45** (a) Place the following substances in order of increasing volatility: CH_4 , CBr_4 , CH_2Cl_2 , CH_3Cl , $CHBr_3$, and CH_2Br_2 . Explain. (b) How do the boiling points vary through this series?
- 11.46** True or false:
 (a) CBr_4 is more volatile than CCl_4 .
 (b) CBr_4 has a higher boiling point than CCl_4 .
 (c) CBr_4 has weaker intermolecular forces than CCl_4 .
 (d) CBr_4 has a higher vapor pressure at the same temperature than CCl_4 .

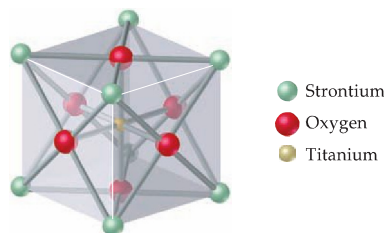
- 11.47** (a) Two pans of water are on different burners of a stove. One pan of water is boiling vigorously, while the other is boiling gently. What can be said about the temperature of the water in the two pans? (b) A large container of water and a small one are at the same temperature. What can be said about the relative vapor pressures of the water in the two containers?
- 11.48** Explain the following observations: (a) Water evaporates more quickly on a hot, dry day than on a hot, humid day. (b) It takes longer to boil water for tea at high altitudes than at lower altitudes.
- 11.49** Using the vapor-pressure curves in Figure 11.24, (a) estimate the boiling point of ethanol at an external pressure of 200 torr; (b) estimate the external pressure at which ethanol will boil at 60 °C; (c) estimate the boiling point of diethyl ether at 400 torr; (d) estimate the external pressure at which diethyl ether will boil at 40 °C.
- 11.50** Appendix B lists the vapor pressure of water at various external pressures.
- (a) Plot the data in Appendix B, vapor pressure (torr) vs. temperature (°C). From your plot, estimate the vapor pressure of water at body temperature, 37 °C.
- (b) Explain the significance of the data point at 760.0 torr, 100 °C.
- (c) A city at an altitude of 5000 ft above sea level has a barometric pressure of 633 torr. To what temperature would you have to heat water to boil it in this city?
- (d) A city at an altitude of 500 ft below sea level would have a barometric pressure of 774 torr. To what temperature would you have to heat water to boil it in this city?
- (e) For the two cities in parts (c) and (d), compare the average kinetic energies of the water molecules at their boiling points. Are the kinetic energies the same or different? Explain.

Phase Diagrams

- 11.51** (a) What is the significance of the critical point in a phase diagram? (b) Why does the line that separates the gas and liquid phases end at the critical point?
- 11.52** (a) What is the significance of the triple point in a phase diagram? (b) Could you measure the triple point of water by measuring the temperature in a vessel in which water vapor, liquid water, and ice are in equilibrium under one atmosphere of air? Explain.
- 11.53** Refer to Figure 11.27(a), and describe all the phase changes that would occur in each of the following cases: (a) Water vapor originally at 0.005 atm and -0.5 °C is slowly compressed at constant temperature until the final pressure is 20 atm. (b) Water originally at 100.0 °C and 0.50 atm is cooled at constant pressure until the temperature is -10 °C.
- 11.54** Refer to Figure 11.27(b), and describe the phase changes (and the temperatures at which they occur) when CO_2 is heated from -80 °C to -20 °C at (a) a constant pressure of 3 atm, (b) a constant pressure of 6 atm.
- 11.55** Sketch a generic phase diagram for a substance that has a more dense solid phase than a liquid phase. Label all regions, lines, and points.
- 11.56** The normal melting and boiling points of O_2 are -218 °C and -183 °C respectively. Its triple point is at -219 °C and 1.14 torr, and its critical point is at -119 °C and 49.8 atm. (a) Sketch the phase diagram for O_2 , showing the four points given and indicating the area in which each phase is stable. (b) Will $\text{O}_2(\text{s})$ float on $\text{O}_2(\text{l})$? Explain. (c) As it is heated, will solid O_2 sublime or melt under a pressure of 1 atm?

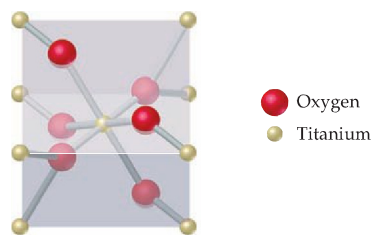
Structures of Solids

- 11.57** (a) Draw a picture that represents a crystalline solid at the atomic level. (b) Now draw a picture that represents an amorphous solid at the atomic level.
- 11.58** Amorphous silica has a density of about 2.2 g/cm^3 , whereas the density of crystalline quartz is 2.65 g/cm^3 . Account for this difference in densities.
- 11.59** Tausonite, a mineral composed of Sr, O, and Ti, has the cubic unit cell shown in the drawing. (a) What is the chemical formula of this mineral? (b) It is easy to see that Ti is coordinated by six oxygen atoms, because the Ti atom is located at the center of the unit cell. To see the full coordination environment of the other ions, we have to consider neighboring unit cells. How many oxygens are coordinated to strontium?

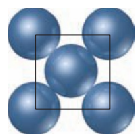


- 11.60** Rutile is a mineral composed of Ti and O. Its unit cell, shown in the drawing, contains Ti atoms at each corner and a Ti atom at the center of the cell. Four O atoms are

on the opposite faces of the cell, and two are entirely within the cell. (a) What is the chemical formula of this mineral? (b) What is the nature of the bonding that holds the solid together? (c) What is the coordination number of each atom?



- 11.61** Iridium crystallizes in a face-centered cubic unit cell that has an edge length of 3.833 Å. The atom in the center of the face is in contact with the corner atoms, as shown in the drawing. (a) Calculate the atomic radius of an iridium atom. (b) Calculate the density of iridium metal.



- 11.62** Aluminum metal crystallizes in a cubic close-packed structure (face-centered cubic cell, Figure 11.34). (a) How many aluminum atoms are in a unit cell? (b) What is the coordination number of each aluminum atom? (c) Assume that the aluminum atoms can be represented as spheres, as shown in the drawing for

Exercise 11.61. If each Al atom has a radius of 1.43 Å, what is the length of a side of the unit cell? (d) Calculate the density of aluminum metal.

- 11.63** An element crystallizes in a body-centered cubic lattice. The edge of the unit cell is 2.86 Å, and the density of the crystal is 7.92 g/cm³. Calculate the atomic weight of the element.
- 11.64** KCl has the same structure as NaCl. The length of the unit cell is 628 pm. The density of KCl is 1.984 g/cm³, and its formula mass is 74.55 amu. Using this information, calculate Avogadro's number.
- 11.65** NaF has the same structure as NaCl. (a) Use ionic radii from Chapter 7 to estimate the length of the unit cell edge for NaF. (b) Use the unit cell size calculated in part (a) to estimate the density of NaF.
- 11.66** What is the coordination number of (a) Na⁺ in the NaCl structure, Figure 11.35; (b) Zn²⁺ in the ZnS unit cell, Figure 11.42(b); (c) Ca²⁺ in the CaF₂ unit cell, Figure 11.42(c)?
- 11.67** Clausthalite is a mineral composed of lead selenide (PbSe). The mineral adopts a NaCl-type structure. The density of PbSe at 25 °C is 8.27 g/cm³. Calculate the length of an edge of the PbSe unit cell.
- 11.68** A particular form of cinnabar (HgS) adopts the zinc blende structure, Figure 11.42(b). The length of the unit cell side is 5.852 Å. (a) Calculate the density of HgS in this form. (b) The mineral tiemannite (HgSe) also forms a solid phase with the zinc blende structure. The length of the unit cell side in this mineral is 6.085 Å. What accounts for the larger unit cell length in tiemannite? (c) Which of the two substances has the higher density? How do you account for the difference in densities?

Bonding in Solids

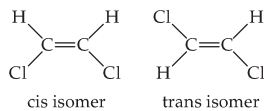
- 11.69** It is possible to change the temperature and pressure of a vessel containing argon gas so that the gas solidifies. (a) What intermolecular forces exist between argon atoms? (b) Is the solid argon a "covalent network solid"? Why or why not?
- 11.70** (a) Silicon is the fundamental component of integrated circuits. Si has the same structure as diamond. Is Si a molecular, metallic, ionic, or covalent-network solid? (b) Silica is SiO₂. What type of solid would you expect silica to form?
- 11.71** What kinds of attractive forces exist between particles in (a) molecular crystals, (b) covalent-network crystals, (c) ionic crystals, (d) metallic crystals?
- 11.72** Indicate the type of crystal (molecular, metallic, covalent-network, or ionic) each of the following would form upon solidification: (a) CaCO₃, (b) Pt, (c) ZrO₂ (melting point, 2677 °C), (d) table sugar (C₁₂H₂₂O₁₁), (e) benzene, (f) I₂.
- 11.73** Covalent bonding occurs in both molecular and covalent-network solids. Why do these two kinds of solids differ so greatly in their hardness and melting points?
- 11.74** Which type (or types) of crystalline solid is characterized by each of the following: (a) high mobility of electrons throughout the solid; (b) softness, relatively low melting point; (c) high melting point and poor electrical conductivity; (d) network of covalent bonds; (e) charged particles throughout the solid.
- 11.75** A white substance melts with some decomposition at 730 °C. As a solid, it does not conduct electricity, but it dissolves in water to form a conducting solution. Which type of solid (Table 11.7) might the substance be?
- 11.76** You are given a white substance that sublimates at 3000 °C; the solid is a nonconductor of electricity and is insoluble in water. Which type of solid (Table 11.7) might this substance be?
- 11.77** For each of the following pairs of substances, predict which will have the higher melting point and indicate why: (a) Ar, Xe; (b) SiO₂, CO₂; (c) KBr, Br₂; (d) C₆Cl₆, C₆H₆.
- 11.78** For each of the following pairs of substances, predict which will have the higher melting point, and indicate why: (a) HF, HCl; (b) C (graphite), CH₄; (c) KCl, Cl₂; (d) LiF, MgF₂.

ADDITIONAL EXERCISES

11.79 As the intermolecular attractive forces between molecules increase in magnitude, do you expect each of the following to increase or decrease in magnitude? (a) vapor pressure, (b) heat of vaporization, (c) boiling point, (d) freezing point, (e) viscosity, (f) surface tension, (g) critical temperature.

11.80 Suppose you have two colorless molecular liquids, one boiling at -84°C , the other at 34°C , and both at atmospheric pressure. Which of the following statements is correct? For those that are not correct, modify the statement so that it is correct. (a) The higher-boiling liquid has greater total intermolecular forces than the other. (b) The lower boiling liquid must consist of nonpolar molecules. (c) The lower-boiling liquid has a lower molecular weight than the higher-boiling liquid. (d) The two liquids have identical vapor pressures at their normal boiling points. (e) At 34°C both liquids have vapor pressures of 760 mm Hg.

11.81 Two isomers of the planar compound 1,2-dichloroethylene are shown here, along with their melting and boiling points.



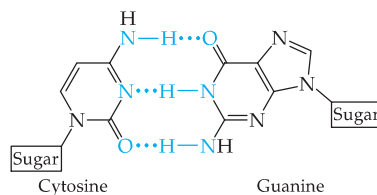
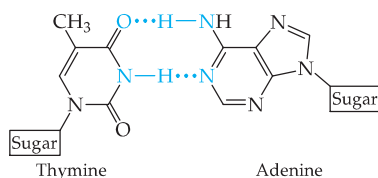
| | | |
|------------------------------------|-------|-------|
| Melting point ($^\circ\text{C}$) | -80.5 | -49.8 |
| Boiling point ($^\circ\text{C}$) | 60.3 | 47.5 |

(a) Which of the two isomers will have the stronger dipole-dipole forces? Is this prediction borne out by the data presented here? (b) Based on the data presented here, which isomer packs more efficiently in the solid phase?

11.82 In dichloromethane, CH_2Cl_2 ($\mu = 1.60\text{ D}$), the dispersion force contribution to the intermolecular attractive forces is about five times larger than the dipole-dipole contribution. Would you expect the relative importance of the two kinds of intermolecular attractive forces to differ (a) in dibromomethane ($\mu = 1.43\text{ D}$), (b) in difluoromethane ($\mu = 1.93\text{ D}$)? Explain.

11.83 When an atom or group of atoms is substituted for an H atom in benzene (C_6H_6), the boiling point changes. Explain the order of the following boiling points: C_6H_6 (80°C), $\text{C}_6\text{H}_5\text{Cl}$ (132°C), $\text{C}_6\text{H}_5\text{Br}$ (156°C), $\text{C}_6\text{H}_5\text{OH}$ (182°C).

11.84 The DNA double helix (Figure 25.40) at the atomic level looks like a twisted ladder, where the "rungs" of the ladder consist of molecules that are hydrogen-bonded together. Sugar and phosphate groups make up the sides of the ladder. Shown are the structures of the adenine-thymine (AT) "base pair" and the guanine-cytosine (GC) base pair:



You can see that AT base pairs are held together by two hydrogen bonds, and the GC base pairs are held together by three hydrogen bonds. Which base pair is more stable to heating?

11.85 Ethylene glycol [$\text{CH}_2(\text{OH})\text{CH}_2(\text{OH})$] is the major component of antifreeze. It is a slightly viscous liquid, not very volatile at room temperature, with a boiling point of 198°C . Pentane (C_5H_{12}), which has about the same molecular weight, is a nonviscous liquid that is highly volatile at room temperature and whose boiling point is 36.1°C . Explain the differences in the physical properties of the two substances.

11.86 Using the following list of normal boiling points for a series of hydrocarbons, estimate the normal boiling point for octane, C_8H_{18} : propane (C_3H_8 , -42.1°C), butane (C_4H_{10} , -0.5°C), pentane (C_5H_{12} , 36.1°C), hexane (C_6H_{14} , 68.7°C), heptane (C_7H_{16} , 98.4°C). Explain the trend in the boiling points.

[11.87] Notice in Figure 11.21 that there is a pressure-reduction valve in the line just before the supercritical CO_2 and dissolved caffeine enter the separator. Suggest an explanation for the function of this valve in the overall process.

11.88 (a) When you exercise vigorously, you sweat. How does this help your body cool? (b) A flask of water is connected to a vacuum pump. A few moments after the pump is turned on, the water begins to boil. After a few minutes, the water begins to freeze. Explain why these processes occur.

[11.89] The following table gives the vapor pressure of hexafluorobenzene (C_6F_6) as a function of temperature:

| Temperature (K) | Vapor Pressure (torr) |
|-----------------|-----------------------|
| 280.0 | 32.42 |
| 300.0 | 92.47 |
| 320.0 | 225.1 |
| 330.0 | 334.4 |
| 340.0 | 482.9 |

(a) By plotting these data in a suitable fashion, determine whether the Clausius-Clapeyron equation is obeyed. If it is obeyed, use your plot to determine ΔH_{vap} for C_6F_6 . (b) Use these data to determine the boiling point of the compound.

[11.90] Suppose the vapor pressure of a substance is measured at two different temperatures. (a) By using the Clausius-Clapeyron equation, Equation 11.1, derive the following relationship between the vapor pressures, P_1 and P_2 , and the absolute temperatures at which they were measured, T_1 and T_2 :

$$\ln \frac{P_1}{P_2} = -\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

(b) Gasoline is a mixture of hydrocarbons, a major component of which is octane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$. Octane has a vapor pressure of 13.95 torr at 25 °C and a vapor pressure of 144.78 torr at 75 °C. Use these data and the equation in part (a) to calculate the heat of vaporization of octane. (c) By using the equation in part (a) and the data given in part (b), calculate the normal boiling point of octane. Compare your answer to the one you obtained from Exercise 11.86. (d) Calculate the vapor pressure of octane at -30 °C.

- [11.91] The following data present the temperatures at which certain vapor pressures are achieved for dichloromethane (CH_2Cl_2) and methyl iodide (CH_3I):

| Vapor Pressure (torr): | 10.0 | 40.0 | 100.0 | 400.0 |
|--|-------|-------|-------|-------|
| T for CH_2Cl_2 (°C): | -43.3 | -22.3 | -6.3 | 24.1 |
| T for CH_3I (°C): | -45.8 | -24.2 | -7.0 | 25.3 |

(a) Which of the two substances is expected to have the greater dipole-dipole forces? Which is expected to have the greater London dispersion forces? Based on your answers, explain why it is difficult to predict which compound would be more volatile. (b) Which compound would you expect to have the higher boiling point? Check your answer in a reference book such as the *CRC Handbook of Chemistry and Physics*. (c) The order of volatility of these two substances changes as the temperature is increased. What quantity must be different for the two substances in order for this phenomenon to occur? (d) Substantiate your answer for part (c) by drawing an appropriate graph.

- 11.92 The elements xenon and gold both have solid-state structures with face-centered cubic unit cells, yet Xe melts at -112 °C and gold melts at 1064 °C. Account for these greatly different melting points.
- 11.93 In Chapter 7 we saw that Li reacts with oxygen to form lithium oxide, Li_2O , while the larger alkali metals react with oxygen to form peroxides (such as Na_2O_2 , K_2O_2 , etc.). The origin of this curious pattern of reactivity is

related to the relative sizes of the cation and anion and the overall stoichiometry. Li_2O crystallizes with a structure called the antifluorite structure. This structure is identical to the fluorite structure shown in Figure 11.42(c), but the cations and anions have been switched. (a) In Li_2O , what are the coordination numbers for each ion? (b) As the cation radius increases, would you expect the coordination number to increase or decrease (assuming the anion size does not change)? (c) Why do you think the antifluorite structure becomes unstable for A_2O ($\text{A} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) compounds of the heavier alkali metal ions?

- 11.94 Gold crystallizes in a face-centered cubic unit cell that has an edge length of 4.078 Å. The atom in the center of the face is in contact with the corner atoms, as shown in the drawing for Exercise 11.61. (a) Calculate the apparent radius of a gold atom in this structure. (b) Calculate the density of gold metal.
- 11.95 (a) Explain why X-rays can be used to measure atomic distances in crystals but visible light cannot. (b) Why can't CaCl_2 have the same crystal structure as NaCl ?
- 11.96 In their study of X-ray diffraction, William and Lawrence Bragg determined that the relationship among the wavelength of the radiation (λ), the angle at which the radiation is diffracted (θ), and the distance between the layers of atoms in the crystal that cause the diffraction (d) is given by $n\lambda = 2d \sin \theta$. (a) X-rays from a copper X-ray tube that have a wavelength of 1.54 Å are diffracted at an angle of 14.22 degrees by crystalline silicon. Using the Bragg equation, calculate the interplanar spacing in the crystal, assuming $n = 1$ (first-order diffraction). (b) Repeat the calculation of part (a) but for the $n = 2$ case (second-order diffraction).
- [11.97] (a) The density of diamond [Figure 11.41(a)] is 3.5 g/cm³, and that of graphite [Figure 11.41(b)] is 2.3 g/cm³. Based on the structure of buckminsterfullerene (Figure 11.43), what would you expect its density to be relative to these other forms of carbon? (b) X-ray diffraction studies of buckminsterfullerene show that it has a face-centered cubic lattice of C_{60} molecules. The length of a side of the unit cell is 14.2 Å. Calculate the density of buckminsterfullerene.

INTEGRATIVE EXERCISES

- 11.98 Spinel is a mineral that contains 37.9% Al, 17.1% Mg, and 45.0% O, by mass, and has a density of 3.57 g/cm³. The unit cell is cubic, with an edge length of 809 pm. How many atoms of each type are in the unit cell?
- 11.99 (a) At the molecular level, what factor is responsible for the steady increase in viscosity with increasing molecular weight in the hydrocarbon series shown in Table 11.4? (b) Although the viscosity varies over a factor of more than two in the series from hexane to nonane, the surface tension at 25 °C increases by only about 20% in the same series. How do you account for this? (c) *n*-Octyl alcohol, $\text{CH}_3(\text{CH}_2)_7\text{OH}$, has a viscosity of $1.01 \times 10^{-2} \text{ kg m}^{-1}\text{s}^{-1}$, much higher than nonane,

which has about the same molecular weight. What accounts for this difference? How does your answer relate to the difference in normal boiling points for these two substances?

- 11.100 Acetone, $(\text{CH}_3)_2\text{CO}$, is widely used as an industrial solvent. (a) Draw the Lewis structure for the acetone molecule, and predict the geometry around each carbon atom. (b) Is the acetone molecule polar or nonpolar? (c) What kinds of intermolecular attractive forces exist between acetone molecules? (d) 1-Propanol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, has a molecular weight that is very similar to that of acetone, yet acetone boils at 56.5 °C and 1-propanol boils at 97.2 °C. Explain the difference.

11.101 The table shown here lists the molar heats of vaporization for several organic compounds. Use specific examples from this list to illustrate how the heat of vaporization varies with (a) molar mass, (b) molecular shape, (c) molecular polarity, (d) hydrogen-bonding interactions. Explain these comparisons in terms of the nature of the intermolecular forces at work. (You may find it helpful to draw out the structural formula for each compound.)

| Compound | Heat of Vaporization (kJ/mol) |
|---|-------------------------------|
| CH ₃ CH ₂ CH ₃ | 19.0 |
| CH ₃ CH ₂ CH ₂ CH ₂ CH ₃ | 27.6 |
| CH ₃ CHBrCH ₃ | 31.8 |
| CH ₃ COCH ₃ | 32.0 |
| CH ₃ CH ₂ CH ₂ Br | 33.6 |
| CH ₃ CH ₂ CH ₂ OH | 47.3 |

11.102 Liquid butane, C₄H₁₀, is stored in cylinders, to be used as a fuel. The normal boiling point of butane is listed as -0.5 °C. (a) Suppose the tank is standing in the sun and reaches a temperature of 35 °C. Would you expect the pressure in the tank to be greater or less than atmospheric pressure? How does the pressure within the tank depend on how much liquid butane is in it? (b) Suppose the valve to the tank is opened and a few liters of butane are allowed to escape rapidly. What do you expect would happen to the temperature of the remaining liquid butane in the tank? Explain. (c) How much heat must be added to vaporize 250 g of butane if its heat of vaporization is 21.3 kJ/mol? What volume does this much butane occupy at 755 torr and 35 °C?

[11.103] Using information in Appendices B and C, calculate the minimum number of grams of propane, C₃H₈(g), that must be combusted to provide the energy necessary to convert 5.50 kg of ice at -20 °C to liquid water at 75 °C.

11.104 In a certain type of nuclear reactor, liquid sodium metal is employed as a circulating coolant in a closed system, protected from contact with air or water. Much like the coolant that circulates in an automobile engine, the liquid sodium carries heat from the hot reactor core to heat exchangers. (a) What properties of the liquid sodium are of special importance in this application? (b) The viscosity of liquid sodium varies with temperature as follows:

| Temperature (°C) | Viscosity (kg m ⁻¹ s ⁻¹) |
|------------------|---|
| 100 | 7.05 × 10 ⁻⁴ |
| 200 | 4.50 × 10 ⁻⁴ |
| 300 | 3.45 × 10 ⁻⁴ |
| 600 | 2.10 × 10 ⁻⁴ |

What forces within the liquid sodium are likely to be the major contributors to the viscosity? Why does viscosity decrease with increasing temperature?

11.105 The vapor pressure of a volatile liquid can be determined by slowly bubbling a known volume of gas through it at a known temperature and pressure. In an experiment, 5.00 L of N₂ gas is passed through 7.2146 g of liquid benzene, C₆H₆, at 26.0 °C. The liquid remaining after the experiment weighs 5.1493 g. Assuming that the gas becomes saturated with benzene vapor and that the total gas volume and temperature remain constant, what is the vapor pressure of the benzene in torr?

11.106 The relative humidity of air equals the ratio of the partial pressure of water in the air to the equilibrium vapor pressure of water at the same temperature, times 100%. If the relative humidity of the air is 58% and its temperature is 68 °F, how many molecules of water are present in a room measuring 12 ft × 10 ft × 8 ft?

11.107 Use a reference source such as the *CRC Handbook of Chemistry and Physics* to compare the melting and boiling points of the following pairs of inorganic substances: (a) W and WF₆, (b) SO₂ and SF₄, (c) SiO₂ and SiCl₄. Account for the major differences observed in terms of likely structures and bonding.