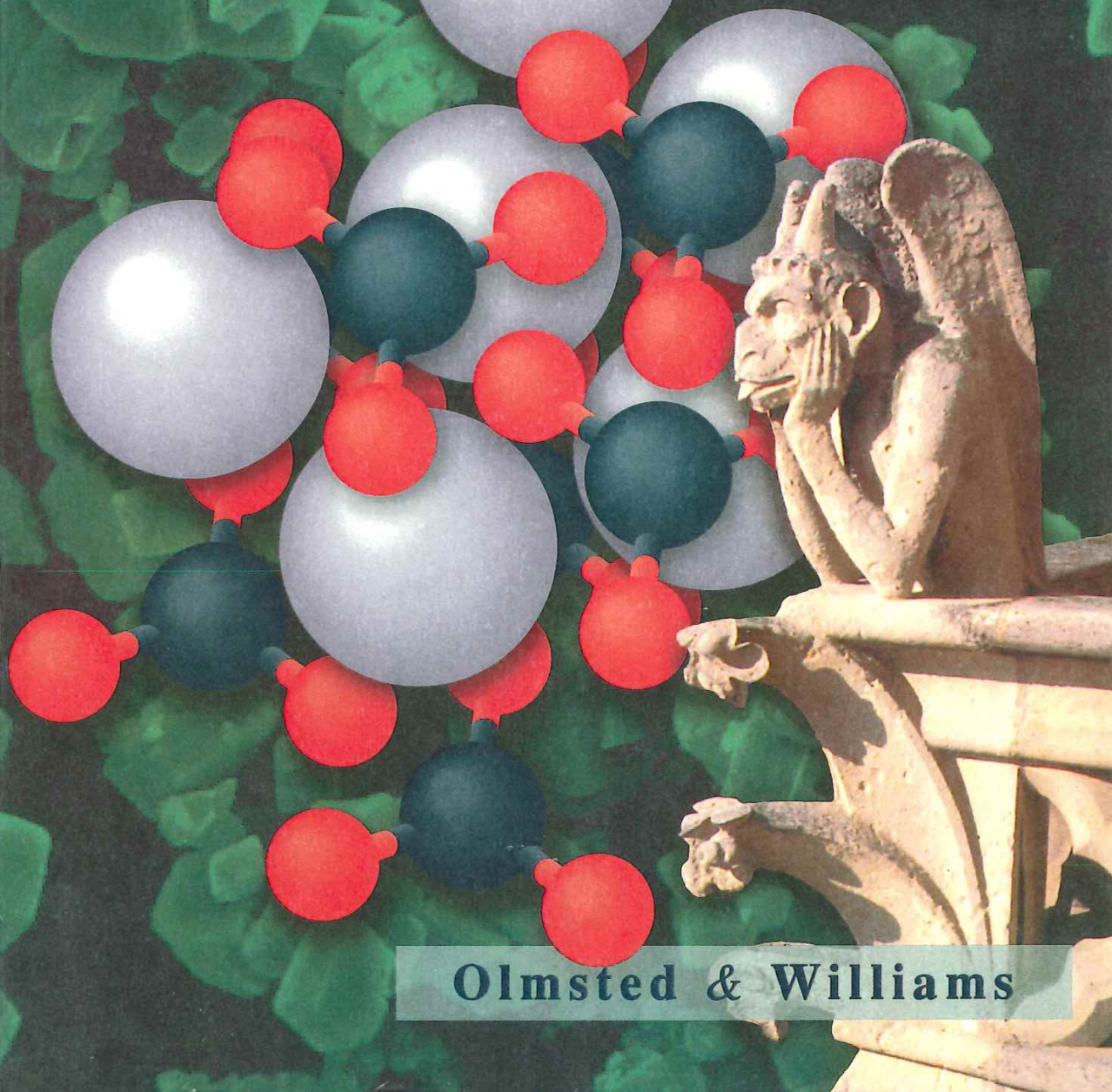


CHEMISTRY

THE MOLECULAR SCIENCE

Second Edition



Olmsted & Williams

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Chapter 10

Effects of Intermolecular Forces

Intermolecular forces give even as simple a molecule as H_2O the capability of forming massive glaciers and lacy snowflakes.



Introduction: Personal Care Products

- 10.1 The Nature of Intermolecular Forces
- 10.2 Types of Intermolecular Forces
- 10.3 Forces in Solids
- 10.4 Order in Solids
- 10.5 The Nature of Solutions
- 10.6 Dual-Nature Molecules: Surfactants and Biological Membranes
- 10.7 Properties of Aqueous Solutions



INTRODUCTION: PERSONAL CARE PRODUCTS

When you take a shower, interaction among molecules is probably the last thing you are likely to think about. Yet, personal care products such as shampoos, hair sprays, and cosmetics contain a wide variety of chemicals whose primary purpose is to modify the forces that exist between molecules, so-called **intermolecular forces**.

Consider, for example, the “smooth” feeling that we associate with clean skin and healthy hair. A hand glides easily over something smooth because the skin encounters little frictional resistance. The attractive forces between molecules are relatively weak. Hair conditioners and body lotions contain substances that coat the skin or hair with an ultrathin layer of molecules that offer low intermolecular forces to a hand or a comb.

Chemical substances can be classified according to whether they have strong attractions to water (hydrophilic) or weak attractions to water (hydrophobic). Water by itself has difficulty removing dirt and grease from clothing and skin because these hydrophobic materials are attracted more strongly to the surface than to water. Soaps and detergents contain molecules that have strong attractive forces to both water and hydrophobic substances. They assist in cleaning by associating with hydrophobic dirt particles to form clumps that are strongly attracted to water.

“Spray-on” products such as hair spray and spray deodorants must combine both strong and weak intermolecular forces. In the can, they must flow easily, or the spray action will become fouled. The ability of molecules to flow easily from place to place requires weak intermolecular forces. After application, the active ingredients must adhere to the target surface, which requires strong intermolecular forces. The ingredients of a successful spray product impart minimal “stickiness” to the solution in the can but maximal “stickiness” after application and evaporation of the solvent.

Ingredients of personal care products must have appropriate intermolecular force characteristics, but they must also be nontoxic and biodegradable. Chemists who work for companies that make such products face challenging chemical design problems. The stakes are high because personal care products are a \$25 billion-plus annual market in the United States alone.

No single substance can provide all the properties desired in a personal care product, so a typical list of ingredients contains a multitude of exotic-sounding chemicals. One protective hand cream lists the following ingredients: water, glyceryl stearate, cetyl alcohol, dimethicone, mineral oil, imidazolidinyl urea, fragrance, sodium lauryl sulfate, and methylparaben. Some of these names occur again later in this chapter; when you encounter them later, you will be able to identify them according to their intermolecular force characteristics.

Earlier chapters emphasize the forces that bind atoms together into molecules. Chapters 8 and 9, for example, describe the bonding that exists *within molecules*, called **intramolecular forces**. Chapter 5 presents the properties of a gas in terms of the ideal gas model, which assumes that the forces acting *between molecules* of a gas are negligible. In reality, there are indeed intermolecular forces acting between molecules. They affect the properties of gases and explain the existence and properties of liquids and solids.

Intermolecular forces are considerably weaker than intramolecular forces. In a liquid, for example, intermolecular forces are weak enough to allow individual molecules to move about relatively freely. In contrast, intramolecular forces are strong enough to prevent atoms from breaking away from the molecules to which they are bonded. Consequently, a discussion of bonding can ignore relatively weak intermolecular interactions. To understand the properties of liquids and solids, however, these interactions must be taken into account. Intermolecular forces “lock” mole-

Solids	Liquids	Gases
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10.1 THE NATURE OF INTERMOLECULAR FORCES

The Halogens

Fluorine and chlorine are gases under ambient conditions. Their molecules move freely throughout their gaseous volume, traveling many molecular diameters

Liquid Br₂Gaseous Cl_2

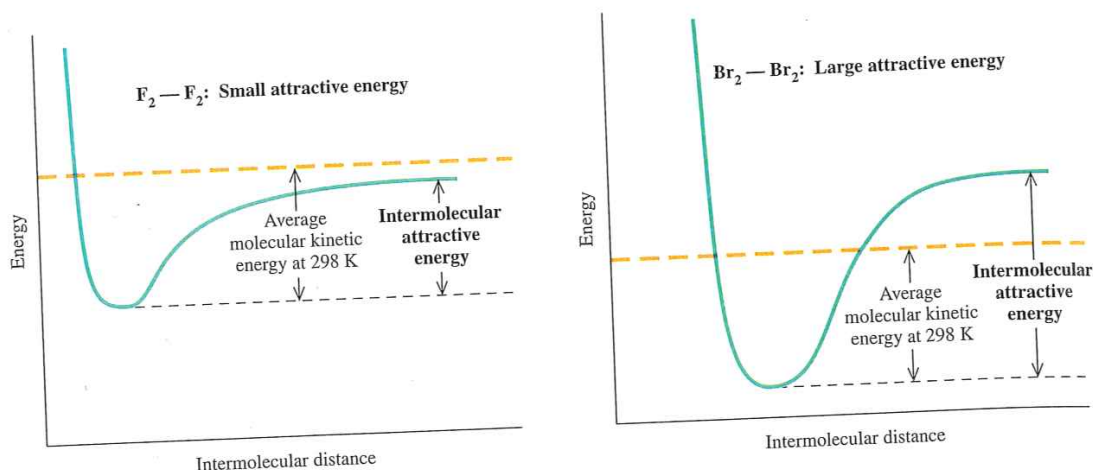
At room temperature and pressure, H, He, N, O, F, Cl, Ne, Ar, Kr, Xe, and Rn are gases, and Hg and Br are liquids. All other elements are solids.



Under normal conditions, chlorine is a pale yellow-green gas, bromine is a dark red liquid, and iodine is a purple crystalline solid.

Figure 10-3

Molecular representations of solid I_2 , liquid Br_2 , and gaseous Cl_2 demonstrate why gases, liquids, and solids behave differently. A gas is mostly empty space, so the molecules are free to move about the entire volume of their container. Molecules in a liquid are packed closely together but can still move past one another. A crystalline solid contains a regular array of molecules that vibrate about favored positions but cannot move freely by one another.

**Figure 10-4**

Intermolecular attractive forces stabilize molecules that are close to one another. The plots show that the attractive energy between bromine molecules is greater than the average kinetic energy of the molecules at room temperature, whereas for fluorine molecules the average kinetic energy exceeds the attractive energy. This is the reason that fluorine is a gas but bromine is a liquid at room temperature and pressure.

before colliding with one another or with the walls of their container. Because much of the volume of a gas is empty space, samples of gaseous F₂ and Cl₂ readily expand or contract in response to changes in pressure. This freedom of motion indicates that the intermolecular forces between these molecules are small.

Molecules of liquid bromine also move about relatively freely, but there is not much empty space between molecules. A liquid cannot be compressed significantly by increasing the pressure because molecules are already in close contact with one another. Also, a liquid does not expand significantly if the pressure above it is reduced. This is because intermolecular forces in a liquid are large enough to prevent the molecules from breaking away from one another.

Solid iodine has even less empty space between molecules than liquid bromine. Furthermore, the molecules in this solid do not move freely past one another. A sample of solid iodine contains highly regular crystals in which I₂ molecules are arranged in ordered arrays. Each molecule vibrates back and forth about a single lowest-energy position, but it cannot slide easily past its neighbors. Like liquids, solids do not expand or contract significantly when pressure decreases or increases.

Whether a substance is a gas, liquid, or solid depends on the balance between the energy of motion of its molecules and the stabilization energy generated by its intermolecular forces. Molecules in a gas remain separated from one another because their kinetic energies are larger than the energies of intermolecular attraction. Molecules in a liquid or solid remain close to one another because they lack sufficient kinetic energy to overcome intermolecular attractive forces.

The graph in Figure 10-4 shows that the intermolecular stabilization energy is substantially greater for Br₂ than for F₂. At room temperature, fluorine molecules have more kinetic energy of motion than the stabilization energy of F₂-F₂ interactions. Bromine molecules have enough kinetic energy to move freely about, but their energy of motion is insufficient to overcome the intermolecular forces that hold them together in the liquid phase. At room temperature, iodine molecules are locked in position in the solid state because the stabilization energy between I₂ molecules is even larger than that between Br₂ molecules.

Real Gases

Although bromine is a liquid under ambient conditions, the red color above the liquid shown in Figure 10-5 suggests that the gas above a sample of liquid bromine contains a substantial number of gaseous Br₂ molecules. Apparently, intermolecular

forces are not sufficient to hold all the bromine molecules in the liquid phase at room temperature. How shall the gas above a sample of liquid bromine be described? The assumption of the ideal gas model—that intermolecular forces in a gas can be neglected—cannot be correct. Under these conditions, intermolecular forces are strong enough to condense most of the molecules into the liquid phase.

The ideal gas model also assumes that molecular sizes can be neglected. However, no substance can be compressed indefinitely. When the distance between molecules gets small enough, repulsive forces among their electron clouds strongly resist further reduction of the volume. This is shown by the steeply rising plots of Figure 10-4. Thus finite molecular sizes also lead to deviations from ideal gas behavior.

What effect do intermolecular forces and molecular volumes have on real gases? In other words, how close do real gases come to ideal behavior? To answer these questions, we can compare experimental values of real gas properties with those computed from the ideal gas equation. A convenient way to make these comparisons is to examine the experimental values of the ratio PV/nRT . For an ideal gas, this ratio must equal 1. For any real gas, the ratio deviates from 1. When attractive forces are strong, molecules are held closer together than in an ideal gas, making V smaller for the real gas and the ratio smaller than 1. When a gas is compressed sufficiently, molecules take up more space than in an ideal gas, making V larger for the real gas and the ratio larger than 1.

At low pressure, the distances between gas molecules are large. Under these conditions, neither intermolecular forces nor molecular sizes significantly affect gas behavior. Consequently, every gas behaves ideally at low enough pressure, and $PV/nRT = 1$. Deviations from ideality show up as the pressure on a gas increases, forcing molecules closer together.

Figure 10-6 shows how PV/nRT varies with pressure for chlorine gas at room temperature. If chlorine were ideal, the PV/nRT ratio would always be 1, as shown by the red line on the graph. Notice in the inset of Figure 10-6 that chlorine behaves very nearly ideally at pressures around 1 atmosphere (atm). In fact, PV/nRT deviates from 1.0 by less than 4% at pressures below 4 atm. As the pressure increases, however, the deviations become increasingly significant. At 100 atm, chlorine is far



Figure 10-5

Even though bromine is a liquid under ambient conditions, enough molecules escape into the gas phase to give the gas above a liquid sample a distinct red color.

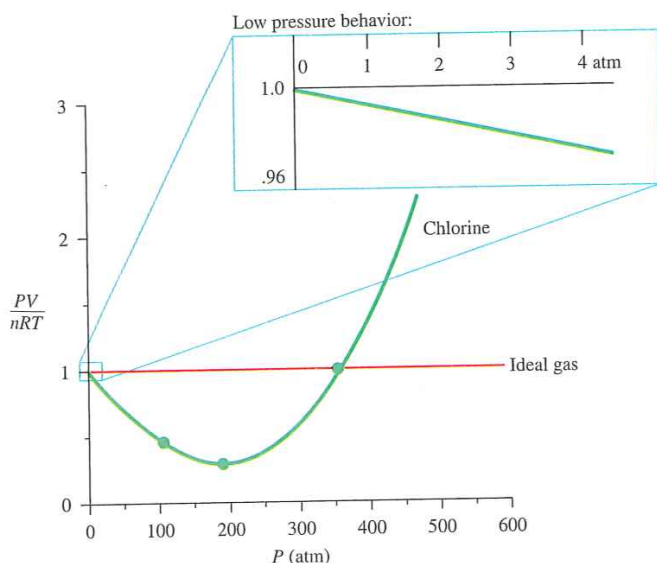
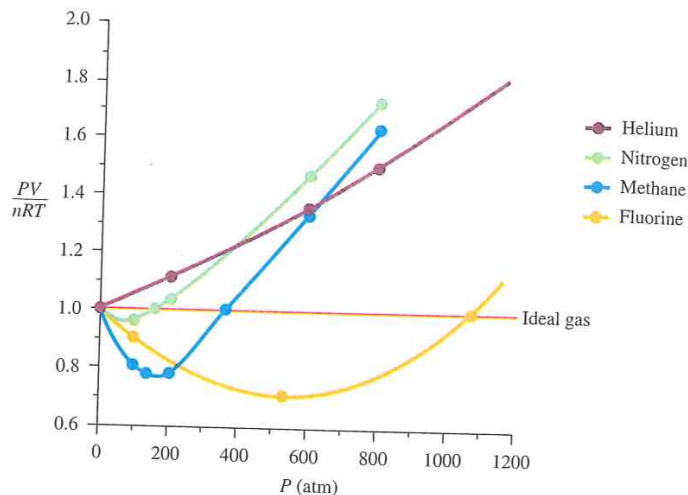


Figure 10-6

Variation in PV/nRT with pressure for chlorine gas at room temperature. The inset at the upper right shows the low-pressure region on an expanded scale.

Figure 10-7

Variation in PV/nRT for He, F₂, CH₄, and N₂ at 300 K. Even substances thought of normally as gases are not completely ideal, especially at high pressure.



Every gas deviates from ideal behavior. Given this fact, does it make sense to use the ideal gas model to discuss the properties of real gases? The answer is "yes," as long as conditions do not become too extreme. The gases with which chemists usually work, such as chlorine, helium, and nitrogen, are nearly ideal at and above room temperature at pressures below about 10 atm.

from ideal because chlorine molecules are close enough together for attractive forces to play a significant role.

Figure 10-6 also indicates that up to about 375 atm pressure, PV/nRT for Cl₂ is smaller than 1, which means that intermolecular attractions hold chlorine molecules closer together than would be the case for an ideal gas. At pressures greater than 375 atm, PV/nRT becomes larger than 1. This is the effect of finite molecular size. At high enough pressure, molecules are so close together that repulsive interactions outweigh attractive ones.

Every gas shows deviations from ideal behavior at high pressure. Figure 10-7 shows PV/nRT for He, F₂, CH₄, and N₂, all of which are gases at room temperature. Notice that PV/nRT for helium increases steadily as pressure increases. Intermolecular forces are too small to reduce the ratio below 1, but the finite size of helium atoms generates deviations from ideality that become significant at pressures above 100 atm.

The van der Waals Equation

Graphs like the ones in Figures 10-6 and 10-7 show how real gases deviate from ideal behavior. It would be useful, however, to have an equation that links the pressure and volume of a real gas. One way to approach real gas behavior is to modify the ideal gas equation to take into account attractive forces and molecular volumes. The result is the **van der Waals equation**, named for the scientist who first proposed it in 1873, Johannes van der Waals:

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT \quad (10-1)$$

Notice that the van der Waals equation adds two correction terms to the ideal gas equation. Each term contains a constant that is different for every gas. The first correction term, n^2a/V^2 , adjusts for attractive intermolecular forces. The van der Waals constant a measures the strength of intermolecular forces for the gas; the stronger the forces, the larger the value of a . The second correction term, nb , adjusts for molecular sizes. The van der Waals constant b measures the size of molecules of the gas; the larger the molecules, the larger the value of b .

Table 10-1

van der Waals Constants

Gas	Formula	a (L ² atm/mol ²)	b (L/mol)
Helium	He	0.0341	0.0237
Neon	Ne	0.211	0.0171
Argon	Ar	1.345	0.0322
Hydrogen	H ₂	0.244	0.0266
Nitrogen	N ₂	1.390	0.0391
Oxygen	O ₂	1.360	0.0318
Carbon monoxide	CO	1.453	0.0395
Fluorine	F ₂	1.156	0.0290
Chlorine	Cl ₂	6.493	0.0562
Carbon dioxide	CO ₂	3.592	0.0427
Water vapor	H ₂ O	5.464	0.0305
Ammonia	NH ₃	4.170	0.0371
Methane	CH ₄	2.253	0.0428
Ethane	C ₂ H ₆	5.489	0.0638
Benzene vapor	C ₆ H ₆	18.00	0.1115

The effects of the two correction factors can be most easily seen by solving Equation 10-1 for P :

$$P = \left(\frac{nRT}{V - nb} \right) - \left(\frac{n^2a}{V^2} \right)$$

The effect of a is to reduce the pressure of a real gas below the value for an ideal gas. This reflects the fact that intermolecular attractions hold molecules together and reduce the forces that they exert on striking the walls of the container. The effect of b is to increase the pressure of a real gas above that of the value for an ideal gas. This reflects the fact that molecular volumes force gas molecules farther apart.

The van der Waals constants for a number of gases appear in Table 10-1, and the magnitude of van der Waals corrections is explored in Sample Problem 10-1.

Sample Problem 10-1

Magnitudes of van der Waals Corrections

Gases such as nitrogen are sold and shipped in compressed gas cylinders. A typical cylinder has a volume of 15.0 L and, when full, contains 62 mol of N₂. After prolonged use, 0.62 mol of N₂ remains in the cylinder. Use the van der Waals equation to calculate the pressures in the cylinder when full and after use, and compare the values to those obtained from the ideal gas equation. Assume $T = 27^\circ\text{C}$.

Method: The van der Waals equation is Equation 10-1. To calculate pressures, we use the rearranged form. The van der Waals constants for N₂ appear in Table 10-1.

$$P = \left(\frac{nRT}{V - nb} \right) - \left(\frac{n^2a}{V^2} \right)$$

For N₂, $a = 1.390 \text{ L}^2 \text{ atm/mol}^2$ and $b = 0.0391 \text{ L/mol}$; $V = 15.0 \text{ L}$ and $T = 27^\circ\text{C} = 300 \text{ K}$.

When the tank is full, $n = 62$ mol:

$$P = \left(\frac{(62 \text{ mol})(0.08206 \text{ L atm/mol K})(300 \text{ K})}{15.0 \text{ L} - (62 \text{ mol})(0.0391 \text{ L/mol})} \right) - \left(\frac{(62 \text{ mol})^2(1.390 \text{ L}^2 \text{ atm/mol}^2)}{(15.0 \text{ L})^2} \right)$$

$$P = \left(\frac{1526 \text{ L atm}}{15.0 \text{ L} - 2.424 \text{ L}} \right) - (23.75 \text{ atm}) = 98 \text{ atm}$$

$$P_{\text{ideal}} = \frac{nRT}{V} = \frac{(62 \text{ mol})(0.08206 \text{ L atm/mol K})(300 \text{ K})}{(15.0 \text{ L})} = 1.0 \times 10^2 \text{ atm}$$

After use, $n = 0.62$ mol:

$$P = \left(\frac{(0.62 \text{ mol})(0.08206 \text{ L atm/mol K})(300 \text{ K})}{15.0 \text{ L} - (0.62 \text{ mol})(0.0391 \text{ L/mol})} \right) - \left(\frac{(0.62 \text{ mol})^2(1.390 \text{ L}^2 \text{ atm/mol}^2)}{(15.0 \text{ L})^2} \right)$$

$$P = \left(\frac{15.26 \text{ L atm}}{15.0 \text{ L} - 0.0242 \text{ L}} \right) - (0.00237 \text{ atm}) = 1.0 \text{ atm}$$

$$P_{\text{ideal}} = \frac{nRT}{V} = \frac{(0.62 \text{ mol})(0.08206 \text{ L atm/mol K})(300 \text{ K})}{(15.0 \text{ L})} = 1.0 \text{ atm}$$

Notice that the van der Waals correction is appreciable (about 2%) at high pressure but is negligible under normal ambient conditions.

◀ We describe the link between kinetic energy and temperature in Chapter 5.

Boiling points and melting points depend on pressure. Unless otherwise noted, values cited in this text refer to 1 atm pressure, the so-called normal boiling and melting points.

Vaporization and Condensation

Because the energy of motion depends on temperature, changing the temperature of a substance changes the balance between intermolecular forces and energy of motion. At some point, temperature changes cause a different phase of the substance to be stable. For example, liquid bromine boils when it is heated to 59 °C at atmospheric pressure. Above this temperature, bromine exists as a gas. Similarly, gaseous chlorine condenses to a liquid when it is cooled to -34 °C at atmospheric pressure. At -101 °C, moreover, liquid chlorine becomes a solid. Fluorine liquefies at -188 °C and solidifies at -220 °C.

Vaporization is the conversion of a liquid into a gas, and condensation is the conversion of a gas into a liquid. At the molecular level, these processes are mirror images of each other. A liquid vaporizes when molecules leave the liquid phase faster than they are captured from the gas. A gas condenses when molecules leave the gas phase more rapidly than they escape from the liquid. At the boiling point these two processes are in dynamic equilibrium, and the rate of escape from the liquid is matched exactly by the rate of capture from the gas.

Similarly, melting is the conversion of a solid into a liquid, and freezing is the conversion of a liquid into a solid. A solid melts when molecules leave the solid phase more rapidly than they are captured from the liquid; a liquid freezes when molecules leave the liquid phase faster than they escape from the solid. The melting point represents a dynamic equilibrium between the two opposing processes of escape and capture.

Boiling points and melting points provide good qualitative indications of the strengths of intermolecular forces. This is because rates of escape and capture depend on the balance between molecular kinetic energies and intermolecular forces of attraction. A substance with large intermolecular forces must be raised to a high temperature before its molecules have sufficient kinetic energy to overcome those forces. A substance with small intermolecular forces must be cooled to a low temperature before its molecules have small enough kinetic energy to coalesce into

a condensed phase. Table 10-2 lists the boiling and melting points of some representative elemental substances.

Liquid Properties

Liquids are intermediate in behavior between gases and solids. Whereas intermolecular forces among gas molecules are weak enough to allow molecules of a gas to move freely throughout their container, intermolecular forces in a solid are strong enough to hold the molecules fixed in place. In a liquid, intermolecular forces confine the molecules to a specific volume, but they are insufficient to keep the molecules from moving from place to place within the body of the liquid. The relative freedom of motion of liquid molecules leads to three liquid properties arising from intermolecular forces: surface tension, adhesion, and viscosity.

A small amount of a liquid tends to take a spherical shape: For example, water drips from a faucet in nearly spherical liquid droplets. The physical property responsible for this behavior is **surface tension**, which measures the resistance of a liquid to an increase in its surface area.

Figure 10-8 illustrates at the molecular level why liquids exhibit surface tension. A molecule in the *interior* of a liquid is completely surrounded by other molecules, each of which exerts attractive forces on its neighbors. A molecule at a liquid *surface*, on the other hand, has other molecules beside it and beneath it but *very few* above it in the gas phase. As a result, the net intermolecular force on molecules at the surface pulls them toward the interior of the liquid.

Molecules at the surface of a liquid are less stable than those within it, so a liquid is most stable when the fewest molecules are at its surface. This occurs when the liquid has minimal surface area. Spheres have less area per unit volume than any other shape, so small drops of a liquid tend to be spheres. Large drops are distorted from ideal spheres by the force of gravity.

Molecules in contact with the surface of their container experience two different sets of forces. First, they are attracted to the other molecules in the liquid, as just described. The intermolecular forces between liquid molecules are called **cohesive forces**. Second, they are attracted to molecules in the container walls. The intermolecular forces between molecules in the wall of a container and the molecules of a liquid are called **adhesive forces**.

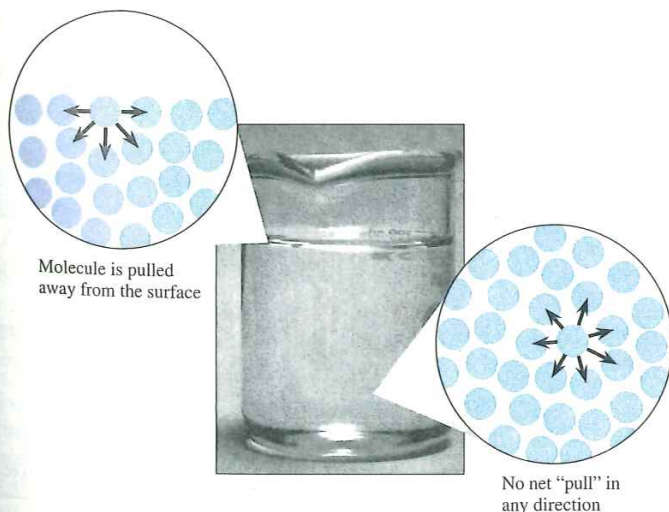


Table 10-2

Substance	Melting and Boiling Points	
	mp (K)	bp (K)
He	0.95*	4.216
H ₂	14.01	20.28
N ₂	63.29	77.4
F ₂	53.53	85.01
Ar	83.78	87.29
O ₂	54.8	90.188
Cl ₂	172.17	239.18
Br ₂	265.9	331.93
I ₂	386.7	457.50
P ₄	317.3	553
Na	370.96	1156.1
Mg	922.0	1363
Si	1683	2628
Fe	1808	3023

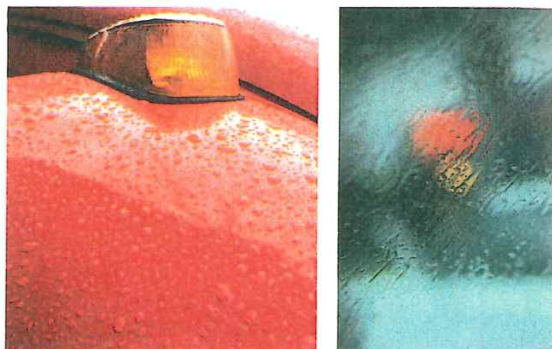
*Under high pressure. He remains liquid at 0 K under normal pressure.

Figure 10-8

In the interior of a liquid (*right*), each molecule experiences equal forces in all directions. A molecule at the surface of a liquid (*left*) is pulled back into the liquid by intermolecular forces.

Figure 10-9

Water in contact with a surface forms spherical droplets when adhesive forces are small, as on a freshly waxed car hood (A), whereas it forms a film when adhesive forces are large, as on a clean windshield (B).



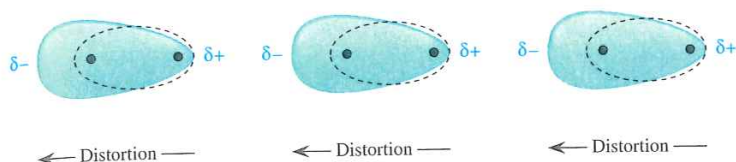
When the molecules of the liquid are attracted more strongly to one another than to the surface, the liquid tends to minimize its contact with that surface. Surface tension causes the liquid to form spherical droplets, as shown in Figure 10-9, A. In contrast, when the molecules of a liquid are attracted more strongly to the surface than to one another, the liquid tends to maximize its contact with that surface. Under these conditions, the liquid wets the surface and tends to form a film, as shown in Figure 10-9, B.

Water can be poured very quickly from one container to another, salad oil pours more slowly, and honey on a cold day seems to take forever. A liquid's resistance to flow is called its **viscosity**; the greater its viscosity, the more slowly the liquid pours. Viscosity measures how easily molecules slide by one another, and this depends on molecular shapes and intermolecular forces. Molecular shape strongly influences viscosity. Liquids such as water, acetone, and benzene, whose molecules are small and compact, have low viscosity. In contrast, large molecules such as the hydrocarbons found in oils tend to get tangled up with each other. Tangling inhibits the flow of molecules and leads to high viscosity. In addition, strong cohesive forces make it harder for molecules to move about.

Molecules move faster as temperature increases, and this allows them to slide by one another more easily. Consequently, viscosity decreases as temperature increases. This dependence is quite noticeable for highly viscous substances such as honey and syrup, which are much easier to pour when hot than when cold.

Section Exercises

- 10.1.1** On the basis of the behavior of the other elements of Group 17, predict whether At_2 will be a gas, liquid, or solid at room temperature. Sketch its intermolecular stabilization energy curve relative to those of F_2 and Br_2 (see Figure 10-4).
- 10.1.2** From Figure 10-7, determine which of the four gases has the largest intermolecular forces and which has the smallest. State your reasoning.
- 10.1.3** Use the data in Table 10-2 to answer the following:
- Predict whether Xe boils at a higher or lower temperature than Ar.
 - List F_2 , N_2 , H_2 , and Cl_2 in order of increasing intermolecular forces.
 - Which group in the periodic table has the smallest intermolecular forces?

**Figure 10-10**

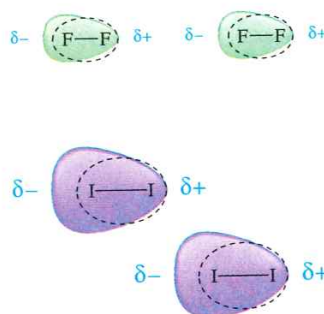
Exaggerated view of how dispersion forces arise. As molecules approach one another, their electron clouds change shape slightly in response to coulombic repulsion between the electrons. This distortion creates a small partial positive charge on one end of each molecule and a small partial negative charge on the other end.

10.2 TYPES OF INTERMOLECULAR FORCES

Intermolecular forces are of two general types: **dispersion forces**, exhibited by all substances, and **dipolar forces**, which exist only for compounds that possess permanent dipole moments (see Section 8.7).

We can explore the nature of dispersion forces by examining the boiling points of the halogens. Fluorine boils at 85 K, chlorine at 239 K, bromine at 332 K, and iodine at 458 K. The data suggest that as the sizes of halogen molecules increase, the magnitudes of their intermolecular forces become larger. To understand this trend, consider what happens when two halogen molecules approach each other. Each molecule contains positive nuclei surrounded by a cloud of negative electrons. As two molecules approach, the nucleus of one molecule attracts the electron cloud of the other. At the same time the two electron clouds repel each other. Electrons are highly mobile, so their orbitals change shape to minimize electron-electron repulsion, as shown in Figure 10-10. This distortion of the electron cloud creates a charge imbalance, giving the molecule a slight positive charge at one end and a slight negative charge at the other. Dispersion forces involve the net attractive forces among molecules generated by all these induced charge imbalances.

The magnitudes of dispersion forces depend on how easy it is to distort the electron cloud of the molecule. The ease of distortion is called **polarizability** because distortion of an electron cloud generates a temporary polarity within the molecule. As Figure 10-11 illustrates, the large electron cloud of an I_2 molecule distorts more readily than the small electron cloud of F_2 . Both molecules contain 14 valence electrons, but those of F_2 are in relatively compact $n = 2$ orbitals, whereas those of I_2 occupy highly diffuse $n = 5$ orbitals. As a result, the valence orbitals of I_2 distort much more readily than those of F_2 , generating larger dispersion forces that make iodine a solid at room temperature, whereas fluorine is a gas. The boiling point trend among the halogens reflects this behavior: The boiling point increases progressively as the molecules become larger and more polarizable. This reasoning is extended to include the elemental noble gases in Sample Problem 10-2.

**Figure 10-11**

Iodine's electron cloud is much larger and more polarizable than fluorine's. Iodine therefore has stronger dispersion forces than fluorine, which is why F_2 is a gas at room temperature but I_2 is a solid.

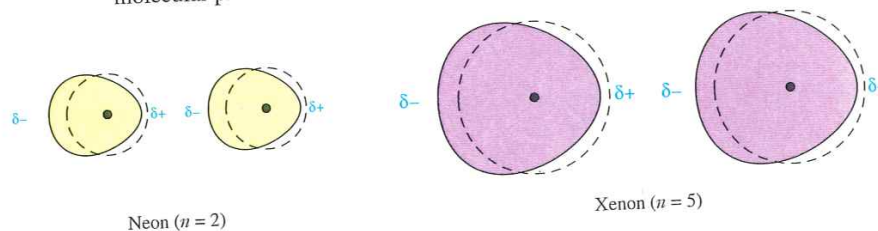
Sample Problem 10-2

Boiling Point Trends

At room temperature, neon and xenon are gases, but both become liquids if the temperature is low enough. Draw a molecular picture showing the relative sizes and polarizabilities of atoms of neon and xenon, and use the picture to determine which substance has a lower boiling point.

Method: The boiling point of a substance depends on the magnitude of its intermolecular forces, which in turn depends on the polarizability of its electron cloud. Monatomic gases contain atoms rather than molecules, so we must assess *interatomic* forces for these substances.

The dispersion forces that act between atoms of rare gases depend on the polarizability of their electron clouds. The valence electrons of neon are in small, $n = 2$ atomic orbitals that have low polarizability, whereas those of xenon are in relatively large, polarizable $n = 5$ orbitals. When two atoms approach each other, the smaller electron cloud of neon distorts less than the larger electron cloud of xenon, as a molecular picture illustrates:



Less polarizability means smaller partial charges and weaker intermolecular forces. Thus neon has the lower boiling point. The experimental values are 166.1 K for Xe and 27.1 K for Ne.

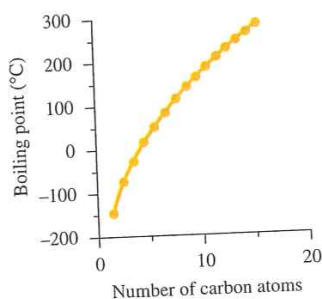


Figure 10-12

The boiling points of alkanes increase with the length of the carbon chain.

It is easier to distort the electron cloud of a large molecule than of a small molecule. Figure 10-12 shows how the boiling points of alkanes change as the carbon chain gets longer. As alkanes get longer, their electron clouds become larger and more polarizable, making dispersion forces larger and raising the boiling point. For example, at room temperature, methane (CH_4) is a gas, pentane (C_5H_{12}) is a liquid, and eicosane ($\text{C}_{20}\text{H}_{42}$) is a waxy solid. Figure 10-13 compares the polarizabilities of pentane and decane.

Among otherwise similar substances, more extended molecules have higher polarizabilities than more compact molecules. This trend is illustrated by the boiling points of the three isomers with the formula C_5H_{12} . Figure 10-14 shows that the highest-boiling isomer, pentane, is most extended and the lowest-boiling isomer, 2,2-dimethylpropane, is most compact, with 2-methylbutane in between.

Dispersion forces exist between all molecules, but some substances remain liquid at much higher temperatures than can be accounted for by dispersion forces alone. Consider 2-methylpropane and acetone, whose structures are shown in Figure 10-15. These two molecules have the same molar mass, similar shape, and nearly the same number of valence electrons (26 vs. 24). They are so similar that the two compounds might be expected to have similar boiling points, but acetone is

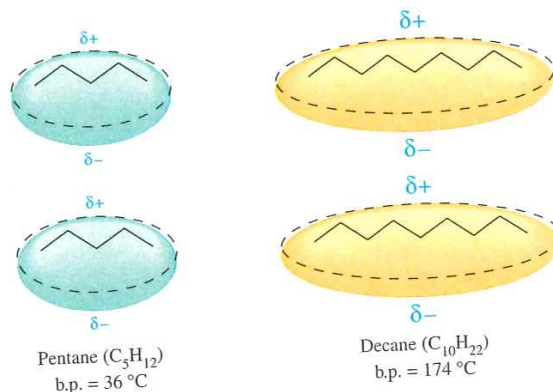


Figure 10-13

Large alkanes have higher boiling points than small alkanes. Their dispersion forces are larger because of the increased polarizability of their larger electron clouds.

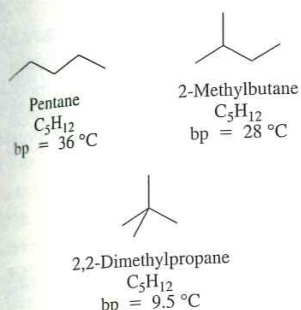


Figure 10-14
The three isomers with chemical formula C_5H_{12} have different boiling points because polarizability increases as molecules become more extended.

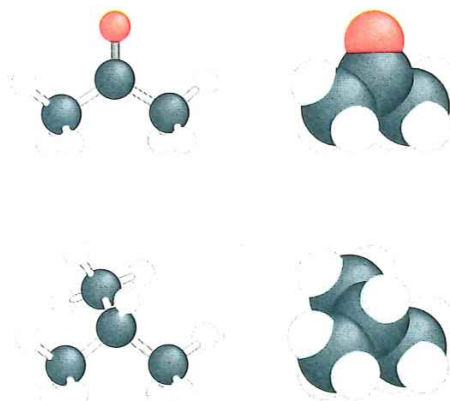
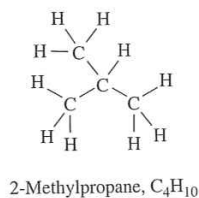
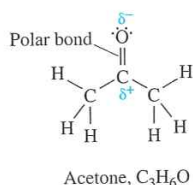


Figure 10-15

Models and Lewis structures of 2-methylpropane and acetone show that they have similar molecular shapes. The important difference between them is the dipole moment resulting from the polar bond in acetone.

a liquid at room temperature, whereas 2-methylpropane is a gas. Acetone boils at 56 °C, whereas 2-methylpropane boils at -12 °C.

Why does acetone remain a liquid at temperatures well above the boiling point of 2-methylpropane? The cause is charge asymmetry in the molecular structure of acetone. Remember from the bonding picture presented in Chapter 8 that chemical bonds are polarized toward the more electronegative atom. Whereas carbon ($\chi = 2.5$) and hydrogen ($\chi = 2.1$) have nearly equal electronegativity, the electronegativity of oxygen is considerably larger ($\chi = 3.5$). Thus a C=O bond of acetone is highly polarized, with a partial negative charge on the oxygen atom and a partial positive charge on the carbon atom.

When two polar acetone molecules approach each other, they align with the positive end of one molecule close to the negative end of the other. In a liquid array, this repeating pattern of head-to-tail alignment gives rise to significant net attractive dipolar forces among the molecules, as illustrated in Figure 10-16.

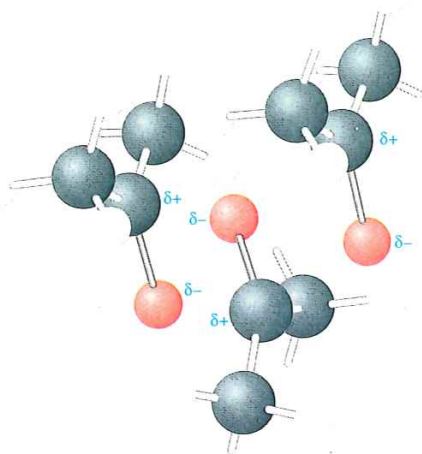


Figure 10-16

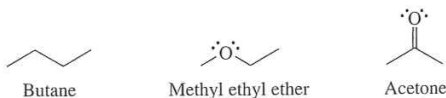
In liquid acetone the permanent dipoles tend to align with positive ends nearer negative ones and negative ends nearer positive ones.

The dispersion forces in 2-methylpropane are about the same as those in acetone, but the addition of dipolar forces makes the total amount of intermolecular attraction between acetone molecules substantially greater than that between molecules of 2-methylpropane. Consequently, acetone boils at a considerably higher temperature than 2-methylpropane. Sample Problem 10-3 provides some additional comparisons of dispersion forces and dipole forces.

Sample Problem 10-3

Boiling Points and Structure

The line structures of butane, methyl ethyl ether, and acetone follow. Explain the trend in boiling points: butane (0 °C), methyl ethyl ether (8 °C), and acetone (56 °C).



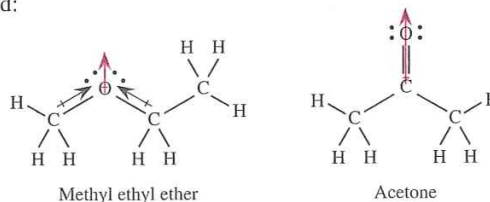
Method: These boiling points can be explained in terms of dispersion forces and dipolar forces. First, assess the magnitudes of dispersion forces, which are present in all substances, and then look for molecular polarity.

Dispersion forces depend on the size of the electron cloud and on the shape of the molecule. A table helps organize the available information:

Substance	Boiling Point	Valence Electrons	Shape
Butane	0 °C	26	Elongated
Methyl ethyl ether	8 °C	26	Elongated
Acetone	56 °C	24	Compact

The table shows that dispersion forces alone cannot account for the range in boiling temperatures. Methyl ethyl ether and butane have the same number of electrons and similar shapes; yet their boiling points are different. Acetone, which has fewer electrons and a more compact shape than the other compounds, has smaller dispersion forces; yet it boils at a higher temperature. The order of boiling points indicates that acetone is a more polar molecule than methyl ethyl ether, which in turn is more polar than butane.

We expect butane to have a low polarity because of the small electronegativity difference between carbon and hydrogen. Acetone and methyl ethyl ether, on the other hand, contain polar C—O bonds. The molecular geometry about the polar C—O bonds reveals why acetone is more polar than methyl ethyl ether. The full Lewis structures of these molecules show that the oxygen atom in the ether has a steric number of 4 and bent geometry. Arrows show the charge displacement for each polar bond:



Notice that the two C—O bond dipoles in methyl ethyl ether partially cancel each other, leaving a relatively small polarity, whereas the polar C—O bond in acetone is unopposed. Thus acetone is more polar than methyl ethyl ether.

Hydrogen Bonding

Methyl ethyl ether is a gas at room temperature (boiling point, or bp, = 8 °C), whereas 1-propanol, shown in Figure 10-17, is a liquid (bp = 97 °C). Both compounds have the same molecular formula, C_3H_8O , and both have chains of four atoms, $C-O-C-C$ and $O-C-C-C$. Consequently, the electron clouds of these two molecules are about the same size, and their dispersion forces are comparable. Each molecule has an sp^3 -hybridized oxygen atom with two polar single bonds, so their dipolar forces should be similar. The very different boiling points of 1-propanol and methyl ethyl ether make it clear that dispersion and dipolar forces do not reveal the entire story of intermolecular attractions.

The forces of attraction between 1-propanol molecules are stronger than those between methyl ethyl ether molecules because of a special intermolecular interaction called a **hydrogen bond**. A hydrogen bond occurs when a highly electronegative atom with a lone pair of electrons acts as an electron donor and partially shares its nonbonding electrons with a positively polarized hydrogen atom. Hydrogen bonds are only 5% to 10% as strong as covalent bonds, but they are comparable to and sometimes stronger than dipolar and dispersion interactions.

There are two requirements for hydrogen bond formation. First, there must be an electron-deficient hydrogen atom to act as electron-pair acceptor. Hydrogen atoms in $O-H$, $F-H$, and $N-H$ bonds meet this requirement. Second, there must be a highly electronegative atom with at least one lone pair of electrons. Three second-row elements, O, N, and F, meet this requirement. Consequently, hydrogen bond formation is restricted to molecules that have hydrogen atoms bonded to fluorine, oxygen, or nitrogen. Figure 10-18 shows representative examples of hydrogen bonding. The hydrogen bonds are shown by dashed lines to indicate the partially bonding nature of these interactions.

Notice from the examples shown in Figure 10-18 that hydrogen bonds can form between *different* molecules (for example, $H_3N \cdots H_2O$) or between *identical* molecules (for example, $HF \cdots HF$). Also notice that molecules can form more than one hydrogen bond (for example, glycine) and that hydrogen bonds can form within a molecule (for example, salicylic acid) as well as between molecules. Sample Problem 10-4 explores the possibilities for hydrogen bond formation.

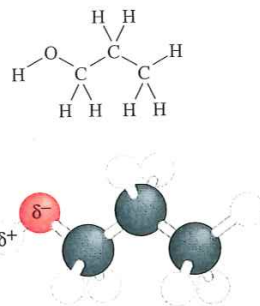


Figure 10-17

The Lewis structure and space-filling model of 1-propanol. The high polarity of the $O-H$ bond results in an electron deficiency on the hydrogen atom and an electron excess on the oxygen atom.

Chlorine and sulfur atoms are also sufficiently electronegative to participate in hydrogen bonding, and there is some evidence for such bonding in HCl . However, the nonbonding electrons on these atoms are in diffuse $3p$ orbitals that do not interact as strongly with a hydrogen atom as electrons in more compact $2p$ orbitals.

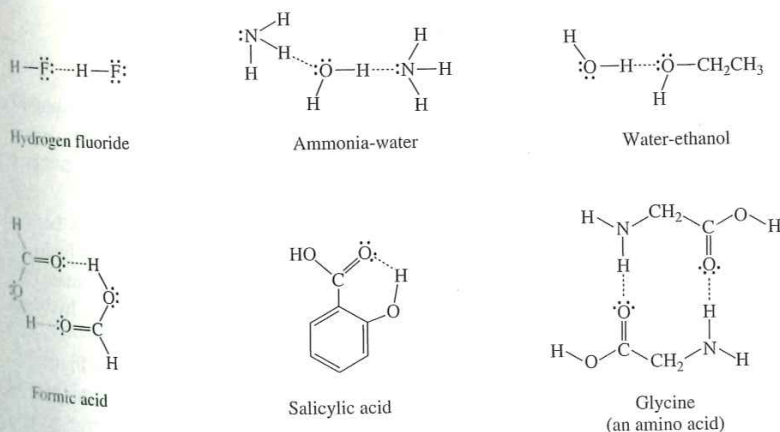


Figure 10-18

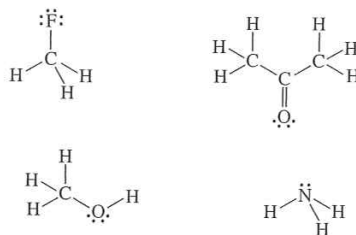
Examples of hydrogen bonding among some small molecules.

Sample Problem 10-4

Formation of Hydrogen Bonds

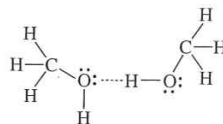
In which of the following systems will hydrogen bonding play an important role: CH_3F , $(\text{CH}_3)_2\text{CO}$ (acetone), CH_3OH , and NH_3 dissolved in $(\text{CH}_3)_2\text{CO}$?

Method: Hydrogen bonds occur when both polar $\text{H}-\text{X}$ bonds and electronegative atoms with nonbonding pairs of electrons are present. Lewis structures provide the best starting point in determining whether these requirements are met:

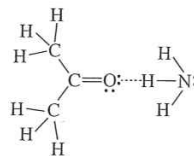


In acetone and CH_3F , there is an electronegative atom with nonbonding pairs, but neither has highly polar $\text{H}-\text{X}$ bonds. Thus there is no hydrogen bonding between molecules of these substances.

The $\text{O}-\text{H}$ bond in CH_3OH meets the requirements for hydrogen bonding. The $\text{O}-\text{H}$ hydrogen atom on one molecule interacts with the oxygen atom of a neighboring molecule:



For a solution of ammonia in acetone, we must examine both components. Acetone has an electronegative oxygen atom with nonbonding pairs, whereas NH_3 has a polar $\text{N}-\text{H}$ bond. Consequently, a mixture of these two compounds displays hydrogen bonding between ammonia's hydrogen atoms and acetone's oxygen atoms:



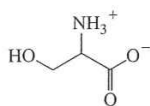
For more practice, draw a similar picture that shows the hydrogen bonding in a solution of acetone in water.

Hydrogen bonding is particularly important in biochemical systems because biomolecules contain many oxygen and nitrogen atoms that participate in hydrogen bonding. For example, the amino acids from which proteins are made contain NH_2 (amino) and CO_2H (carboxylic acid) groups. Four different types of hydrogen bonds exist in these systems: $\text{O}-\text{H}\cdots\text{N}$, $\text{N}-\text{H}\cdots\text{O}$, $\text{O}-\text{H}\cdots\text{O}$, and $\text{N}-\text{H}\cdots\text{N}$. Hydrogen bonding between glycine molecules is shown in Figure 10-18, and Sample Problem 10-5 provides further illustrations. We examine more details of hydrogen bonding in biomolecules in Chapter 11.

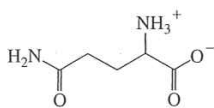
Sample Problem 10-5

Identifying Hydrogen Bonding Sites

In aqueous solution, amino acids undergo intramolecular proton transfer to form ions. The line structures of two amino acid ions, serine and glutamine, follow. For each molecule, identify the hydrogen atoms that can form hydrogen bonds and the electronegative atoms to which hydrogen bonds can form.

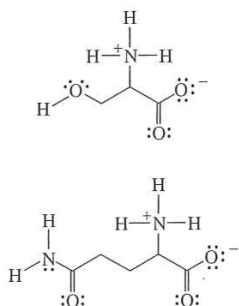


Serine
 $C_3H_7NO_3$

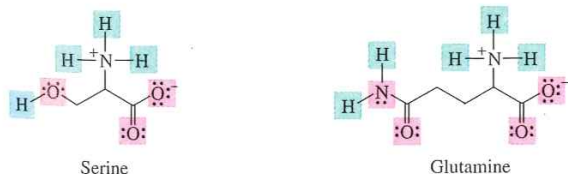


Glutamine
 $C_5H_{10}N_2O_3$

Method: Hydrogen atoms in polar H—X bonds can form hydrogen bonds with lone pairs on other nitrogen, oxygen, or fluorine atoms. To identify hydrogen bonding possibilities, we need Lewis structures to determine the locations of nonbonding pairs of electrons. Carbon atoms are never involved in hydrogen bonds, so we can ignore the carbon framework of the molecules. The following partial Lewis structures show the nonbonding pairs of electrons and the polar H—X bonds:



Any N—H or O—H hydrogen atom in these molecules can participate in hydrogen bonding. These are highlighted in blue in the following structures. The N atoms and O atoms with lone pairs of electrons can also participate in hydrogen bonding. These atoms are highlighted in red.



Serine

Glutamine

Binary Hydrogen Compounds

Boiling points of the binary hydrogen compounds illustrate the interplay among dispersion, dipolar, and hydrogen bonding forces. The graph in Figure 10-19 shows that there are regular periodic trends in the boiling points of these compounds. Except for the second-row elements, the boiling points of the binary hydrogen compounds increase moving down each column of the periodic table. This trend can be attributed to increasing dispersion forces: The larger the molecular valence orbitals, the stronger the dispersion forces and the higher the boiling point. In Group 16, for example, H_2S (eight valence e^- , $n = 3$) boils at -60°C , whereas H_2Se (eight valence e^- , $n = 4$) and H_2Te (eight valence e^- , $n = 5$) boil at -41°C and -4°C , respectively.

Comparing compounds in the same row, we find that the Group 14 compound, XH_4 , consistently boils lower than either of its neighbors. The XH_4 molecules are tetrahedral and symmetric; thus they have zero dipole moment. The presence of lone pairs in all the other compounds of this set results in dipole moments, increasing the intermolecular forces and boiling points. This effect is not dramatic, however, because the electronegativity difference is relatively small between hydrogen ($\chi = 2.1$) and elements in Groups 15 to 17 (χ varies between 1.9 and 3.0 beyond row 2).

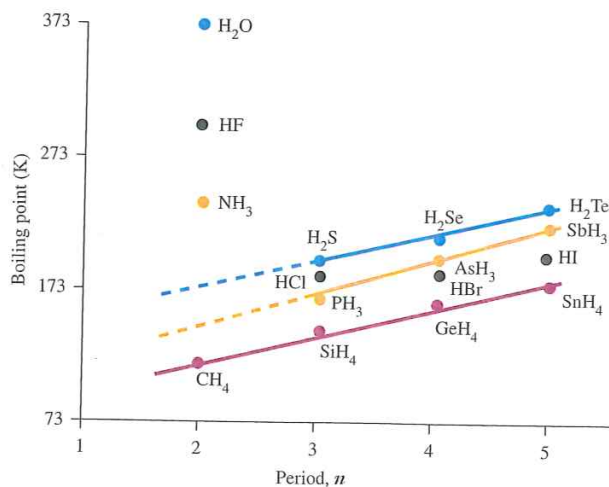
Ammonia, water, and hydrogen fluoride depart dramatically from the periodic behavior illustrated in Figure 10-19. This is because their molecules experience particularly large intermolecular forces resulting from hydrogen bonding. In hydrogen fluoride, for instance, partial donation of an electron pair from the highly electronegative fluorine atom of one HF molecule to the electron-deficient hydrogen atom of another HF molecule creates a hydrogen bond. Similar interactions among many HF molecules result in a network of hydrogen bonds that gives HF a boiling point much higher than those of HCl, HBr, and HI.

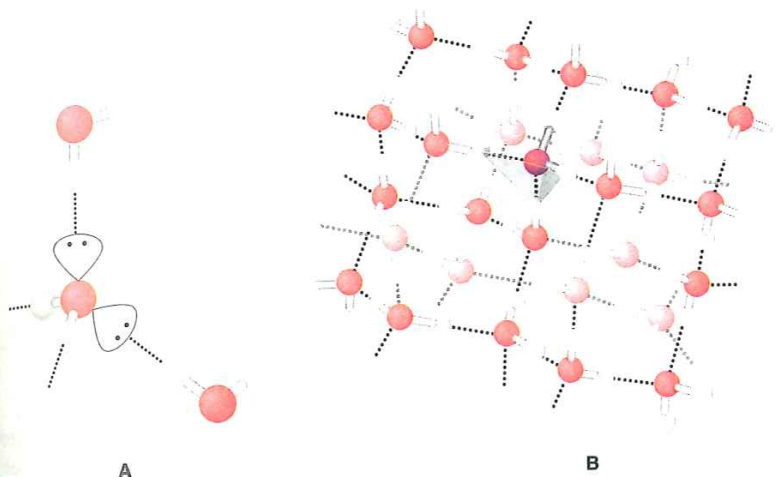
Water has a substantially higher boiling point than hydrogen fluoride, which indicates that the overall strength of hydrogen bonding in H_2O is greater than that in HF. Fluorine has the highest electronegativity, however, so the strongest *individual* hydrogen bonds are those in HF. The higher boiling point of water reflects the fact that it forms more hydrogen bonds *per molecule* than hydrogen fluoride.

Every hydrogen atom in liquid HF is involved in a hydrogen bond, but there is only one polar hydrogen atom per molecule. Thus each HF molecule participates in

Figure 10-19

Periodic trends in the boiling points of binary hydrogen compounds. Notice that H_2O , HF, and NH_3 are exceptions to the trends.



**Figure 10-20**

The structure of ice. **A**, Each oxygen atom is at the center of a distorted tetrahedron of hydrogen atoms. The tetrahedron is composed of two short covalent O—H bonds and two long H····O hydrogen bonds. **B**, Water molecules are held in a network of these tetrahedra.

two hydrogen bonds with two other HF partners. There is one hydrogen bond involving the partially positive hydrogen atom and a second involving the partially negative fluorine atom. In contrast, a water molecule has *two* hydrogen atoms that can form hydrogen bonds and *two* nonbonding electron pairs on each oxygen atom. This permits every water molecule to form *four* hydrogen bonds.

Hydrogen bonding in liquid water and, even more strikingly, in solid ice creates a three-dimensional network that puts each oxygen atom at the center of a distorted tetrahedron. Figure 10-20 shows that two arms of the tetrahedron are regular covalent O—H bonds, whereas the other two arms of the tetrahedron are hydrogen bonds to two different water molecules.

Dispersion forces, dipole interactions, and hydrogen bonds are all much weaker than covalent intramolecular bonds. For example, the average C—C bond energy is 345 kJ/mol, whereas dispersion forces are just 0.1 to 5 kJ/mol for small alkanes such as propane. Dipolar interactions between polar molecules such as acetone range from 5 to 20 kJ/mol, and hydrogen bonds vary from 5 to 50 kJ/mol.

◀ Recall from Chapter 9 that bond energy is the amount of energy required to break 1 mol of a particular bond. Table 9-2 lists bond energies.

Section Exercises

- 10.2.1** Explain the following differences in boiling points:
- Kr boils at $-152\text{ }^{\circ}\text{C}$, and propane boils at $-42\text{ }^{\circ}\text{C}$.
 - $\text{C}(\text{CH}_3)_4$ boils at $10\text{ }^{\circ}\text{C}$, and CCl_4 boils at $77\text{ }^{\circ}\text{C}$.
 - N_2 boils at $-196\text{ }^{\circ}\text{C}$, and CO boils at $-191.5\text{ }^{\circ}\text{C}$.
- 10.2.2** Acetone and methanol have nearly equal boiling points. What types of intermolecular forces does each exhibit? What does the similarity in boiling points tell you about the relative magnitudes of each type of force in these two compounds?
- 10.2.3** There are nine important hydrogen bonding interactions. One of them is $\text{O}-\text{H}\cdots\text{O}$. Draw the other eight. For each of the nine, draw a Lewis structure of a specific example using real molecules.

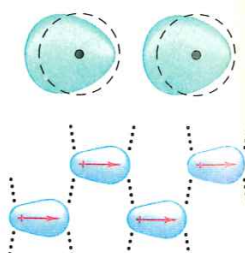
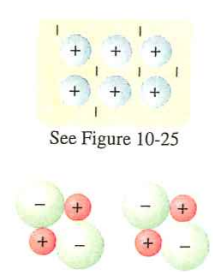
10.3 FORCES IN SOLIDS

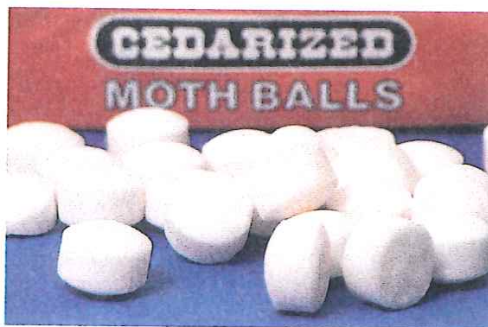
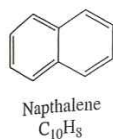
One of the most active areas of research in modern chemistry, physics, and engineering is the development of new solid materials. Solids play an ever-expanding role in society, from complex materials that act as high-temperature superconductors, to heat-resistant tiles for the outer "skin" of the space shuttle, to new tissue-compatible solids used for surgical implants. In this section, we describe the various forces that exist in solids.

Magnitudes of Forces

The melting points of the elements presented in Table 10-2 span an immense range, from <15 K (H_2) to >1500 K (Si and Fe). This reveals that the forces holding solids together range from very small to extremely large. In addition to the intermolecular forces described in Section 10.2, solids can be bound together by strong intramolecular forces of three types: covalent bonds, metallic bonds (with delocalized electrons), and ionic interactions. This gives rise to four distinct types of solids, each characterized by a different type of force. Table 10-3 contrasts the forces and energies in these four types of solids. The molecules (or atoms) of a **molecular solid** are held in place by the types of forces already discussed in this chapter: dispersion forces, dipolar interactions, and/or hydrogen bonds. The atoms of a **metallic solid** are held in place by the delocalized bonding described in Chap-

Table 10-3

Forces in Different Types of Solids					
Solid Type	Attractive Force	Energy (kJ/mol)	Example	Melting Point (K)	Molecular Picture
Molecular	Dispersion	0.05-40	Ar	83.78	 See Figure 10-20
Molecular	Dipolar	5-25	HCl	158	
Molecular	H bonding	10-40	H_2O	273	
Metallic	Delocalized bonding	75-1000	Cu	1356.6	 See Figure 10-25
Network	Covalent	150-500	SiO_2	1983	
Ionic	Coulombic	400-4000	NaCl	1074	

**Figure 10-21**

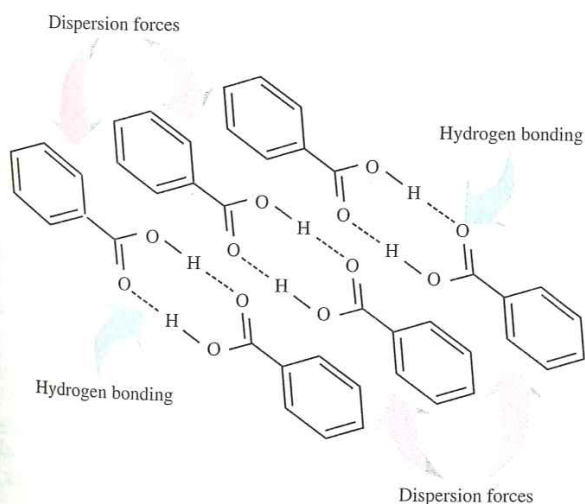
Naphthalene is a planar molecule whose bonding is similar to that of benzene, as described in Chapter 9. Naphthalene crystals are held together by dispersion forces generated primarily by the electrons of the highly polarizable π system. Naphthalene is an effective moth repellent.

ter 9. A **network solid** contains an array of covalent bonds linking every atom to its neighbors. Finally, an **ionic solid** contains cations and anions that are attracted to each other by coulombic interactions.

Molecular Solids

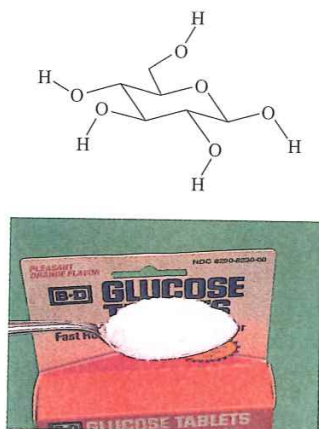
Molecular solids are aggregates of molecules bound together by intermolecular forces. Substances that are gases under normal conditions form molecular solids when they condense at low temperature. Many larger molecules have sufficient dispersion forces to exist as solids at room temperature. One example is naphthalene ($C_{10}H_8$), a white solid that melts at 80°C . Naphthalene has a planar structure with a cloud of 10 delocalized π electrons that lie above and below the molecular plane. Naphthalene molecules are held in the solid state by strong dispersion forces among these highly polarizable π electrons (Figure 10-21).

In addition to dispersion forces, molecular solids often involve dipolar interactions and hydrogen bonding. Benzoic acid ($C_6H_5CO_2H$) is a particularly clear-cut example, as illustrated in Figure 10-22. Molecules of benzoic acid are held in place

**Figure 10-22**

Crystals of benzoic acid contain pairs of molecules held together head to head by hydrogen bonds. These pairs then form stacks, which are held together by dispersion forces.



**Figure 10-23**

The intermolecular forces in glucose are dominated by hydrogen bonding because of the five OH groups in each molecule. Glucose is the sugar normally found in blood and human tissues.

by a combination of dispersion forces among the π electrons and hydrogen bonding among the CO_2H groups. With fewer π electrons, benzoic acid has weaker dispersion forces than naphthalene, but its hydrogen bonding gives benzoic acid the higher melting point: 122 °C.

The effect of extensive hydrogen bonding is revealed by the sugar glucose ($\text{C}_6\text{H}_{12}\text{O}_6$), whose melting point is 155 °C. The structure in Figure 10-23 shows that glucose has five $-\text{OH}$ groups, each of which is capable of forming hydrogen bonds to its neighboring molecules. Although glucose lacks the highly polarizable π electrons found in naphthalene and benzoic acid, the sugar has the highest melting point of the three compounds.

The molecules of a molecular solid retain their individual properties. Solid iodine, for example, is violet because individual I_2 molecules absorb visible light, as shown by the fact that iodine vapor is also violet. Moth balls repel moths because naphthalene molecules that escape into the gas phase are toxic to moths, and glucose tastes sweet because the taste buds recognize the shape of an individual glucose molecule.

Network Solids

Box 9-3 describes the forms of elemental carbon. Fullerene, consisting of discrete C_{60} units, is a molecular solid. Diamond and graphite, on the other hand, consist of extensive networks of covalently bonded carbon atoms. These are network solids. In sharp contrast to molecular solids, network solids have very high melting points. Compare, for example, the behavior of phosphorus and silicon, which are third-row neighbors in the periodic table. As listed in Table 10-2, phosphorus (a molecular solid containing discrete P_4 units) melts at 317.3 K, whereas silicon (a network solid in which covalent bonds among Si atoms connect all the atoms) melts at 1683 K. The reason is evident from Table 10-3: Covalent bond strengths are much greater than the attractive energy generated by intermolecular forces. Solid silicon cannot melt until a significant fraction of the Si—Si covalent bonds have broken. The average Si—Si bond energy is 220 kJ/mol, whereas intermolecular forces are less than 40 kJ/mol.

The vast array of covalent bonds in a network solid compels us to think of the entire structure as one giant “molecule.” Each atom in diamond and graphite is linked to all the other atoms through a network of covalent bonds. Bonding patterns determine the properties of network solids. Diamond and graphite have very different physical and chemical properties arising from their different bonding patterns. As described in Box 9-3, diamond contains a three-dimensional array of σ bonds, whereas graphite has a two-dimensional array of σ bonds supplemented by delocalized π bonding. The two-dimensional layers of graphite are held together only by dispersion forces. As a result, the planes of carbon atoms slide past one another readily, making graphite brittle and a lubricant. In contrast, because of its three-dimensional network of strong covalent bonds, diamond is extremely strong and an excellent abrasive.

Several oxides and sulfides display the characteristics of network solids. The bond network of silica appears in Section 8.5. Other examples are titania (TiO_2) and alumina (Al_2O_3). These materials have extremely high melting points because of the networks of strong X—O bonds holding their atoms together. Like graphite, MoS_2 is a two-dimensional network solid that serves as a solid lubricant. Some network sulfides have nonstoichiometric compositions. Examples are $\text{Cr}_{0.88}\text{S}$ and $\text{Fe}_{0.86}\text{S}$. Of course, fractional atoms do not exist in these materials; rather, for every 100 atoms of S in the network there are 88 atoms of Cr or 86 atoms of Fe.

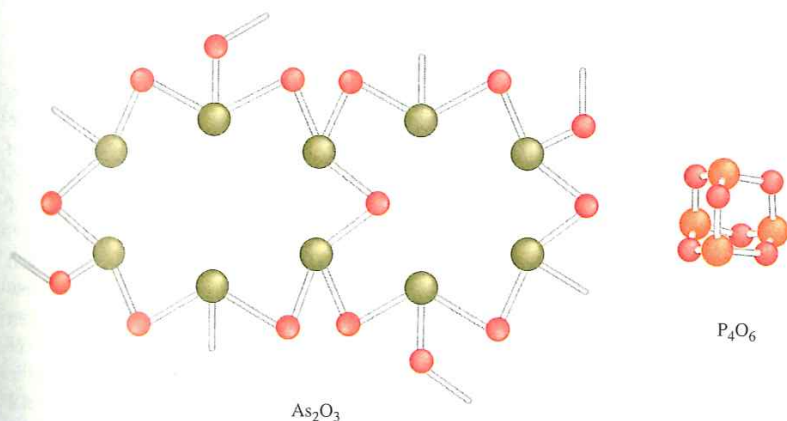
Covalent bonds make network solids extremely durable. Geological examples include the “everlasting sands” and granite formations such as the Rock of Gibralt-

tar. Diamonds and other valuable gemstones are network solids, too. Rubies and sapphires are covalent crystals of aluminum oxide with small amounts of colored transition metal ion impurities. Carborundum is a 1:1 covalent solid of silicon and carbon that has the same lattice structure as diamonds. Carborundum is considerably less expensive than diamond but almost as strong and wear resistant, so it is used for the edges of cutting tools. Sample Problem 10-6 compares the structures and properties of a covalent solid and a molecular solid.

Sample Problem 10-6

Network and Molecular Solids

Whereas SiO_2 melts at 1710°C , other nonmetal oxides melt at much lower temperatures. For example, P_4O_6 melts at 25°C , and As_2O_3 sublimes directly to the gas phase at 315°C . Referring to the following bonding pictures and to the bonding pattern of silica in Figure 8-18, describe the forces that hold these solids together.



Method: Solids may be network, ionic, metallic, or molecular, with different forces accounting for the stability of each type. Because these are nonmetal oxides, they cannot be described as metallic. None of these oxides contains ions, so they must be network or molecular. The bonding patterns provide the information needed to categorize the three compounds and explain their melting temperatures.

SiO_2 : The bonding pattern in silica is a three-dimensional array of strong covalent bonds. Many of these bonds must be broken before silica melts. Silica melts at 1710°C because its three-dimensional covalent bonding network is highly stable.

As_2O_3 : The bonding picture shows a two-dimensional network of covalent bonds with no bonding between molecular planes. In this respect, arsenic trioxide is similar to graphite. It sublimes at a relatively low temperature, indicating that a small amount of energy is required to disrupt this planar bonding network. Actually, when As_2O_3 sublimes, it forms As_4O_6 molecules whose bonding pattern resembles that of P_4O_6 . Thus much of the energy required to break the planar bonding network is recovered through the formation of new $\text{As}-\text{O}$ bonds.

P_4O_6 : The molecular structure shows that P_4O_6 is composed of discrete molecular units rather than an array of covalent bonds. Strong covalent bonding holds the atoms in each molecule together, but each molecular unit is attracted to others only by dispersion forces. In this molecular solid, little energy is required to overcome dispersion forces and allow P_4O_6 molecules to move around in the liquid state.



Sodium is so soft that it can be cut with a knife.

Metallic Solids

As described in Section 9.6, the bonding in solid metals consists of electrons in highly delocalized valence orbitals. There are so many such orbitals that they form energy bands, giving the valence electrons high mobility. Consequently, each metal atom can be viewed as a cation embedded in a “sea” of mobile valence electrons. The properties of metals can be explained on the basis of this picture. The most obvious of these properties, electrical conductivity, is discussed in Section 9.6.

Metals display a range of melting points, indicating that the strength of metallic bonding is variable. The elements in Group 1 are quite soft and melt near room temperature. Sodium, for example, melts at 98 °C and cesium at 28.5 °C. Bonding is weak in these metals because each atom of a Group 1 metal contributes only one valence electron to the bond-forming energy band of these solids. Metals near the middle of the *d* block, on the other hand, are very hard and among the highest-melting substances known. Tungsten melts at 3407 °C, rhenium at 3180 °C, and chromium at 1857 °C. Atoms of these metals contribute two *s* electrons and several *d* electrons to the bond-forming energy band, leading to extremely strong metallic bonding.

Metals are ductile and malleable, meaning they can be drawn into wires or hammered into thin sheets. When a piece of metal is formed into a new shape, its atoms change position. Because the bonding electrons are fully delocalized, however, changing the positions of the atoms does not cause corresponding changes in the energy levels of the electrons. The “sea” of electrons is largely unaffected by the pattern of metal cations, as Figure 10-24 illustrates. Thus metals can be forced into many shapes, including sheets and wires, without destroying the bonding nature of their filled bands of delocalized orbitals.

Among the transition metals, a range of properties is encountered. Copper and silver are much better electrical conductors than chromium. Tungsten has very low ductility. Mercury is a liquid at room temperature. All these differences result from variations in numbers of valence electrons. A transition metal such as vanadium or chromium has five or six valence electrons per atom; all occupy bonding orbitals in the metal lattice. As a result, there are strong attractive forces among the metal atoms, and vanadium and chromium are strong and hard. Beyond the middle of the transition metal series, the additional valence electrons occupy antibonding orbitals, which reduces the net bonding. This effect is most pronounced at the end of the *d* block, where the number of antibonding electrons nearly matches the number of

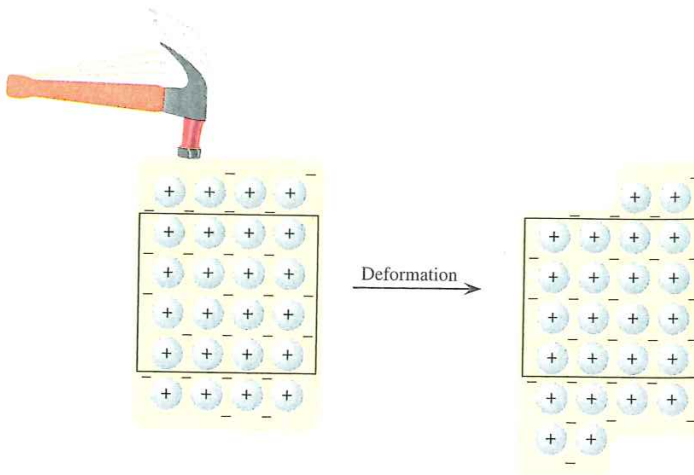


Figure 10-24

When a metal changes shape, its atoms shift position. However, because the valence electrons are fully delocalized, the energy of these electrons is unaffected.

bonding electrons. Zinc, cadmium, and mercury, with d^{10} configurations, have melting temperatures that are more than 600 °C lower than those of their immediate neighbors.

Ionic Solids

As described in Chapter 7, ionic solids contain cations and anions that are strongly attracted to each other through coulombic interactions. Such forces are *interionic* rather than *intermolecular*. Ionic solids must be electrically neutral, so their stoichiometries are determined by the charges carried by the positive and negative ions. These in turn are determined by the positions of the elements in the periodic table.

Many ionic solids contain metal cations and polyatomic anions. Here again, the stoichiometry of the solid is dictated by the charges on the ions and the need for the solid to maintain electrical neutrality. Some examples of 1 : 1 ionic solids containing polyatomic anions are NaOH, KNO_3 , CuSO_4 , BaCO_3 , and NaClO_3 . Some metallic ores have 1 : 1 stoichiometry but contain more exotic anions, such as scheelite, CaWO_4 (contains WO_4^{2-}); zircon, ZrSiO_4 (contains SiO_4^{4-}); and ilmenite, FeTiO_3 (contains TiO_3^{2-}).

Ionic solids can contain more than one cation or anion. For example, the ore apatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$, contains both phosphate and fluoride anions. The mineral beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, contains beryllium and aluminum cations as well as the $\text{Si}_6\text{O}_{18}^{12-}$ polyatomic anion. An even more complicated example is garnierite, $(\text{Ni,Mg})_6\text{Si}_4\text{O}_{10}(\text{OH})_2$, which has a variable composition of Ni^{2+} and Mg^{2+} . Although variable in relative proportions, there are always a total of six cations for every anion of $\text{Si}_4\text{O}_{10}^{10-}$ and two anions of OH^- .

One of the most exciting developments in materials science in recent years involves mixed oxides containing rare earth metals. Some of these compounds have been found to be **superconductors** (Box 10-1). That is, below a certain temperature they can carry immense electrical currents without losses resulting from resistance. Before 1986, it was thought that this property was limited to a few metals at temperatures below 25 K. Then it was found that a mixed oxide of lanthanum, barium, and copper showed superconductivity at around 30 K.

Intense research efforts soon determined that the mixed oxide $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ($x \sim 0.1$) is superconducting at 77 K. This was a huge jump in the temperature at which superconductivity occurs, bringing the phenomenon to a temperature that can be routinely achieved by using inexpensive liquid nitrogen as a coolant. Moreover, the compound is relatively easy to make. Three simple ionic salts, Y_2O_3 , BaCO_3 , and CuO , are ground together in the correct stoichiometric ratio and heated to 950 °C. The mixture is cooled and pressed into pellets, after which the pellets are sintered—heated to just below their melting point—to bind the grains in the pellets tightly together. Finally, the pellets are heated in oxygen at around 550 °C.

This yttrium-containing material displays a characteristic that is unexpected in traditional chemistry but relatively common in solids: nonstoichiometric composition. When the substance contains a stoichiometric amount of oxygen ($x = 0$ or 1), it has inferior superconducting properties. A slight deviation from stoichiometric composition is required for optimal superconducting behavior. In addition, the copper cations display deviations from integral stoichiometry. Assigning characteristic charges to the other elements (+3 for Y, +2 for Ba, and -2 for O), we find that Cu must have an average charge of $+6.8/3 = 2.27$ when $x = 0.1$. Because fractional charges are impossible, this means that most of the Cu atoms in the substance bear +2 charges, but a few have +3 charge. We return to nonstoichiometric compositions of solid materials in Section 10.4.

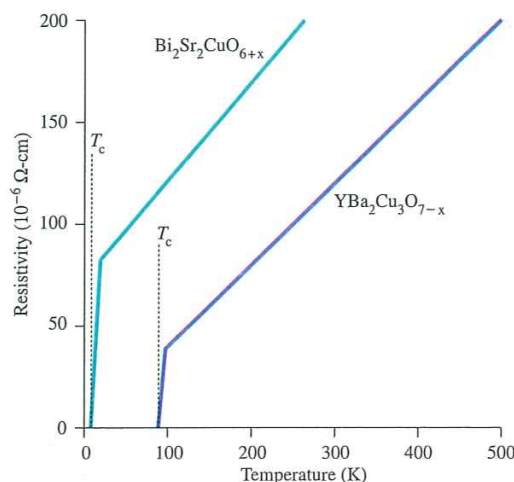
Superconductors

Trains that run on frictionless tracks, high-voltage power lines that span the country without power losses, new magnetic resonance imaging (MRI) machines hundreds of times more powerful than the ones in use today, computer chips smaller yet faster and with much larger capacities than the present generation—these are not predictions from science fiction but potential applications of room-temperature superconductors. Such devices do not exist today, but chemists and physicists believe that they may be possible. Many research groups around the world are developing new materials in hopes of reaching this spectacular goal.

All metals conduct electricity because, as described in Chapter 9, their valence electrons are highly mobile, allowing easy flow of charge. In normal electrical conductors, the charge flow is always accompanied by some losses because of resistive heating. Qualitatively, you can think of the electrons being slowed in their travels through a conductor by “bumping into” atoms along their paths.

In contrast to normal conductivity, superconductivity is characterized by zero electrical resistance. Electrons move freely through a superconductor without any friction. A superconductor can carry immense amounts of current without losses resulting from heating. Coupled with this electrical property is an equally unique magnetic property: Magnetic fields cannot penetrate into superconductors.

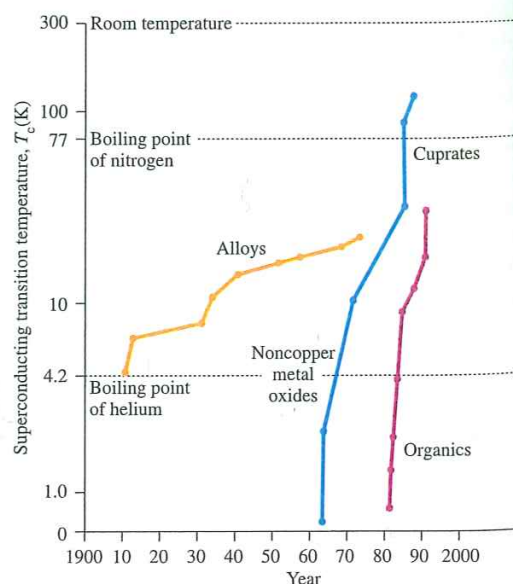
A material that displays superconductivity does so only below a critical temperature, T_c . Above T_c the material displays normal conductivity, but as the temperature drops below T_c , its resistance abruptly disappears. This dramatic change is analogous to the abrupt change in fluidity when a solid melts. The transition from the normal state to the superconducting state, like the transition from solid to liquid state, is a phase transition.



Just as different substances melt at different characteristic temperatures, the transition between normal and superconductivity occurs at different temperatures for different materials. In general, however, T_c is very low, often below 4.2 K, the boiling point of liquid helium. For this reason, any device that makes use of superconductivity must be immersed in a bath of liquid helium. Little wonder that superconductivity was not discovered until early in this century and remained a laboratory curiosity until the mid-1980s.

The story of superconductivity begins with Heike Kamerlingh Onnes, a Dutch physicist who discovered how to liquefy helium in the early 1900s. Liquid helium provided Kamerlingh Onnes with the ability to cool materials to 4.2 K, and he set out to study the properties of materials at this very low temperature. In 1911, his measurements on mercury revealed that at 4.2 K its electrical resistivity abruptly became too low to measure. He had discovered superconductivity.

Over the next 6 decades, many metallic superconductors were discovered, not only among pure metals such as Al, Pb, Th, and Nb, but also in various alloys. Niobium alloys are particularly good superconductors, and in 1973 a niobium alloy, Nb_3Ge , was found to have $T_c = 23$ K, the highest known value for a metal superconductor. This was very slow progress in the search for high-temperature superconductors. In more than 6 decades, the highest temperature observed for superconductivity had advanced only 19 K, from 4.2 to 23 K.



An unprecedented breakthrough came in a quite different type of material: mixed metal oxides. Metal oxide superconductors, such as NbO, had been discovered in the 1930s, all with $T_c < 10$ K. Then in 1986 a ceramic oxide with formula $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ was found to show superconductivity at 30 K. This material held the record for less than a year, because $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, with $T_c = 92$ K, was discovered in 1987. A year later, $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ was found to have $T_c = 125$ K, and the record in the mid-1990s is held by $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9$, with $T_c = 135$ K.

Ceramic oxide superconductors have crystal structures that display distinct layers. The Cu-containing superconductors contain planes of CuO_2 . These planes alternate with layers containing oxygen and the other metals that make up the superconductor. Superconductivity takes place in the CuO_2 planes. One of the simplest structures is illustrated here; the detailed crystal structures of these materials are often complex.

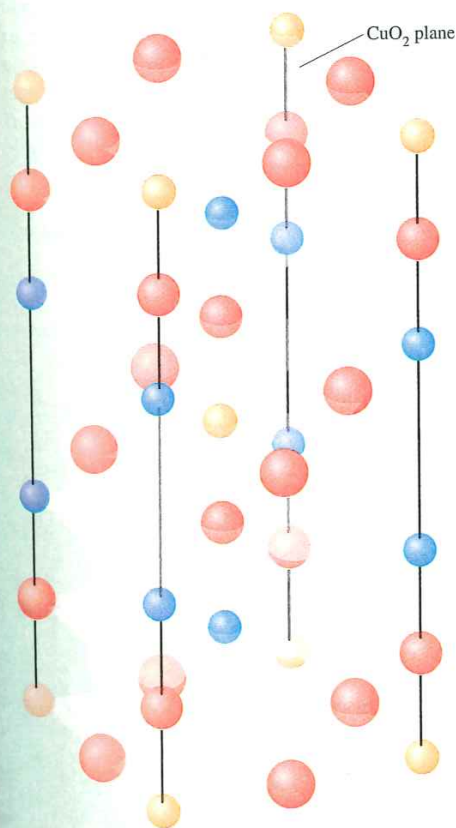
At 135 K, superconductivity is nearly an order of magnitude higher in temperature than it was a decade ago, but it is still far from room temperature. Just as the ceramic oxides leapfrogged past metals to become the leading

superconductors, some researchers believe that organic-based superconductors hold the best hope for the future. The first organic superconductor was discovered in 1981, and within 10 years the highest T_c for an organic-based superconductor rose from < 1 K to 33 K. The current organic record holder is a composite of fullerene and alkali metals, $\text{Cs}_2\text{RbC}_{60}$. This material is a molecular solid with a relatively simple crystal structure. Fullerene molecules form a face-centered cubic structure (visualize Figure 10-30 with the C_{60} balls in place of the ions), with the alkali metal atoms nesting in the interstitial spaces between balls.

Temperature is not the only impediment to the commercialization of superconductors. For many applications, a superconductor must first be drawn into a wire. Ceramic oxides, the best available superconductors at present, lack the ductility needed for wire formation. Recently, however, workers at Los Alamos National Laboratory devised a way to make a flexible tape that has good superconductivity at 77 K.

The process exemplifies the high-technology techniques used in contemporary materials research. The base material is a tape made of an inexpensive nickel alloy. The tape is coated with an aligned layer of cubic zirconia (ZrO_2). First, a beam of gaseous argon ions strips zirconia particles from a block and deposits them on the alloy. At the same time, a second argon ion beam strikes the film at a specific angle, causing the depositing particles to line up properly. Finally, a high-power pulsed laser vaporizes a $\text{YBa}_2\text{Cu}_3\text{O}_7$ superconductor and redeposits it on the zirconia surface, forming an oriented superconducting film 1 to 2 μm thick.

Flexible tapes that superconduct at the temperature of liquid nitrogen provide promise of accelerating uses for superconductors in motors, generators, and even electric transmission lines. Meanwhile, superconducting magnets cooled to the temperature of liquid helium already are in use. High-field nuclear magnetic resonance (NMR) spectrometers have become standard instruments in chemical research laboratories, and the same type of machine (called an *MRI spectrometer*) is used for medical diagnosis in hospitals worldwide.



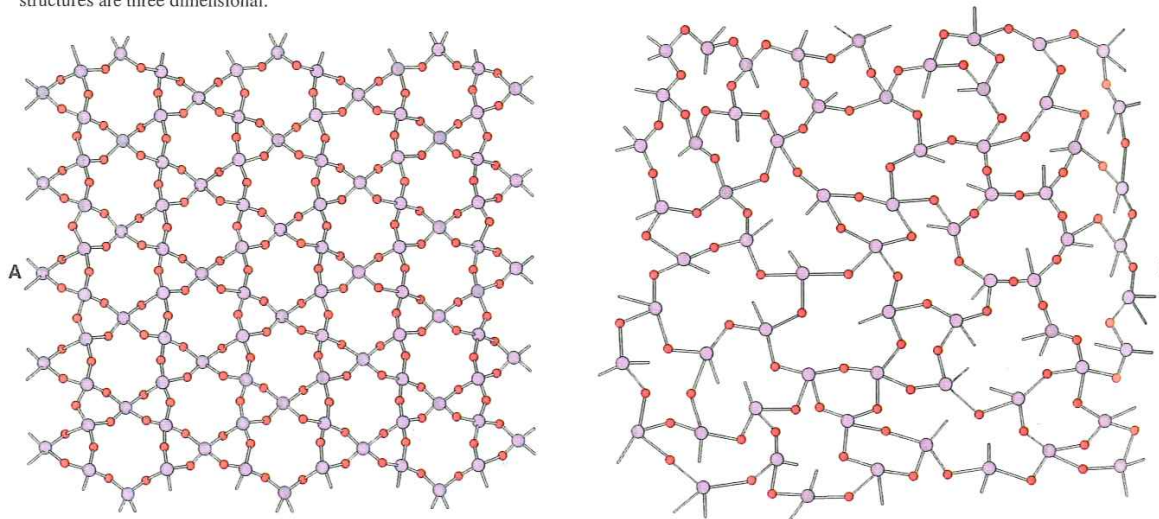
Section Exercises

- 10.3.1** Describe the forces that exist in (a) solid CO_2 (dry ice); (b) crystalline yellow elemental sulfur, S_8 ; (c) tin (soft, malleable, mp = 232°C); and (d) Li_2O .
- 10.3.2** Arrange the following in order of increasing melting point and explain the reasons for your rankings: C (diamond), F_2 , K, and Co.
- 10.3.3** Determine the chemical formulas of the following ionic substances:
 (a) Magnesium phosphate
 (b) Spodumene, a mineral containing Li, Al, and $\text{Si}_2\text{O}_6^{4-}$
 (c) The superconducting oxide that contains Bi^{3+} , Sr^{2+} , and Cu^{2+} in 2:2:1 atomic ratio

Amorphous comes from Greek *a*, meaning “without,” and *morph*, meaning “form.”

Figure 10-25

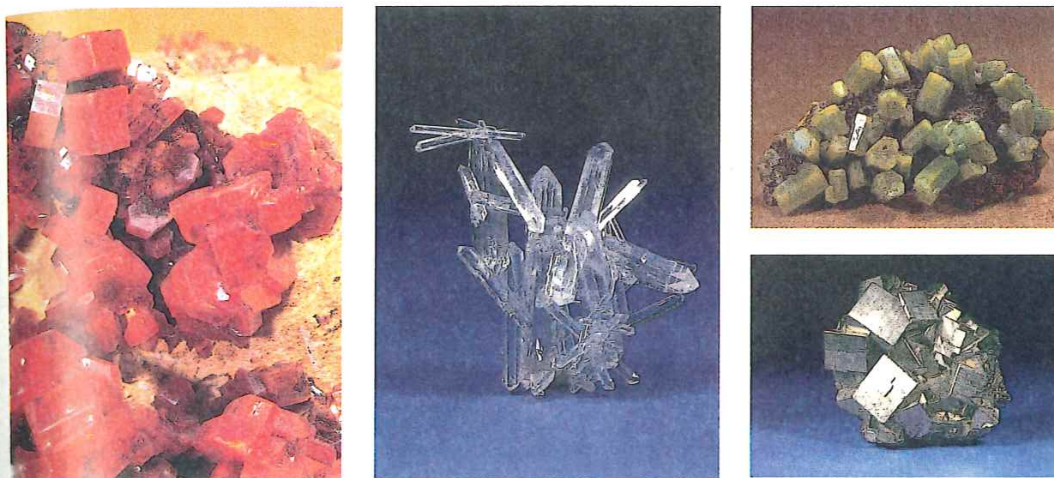
A, Quartz is a crystalline form of silicon dioxide containing a three-dimensional array of SiO_2 units linked by highly regular covalent bonding. B, Silica glass also has a three-dimensional array of SiO_2 units, but in this case the bond arrangement is irregular, and the solid is amorphous. Both A and B are two-dimensional representations. The actual structures are three dimensional.



10.4 ORDER IN SOLIDS

In gases and liquids, molecules are in constant motion, continuously changing their positions. In a solid, in contrast, atoms, molecules, or ions are in fixed positions. Their motions are restricted to vibrations about preferred locations. Many solids display a highly regular repeating pattern of organization; these solids are classified as **crystalline solids**. Diamonds, sugar crystals, quartz, and table salt are examples of crystalline solids. In other solids, the arrangement of particles is irregular, with no observable pattern. These **amorphous solids** include cotton candy, glass, and wax.

Whether a solid sample of a particular substance is crystalline or amorphous depends largely on how the solid is prepared. Silicon dioxide, for example, exists in both forms. Quartz is a crystalline form of silicon dioxide found in minerals all over the world. Each tetrahedral silicon atom is bonded to a total of four oxygens in a highly symmetrical three-dimensional network. This strong bonding network gives silicon dioxide its high melting point of 1710°C . Slow cooling of molten SiO_2 gives crystalline quartz, but rapid cooling gives an amorphous glass. Figure 10-25 shows molecular representations of quartz and glass. Both structures are three-dimensional networks, but the two-dimensional views given in the figure are sufficient to show the differences between crystalline and amorphous solids.

**Figure 10-26**

Shown here are $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$ (vanadinite) (left), SiO_2 (quartz) (center), $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ (pyromorphite) (top right), and FeS_2 (pyrite) (bottom right).

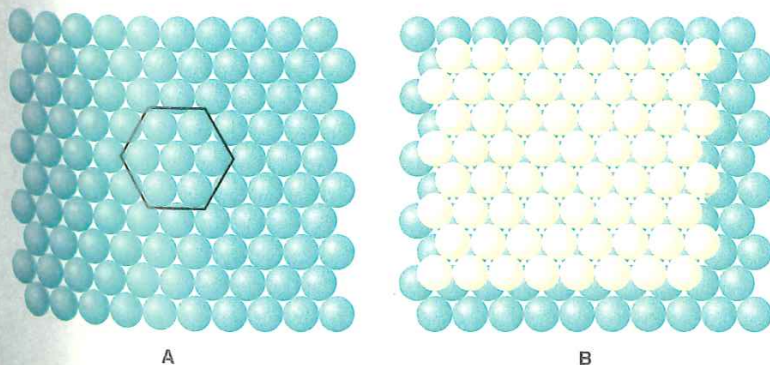
Some of the most valued materials of society are precious gemstones, which are crystals of rare and richly colored minerals. The following general features characterize crystalline solids:

1. Crystals are uniform in structure. Crystals of a particular substance have common geometrical features regardless of how they are formed.
2. The shape of a crystal is characterized by its parallel faces and edges. The edges of a crystal usually intersect at characteristic angles.
3. When a crystal breaks into smaller pieces, fragmentation occurs along crystal edges. The smaller pieces have the same characteristic angles as the original crystal.
4. Crystals have a high degree of symmetry (Figure 10-26).

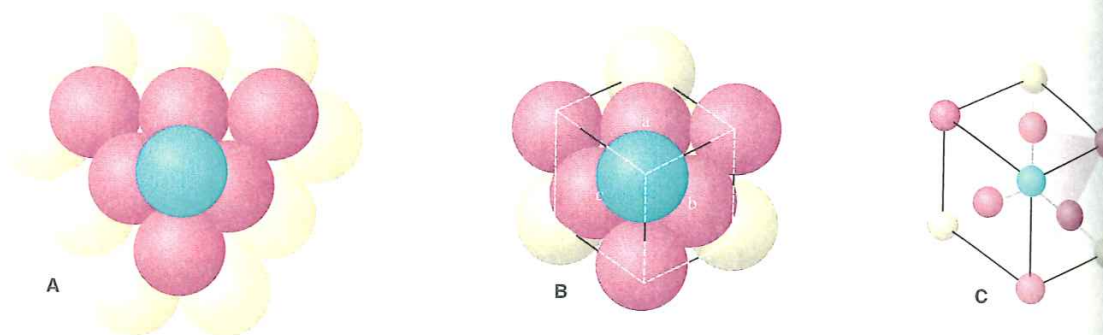
Close-Packed Crystals

A solid is most stable when each atom, molecule, or ion is as close to as many others as possible, thus maximizing intermolecular attraction. An arrangement that accomplishes this is described as a **close-packed structure**. Close-packed structures have atoms or molecules arranged so that the empty space around them is minimized.

To visualize a close-packed atomic solid, think of the atoms as spheres placed as compactly as possible. Begin by assembling a single planar layer as shown in Figure 10-27, A. Notice that the most compact planar arrangement places each

**Figure 10-27**

A, Spheres close-packed in a layer generate a hexagonal pattern. B, When a second layer is packed on top of the first, each sphere in the second layer nestles in the dimple created by three adjacent spheres in the lower layer. The second layer has two different sets of dimples, one directly above the spheres in the first layer (red) and the other offset from the spheres in the layer above it (unshaded).

**Figure 10-28**

Three views of the hexagonal layers contained within a face-centered cubic array. **A**, A view from above of three hexagonal layers, with all but one atom removed from the top layer. **B**, A view from above showing an outline of the cube and atoms from three successive layers that make up the cubic array. **C**, A view of the cube from the side, with the atoms of the middle hexagonal layer screened for emphasis.

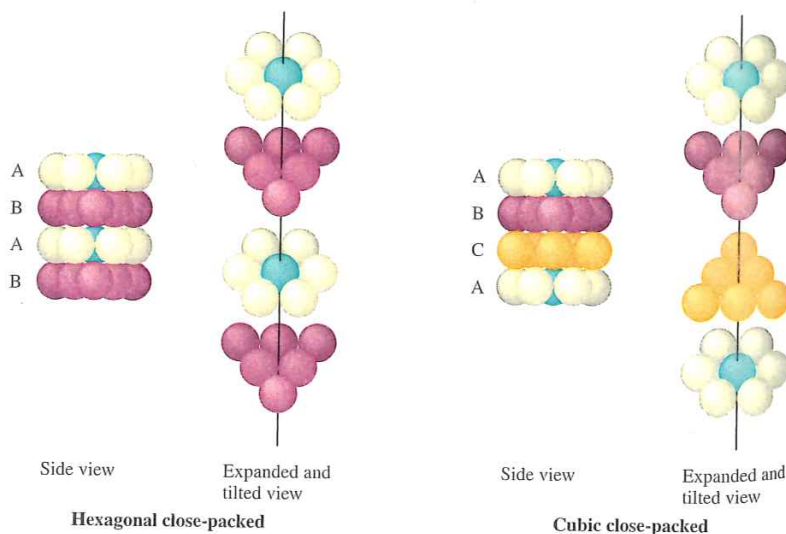
sphere within a regular hexagon formed by six others. Each sphere has six nearest neighbors in the plane. Now add a second layer of spheres. To achieve a most compact arrangement, each sphere will nestle in one of the “dimples” between a trio of spheres in the first layer, as shown in Figure 10-27, **B**. This adds three more nearest neighbors for each sphere. As additional spheres are added, the second layer eventually looks identical to the lower layer, except that it is offset slightly to allow the spheres to nestle in the dimples formed by the layer below.

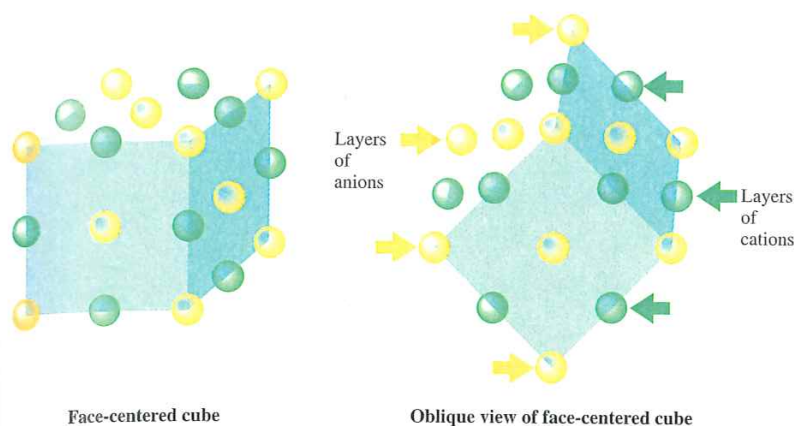
Now consider adding a third layer of spheres. This new layer is like the other two, but it can be placed in two different ways because there are two sets of dimples in the second layer. One set is located directly above the spheres in the first layer. If spheres in the third layer lie in these dimples, the third layer is directly above the first, and the resulting three-dimensional structure is a **hexagonal close-packed structure**. If spheres in the third layer lie in the other set of dimples, the third layer is offset from both of the lower layers. This arrangement is a **cubic close-packed structure**. Either way, addition of a third layer adds three more nearest neighbors for each sphere. In these close-packed structures, each sphere has 12 nearest neighbors: six in the same plane, three above, and three below.

To see the cubes in a cubic close-packed structure, we need to remove all but one of the atoms from the top layer, as shown in Figure 10-28, **A**. The remaining atom from this top layer (shown in green in the figure) defines one corner of a cube.

Figure 10-29

Side and expanded views of hexagonal and cubic close-packed crystal types. In the hexagonal close-packed structure, spheres on both sides of any plane are in the same positions, and the third layer is directly above the first. In the cubic close-packed structure, layers take up three different positions, and the fourth layer is directly above the first.



**Figure 10-30**

Ionic crystals such as NaCl contain face-centered cubic arrangements of each ion. In this view a cube is drawn with the cations, shown as yellow spheres, at its corners and in the centers of the faces. The anions, shown as blue spheres, occupy positions at the center of each edge of the cube. A view from an oblique angle reveals that this structure contains alternating hexagonal planar arrays of cations and anions.

Each face of the cube contains an atom at each corner and one in the center, as shown by Figure 10-28, *B*. Three atoms from the second layer (shown in maroon in the figure) lie at corners of the cube, and three other atoms from the second layer (labeled *a*, *b*, and *c* in the figure) fall in the centers of three faces of the cube. Three additional corners of the cube are occupied by atoms from the third layer (shown in grey in the figure). Figure 10-28, *C*, shows that the atoms from one hexagonal layer fall along a diagonal plane through the cube. Because each face of this cube contains an atom at its center, this array is also known as the **face-centered cubic structure**.

The exploded views in Figure 10-29 show yet another way of looking at the hexagonal and cubic close-packed crystalline types. In the hexagonal close-packed structure, notice that the *third* layer lies directly above the first, the fourth above the second, and so on. Thus the layers can be labeled ABAB, and so on. In the cubic close-packed structure, the third layer is offset from the other two, but the *fourth* layer is directly above the first. Thus this arrangement can be labeled ABCABC and so on.

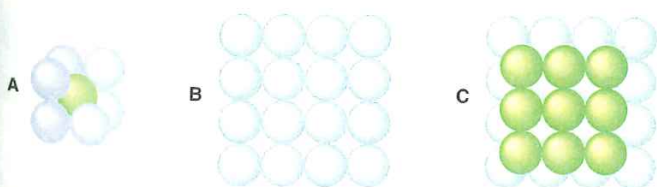
Atoms and molecules with spherical symmetry often form crystals with hexagonal or cubic close-packed geometry. For instance, magnesium and zinc crystallize with their atoms in a hexagonal close-packed array. Silver, aluminum, and gold, on the other hand, crystallize in the cubic close-packed arrangement. Argon solidifies at low temperature as a cubic close-packed crystal, and neon can solidify in either form.

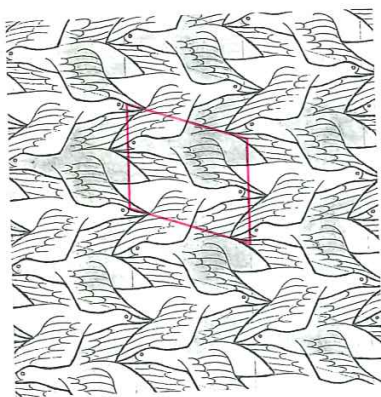
The packing in ionic crystals requires that ions of opposite charges alternate with one another to maximize interionic attraction. For many 1:1 ionic crystals such as NaCl, the most stable arrangement is two interlocking face-centered cubic arrays, as is illustrated in Figure 10-30.

Another type of arrangement, which is shown in Figure 10-31, *A*, is a **body-centered cubic structure**. A body-centered cube can be constructed by assembling

Figure 10-31

A body-centered cubic array is made up of layers of spheres arranged in a square pattern. The basic pattern (*A*) has one corner sphere removed to reveal the sphere nested in the center of the cube. The array can be constructed by laying down a square layer of spheres (*B*) and then placing a second square layer in the dimples between the spheres (*C*). A third layer directly above the first completes the cubes.



**Figure 10-32**

M.C. Escher used repeating patterns to create works of art with exquisite symmetry. The repeating patterns in Escher's work are two-dimensional analogs of the unit cells that define the symmetry of a crystalline solid. A unit cell for this drawing is highlighted on the figure. The entire drawing can be generated by repeated use of this unit cell.

a set of spheres in a *square* array, as shown in Figure 10-31, *B*, and then nesting a second set of spheres in the dimples of the first set, as shown in Figure 10-31, *C*. This arrangement gives a second square array, on which yet another set can be nested. In this arrangement, each sphere has 8 nearest neighbors rather than 12. The packing is not quite as compact as in close-packed arrays, but some metals are more stable when bonded to 8 neighbors rather than to 12. All the alkali metals, as well as iron and the transition metals from Groups 5 and 6, adopt this atomic arrangement.

Unit Cells

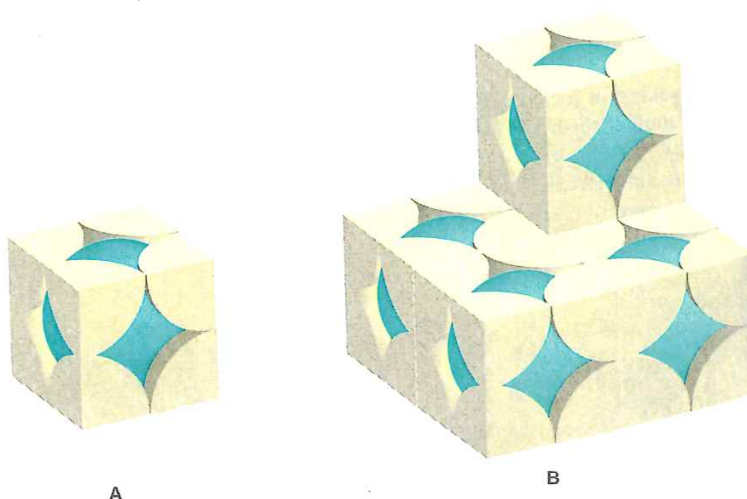
Any crystal is a vast array of atoms, molecules, or ions arranged in some regular repeating pattern. Because the pattern repeats exactly, every crystal has one smallest unit from which the entire pattern can be assembled. This minimum unit is called a **unit cell**. The idea of the unit cell is illustrated in two dimensions by the art of M. C. Escher, as shown in Figure 10-32. Escher often used symmetrical patterns aligned together to create an overall design. The repeating units can be visualized as "tiles" placed edge to edge. In Figure 10-32, each "tile" is a parallelogram. A unit cell in a crystal is a three-dimensional fragment stacked together like a set of blocks. The faces of unit cells can be squares, rectangles, or parallelograms.

The body-centered cubic crystal provides one of the simplest illustrations of three-dimensional unit cells. The unit cell for such a crystal is a cube (Figure 10-33, *A*). Notice that the unit cell has one complete atom in the exact center of the cube. The corners of the cube are defined by the centers of eight other atoms. Thus this cube contains a central atom and portions of eight additional atoms. The body-centered cubic crystal is built by stacking together many unit cells, as shown in Figure 10-33, *B*. It takes eight stacked unit cells to complete one of the corner atoms, so each unit cell contains one eighth of an atom at each of its corners. The cell has eight such corners, giving eight one-eighth parts of atoms in addition to the complete atom in the center. Adding all these together gives a total of two atoms in each unit cell.

Up to now, we have described the crystalline arrays favored by spherical objects such as atoms, but most molecules are far from spherical. The photos of stacks of produce in Figure 10-34 illustrate that nonspherical objects require more elaborate

Figure 10-33

A. The unit cell of iron, which forms body-centered cubic crystals. There is an iron atom at the center of the unit cell, and each of the eight corners contains one eighth of an iron atom, for a total of two complete atoms per unit cell. **B.** Unit cells stacked together. Four unit cells touch at the center, forming half of an iron atom. When a second set of four unit cells is placed on top of the first, the iron atom becomes complete and is surrounded by the eight iron atoms in the centers of the eight unit cells used in the assembly.



A

B



Figure 10-34
Nonspherical objects such as bananas require more elaborate packing schemes than spherical objects such as oranges.

arrays to achieve maximal stability. Compare the stack of bananas with the stack of oranges. Just as the stacking pattern for bananas is less symmetrical than that for oranges, the structural patterns of most molecular crystals are less symmetrical than crystals of spherical atoms, reflecting the lower symmetry of the molecules that make up the crystal.

Amorphous Solids

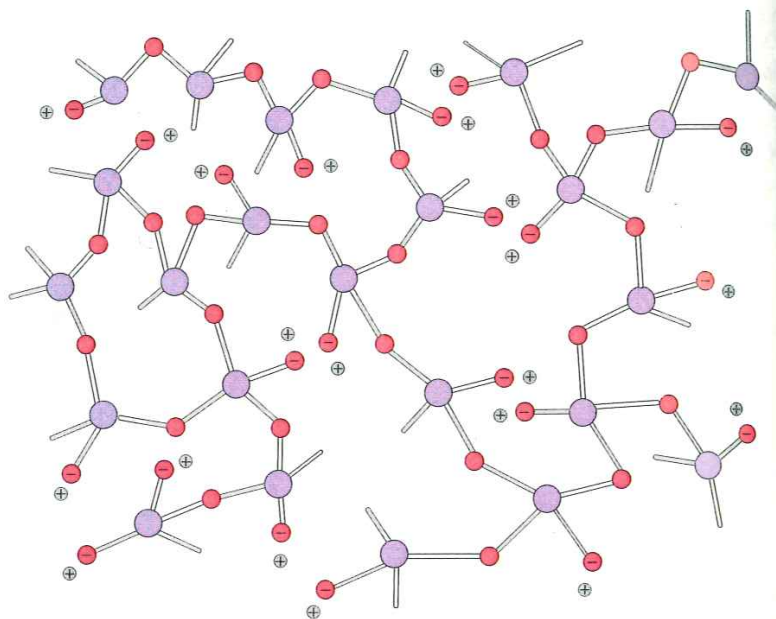
Solid materials are most stable in crystalline form, so when a liquid is cooled slowly, it generally solidifies as crystals. When solids form rapidly, on the other hand, their atoms or molecules may become locked into positions other than those of a regular crystal, giving amorphous materials. Ordinary cane sugar is crystalline as it comes from the package, but it forms an amorphous solid when it is carefully heated until it melts and then is cooled rapidly. Cotton candy contains long threads of amorphous sugar.

What we call **glass** is an entire family of amorphous solids based on silica (SiO_2). Pure silica is usually found as crystals containing the regular array of covalent bonds shown in Figure 10-22. Quartz contains crystals of pure silica. When quartz is melted and then quickly cooled, however, it forms fused silica, an amorphous solid glass. Silica glass has many desirable properties. It resists corrosion, transmits light well, and withstands wide variations in temperature. Unfortunately, pure silica is very difficult to work with because of its high melting point (1710°C). As a result, silica glass is used only for special applications.



Figure 10-35

Adding sodium oxide to quartz glass breaks some of the Si—O covalent bonds to create terminal O^- ions associated with Na^+ cations. This softens the glass, reducing its melting point.



Sodium oxide (Na_2O) is mixed with silica to make glass that can be shaped at a lower temperature. Sodium oxide is ionic, and it breaks the Si—O—Si chain of covalent bonds, as shown in Figure 10-35. This weakens the lattice strength of the glass, lowers its melting point, and reduces the viscosity of the resulting liquid. However, the weakened lattice also means that glass made from sodium and silicon oxides is vulnerable to chemical attack.

A desirable glass melts at a reasonable temperature, is easy to work with, and yet is chemically inert. Such a glass can be prepared by adding a third component that has bonding characteristics intermediate between those of purely ionic sodium oxide and those of purely covalent silicon dioxide. Several different components are used, depending on the properties desired in the glass.

The glass used for windowpanes and bottles is soda-lime-silica glass, a mixture of sodium oxide, calcium oxide, and silicon dioxide. The addition of CaO strengthens the lattice enough to make the glass chemically inert to most common substances. (Strong bases and HF , however, attack this glass.) Pyrex, the glass used in coffeepots and laboratory glassware, can withstand rapid temperature changes that would crack soda-lime-silica glass. Pyrex is a composite of B_2O_3 , CaO , and SiO_2 . Lenses and other optical components are made from glass that contains PbO . Light rays are strongly bent as they pass through lenses made of this glass. Colored glasses are obtained by adding small amounts of colored metal oxides such as Cr_2O_3 (amber), NiO (green), or CoO (brown).

Many materials used in this age of plastics are amorphous solids composed of extremely large molecules called *polymers*. Polymeric solids are intermediate between molecular and covalent solids. They have discrete but extremely large molecules held together by dispersion forces and/or hydrogen bonds. Because the molecules are so large, their covalent bonding plays an important role in determining the properties of the solid. A “plastic” can be shaped and molded because the inter-

► We discuss polymers and other huge molecules in Chapter 11.

molecular forces between polymer molecules are weaker than chemical bonds, but a plastic has relatively high strength because its long-chain molecules are held together by strong covalent bonds.

Crystal Imperfections

The two extremes of ordering in solids are perfect crystals with complete regularity and amorphous solids that have little order. Most solid materials fall in between these extremes. That is, they are crystalline but contain defects. **Crystalline defects** can profoundly alter the properties of a solid material, often in ways that have useful applications. Doped semiconductors, described in Section 9.6, are solids into which impurity “defects” are deliberately introduced in order to modify electrical conductivity. Gemstones are crystals containing impurities that give them their color. Sapphires and rubies both are imperfect crystals of colorless Al_2O_3 ; Ti^{3+} or Fe^{3+} makes sapphires blue, and Cr^{3+} makes rubies red.

As noted earlier, yttrium-barium-copper superconductors have optimal properties when they have a slight deficiency of oxygen. This departure from stoichiometric composition is created by defects in the crystal structure. The superconductor crystal has oxygen anions missing from some positions in the crystal lattice, and the number of missing anions can vary sufficiently to give the material a nonstoichiometric overall composition. For the solid to remain electrically neutral when its anion content varies, some of the cations must take on different charges. The copper cations in the superconductor can have a +2 or +3 charge. The relative number of Cu^{3+} ions decreases as oxygen anions are removed from the structure.

Defects also play important roles in the properties of metals. For example, small amounts of impurities are deliberately added to iron to improve its mechanical properties. Pure iron is relatively soft and easily deformed, but the addition of a small amount of carbon creates steel, a much harder material. Carbon atoms fill some of the open spaces between iron atoms in the crystalline structure of steel. Although they fit easily into these spaces, their presence reduces the ability of adjacent layers of iron atoms to slide past each other, as Figure 10-36 illustrates.

This section describes only a few of the features of order and disorder in solid materials. The rapidly growing field of materials science addresses these and many other atomic and molecular aspects of solids that determine the technologically useful properties of materials.

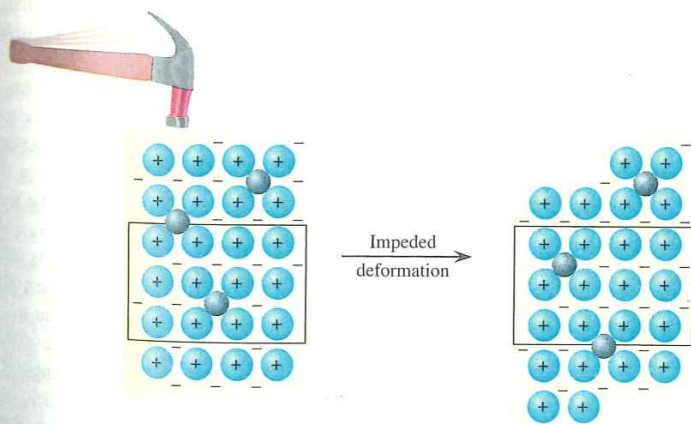


Figure 10-36

The presence of even a few carbon atoms (black circles) in the interstitial holes in an iron lattice makes it more difficult for atomic layers to slide past each other.

Section Exercises

- 10.4.1** Predict the angles found in the crystalline fragments broken from a hexagonal close-packed crystal. What additional angles would be found in fragments from cubic close-packed crystals? (HINT: Think about the angles found in hexagons and cubes.)
- 10.4.2** The unit cell of cubic close-packed crystals is a cube defined by the centers of spheres at its eight corners; there is an additional sphere embedded in the center of each face (see Figure 10-28, C). Draw this unit cell. Determine what fraction of each type of atom (corner and center of face) is within the unit cell. (HINT: How many unit cells must be stacked together to give one complete face atom?)
- 10.4.3** Carbon atoms in steel occupy interstitial positions, as shown in Figure 10-36. Manganese atoms, which are also added to steel to increase its hardness, occupy substitutional positions; that is, they replace iron atoms in the crystalline structure. Draw an atomic picture of a portion of manganese-containing steel.

10.5 THE NATURE OF SOLUTIONS

The discussion so far has focused primarily on pure substances, but most of the chemistry that occurs in the world involves mixtures. Recall from Chapter 1 that a homogeneous mixture of chemical substances is commonly called a **solution**. The component that determines the state of the solution is the **solvent**. Normally, this component is present in greatest quantity. All other substances in the solution are called **solutes**. Solutions have special properties that are described in the next several sections.

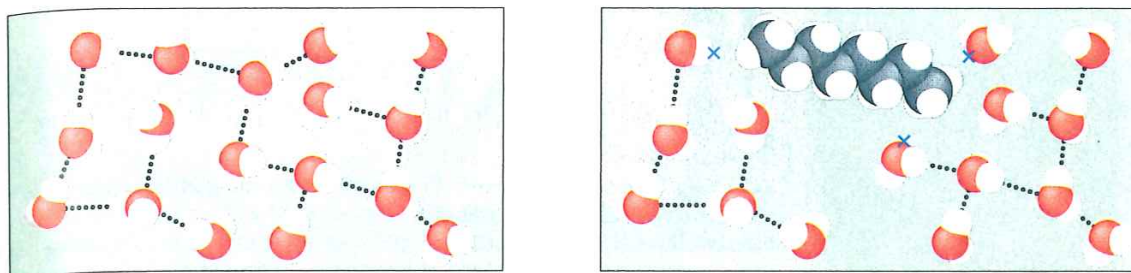
Most people think of solutions as liquid mixtures. The oceans, for example, are liquid solutions in which water is the solvent and dissolved ions, gases, and molecules are the solutes. Vinegar is a liquid solution of acetic acid in water, and gasoline is a liquid solution that contains many different hydrocarbons. Gases can be solutions as well. The most familiar example is the Earth's atmosphere, a solution of nitrogen, oxygen, and small amounts of several other gases. Even solids can be solutions. For instance, brass is a solution of copper and zinc, and steel is a solution of small amounts of carbon and manganese dissolved in iron.

A solution is characterized by its concentration, which can vary. For example, adding more sugar to a cup of coffee makes the solution more concentrated in sugar. The concentration of pollutants in the air is higher in urban areas than in rural ones. Steel can be made harder and stronger by controlling the concentration of carbon dissolved in iron.

Except for gaseous solutions, there is usually an upper limit to the amount of solute that will dissolve in a given amount of solvent. When that limit has been reached, the solution can hold no more solute and is said to be **saturated**. The concentration of a saturated solution is called the **solubility** of the substance in that particular solvent. Concentration is usually expressed as a molarity or as the mole fraction of the solute.

Whether or not a given substance dissolves in a liquid depends largely on intermolecular coulombic forces of attraction. These interactions are of three types: those between ions or molecules of the pure solute, those between solvent molecules, and those between solvent and solute in the solution. The balance among these forces of attraction results in wide variations in solubility. For example, the room-temperature solubility of NaCl in water is about 6 M, that of AgCl is only 10^{-5} M, and that of NaCl in gasoline is virtually zero. Some substances form solu-

◀ Molarity (*M*) is defined in Section 3.7, and mole fraction (*X*) is defined in Section 5.5.

**Figure 10-37**

Left, A collection of water molecules has an intricate hydrogen-bonding network (blue lines). Right, The presence of an octane molecule disrupts the hydrogen bonds marked with Xs.

tions in all proportions and are said to be completely **miscible**. Acetone and water, for example, can be mixed in any proportion from pure water to pure acetone. A few salts, such as $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$, mix with hot water in any proportion.

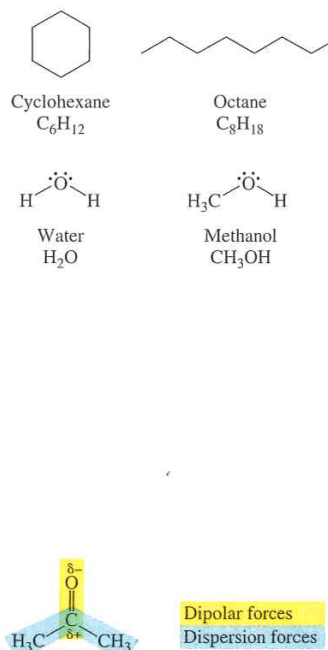
Miscibility of Liquids

Substances that dissolve in each other usually have similar types of intermolecular interactions, a generalization that can be summarized by the expression *like dissolves like*. As a result, one liquid dissolves in another if the forces of attraction between molecules of the two different substances are comparable to the interactions between molecules of the same type.

When two liquids are mixed, all three sets of intermolecular interactions must be assessed. Consider water, methanol, octane, and cyclohexane, all of which are liquids at room temperature. Water and methanol are miscible because the molecules in both the pure liquids and their mixtures form many hydrogen bonds. Octane and cyclohexane are also completely miscible because the molecules in both the pure liquids and their mixtures interact through the dispersion forces caused by their polarizable electron clouds. In contrast, water and octane are nearly insoluble in each other. When mixed, octane and water partition into distinct layers, one of nearly pure water and the other of nearly pure octane. Water and cyclohexane are also insoluble in each other and form two layers when mixed.

The solubilities of water, methanol, octane, and cyclohexane in one another are examples of like dissolving like. Water and methanol form hydrogen bonds. When these liquids are mixed, the degree of hydrogen bonding in the solution is about the same as in either of the pure liquids. Likewise, dispersion forces in solutions of octane and cyclohexane are about the same as those in the pure liquids. As Figure 10-37 shows, however, octane molecules cannot dissolve in water unless they disrupt part of water's hydrogen bonding network. Octane does not form hydrogen bonds, so the only forces of attraction between water molecules and octane molecules are dispersion forces. Because hydrogen bonds are stronger than dispersion forces, the cost of disrupting water's hydrogen bonding network is far greater than the stability gained from octane-water dispersion forces.

Some liquids can interact with other substances in multiple ways. Acetone, for instance, has a polar $\text{C}=\text{O}$ bond and a three-carbon bonding framework (Figure 10-38). The bonding framework is similar to that of a hydrocarbon, so acetone mixes with cyclohexane. The polar $\text{C}=\text{O}$ group makes acetone miscible with other polar molecules such as acetonitrile (CH_3CN). Finally, the polar oxygen atom in acetone has lone pairs of electrons that can form hydrogen bonds with hydrogen atoms of ammonia or water. Because of its versatility, acetone is an important industrial solvent. It is also used in laboratories to clean and rinse glassware. Sample Problem 10-7 treats several alcohols, which also display multiple types of interactions.

**Figure 10-38**

Acetone is a versatile solvent because it will dissolve many substances. The three-carbon chain is compatible with nonpolar molecules such as octane and cyclohexane, whereas the polar $\text{C}=\text{O}$ bond is compatible with other molecules such as methanol and water.

Sample Problem 10-7

Solubility Trends

Give a molecular explanation for the following trend in alcohol solubilities in water:

Propanol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	Completely miscible
Butanol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	1.1 M
Pentanol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	0.30 M
Hexanol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	0.056 M

Method: Solubility limits depend on the relative magnitude of the destabilization that occurs when solvent bonding networks are disrupted, compared with the stabilization generated by solute-solvent interactions. This problem refers to a series of aqueous solutions, which are dominated by hydrogen-bonding interactions.

When any alcohol dissolves in water, the hydrogen-bonding network of water is disrupted by the nonpolar hydrocarbon part of the alcohol. Counterbalancing these disruptions, hydrogen-bonding interactions are generated in the solution between the —OH groups of the alcohol and water molecules.

As the nonpolar region of an alcohol grows longer, more and more hydrogen bonds are disrupted by each solute molecule. At the same time, each alcohol listed has only one —OH group, so the amount of compensating solute-solvent hydrogen bonding is the same for all the alcohols.

This explains why longer-chain alcohols are progressively less soluble in water. As the hydrocarbon chain gets longer, more destabilization is involved in inserting the alcohol into the water matrix, so the alcohol becomes less soluble as the chain grows.

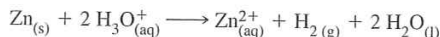
Solubility of Solids

Like dissolves like also describes the solubility properties of solids. There are four different kinds of solids: network, ionic, molecular, and metallic. Each is held together by a different kind of interaction, so each has its own solubility characteristics.

Network solids such as diamond, graphite, or silica cannot dissolve without breaking covalent chemical bonds. Because intermolecular forces of attraction are always much weaker than covalent bonds, solvent-solute interactions are never strong enough to offset the energy cost of breaking bonds. Covalent solids are insoluble in all solvents, but they may be attacked chemically by some liquids or vapors.

Metals also are difficult solids to dissolve because they contain extensive delocalized bonding networks that must be disrupted before the metal can dissolve.

When an alkali metal contacts water or when other metals such as Ca, Zn, or Fe are treated with aqueous acid, the metal *reacts* with the solution, producing hydrogen gas and a solution of the metal cation (for example, Na^+ and Ca^{2+}). This process differs from other solution processes in that the solute undergoes a chemical transformation. The aqueous medium dissolves the metal by a chemical reaction that converts it into soluble cations. Zinc metal, for example, reacts with hydrochloric acid to generate H_2 gas and Zn^{2+} cations in solution:



The solution produced when zinc reacts with hydrochloric acid is an aqueous solution of zinc ions, not a solution of zinc metal in water. If this solution is boiled to dryness, the remaining solid is ZnCl_2 , not zinc metal.

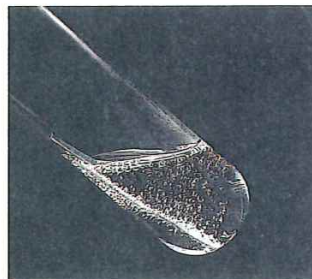
◀ Recall from Section 4.6 that strong acids generate hydronium ions in aqueous solution. The reaction of metals with acids is discussed in Section 4.7.

A few metals *react* with water, and several *react* with aqueous acids, but no metals will simply *dissolve* in water. Likewise, metals do not dissolve in nonpolar liquid solvents.

Metals are insoluble in common liquid solvents but can dissolve in each other (like dissolves like). A mixture of substances with metallic properties is called an **alloy**. Some alloys are solutions, and others are heterogeneous mixtures. Brass, for instance, is a homogeneous solution of copper (20% to 97%) and zinc (80% to 3%), but common plumber's solder is a heterogeneous alloy of lead (67%) and tin (33%). When solder is examined under a microscope, separate regions of solid lead and solid tin can be seen. When brass is examined, no such regions can be detected.

Mercury, the only metal that is a liquid at room temperature, dissolves a number of metals to give liquid solutions. Any solution of another metal dissolved in mercury is called an **amalgam**. Metals close to mercury in the periodic table, such as silver, gold, zinc, and tin, are particularly soluble in mercury. An amalgam of silver, tin, and mercury has been used widely to make dental fillings. When the intermetallic compound Ag_3Sn is ground with mercury, it forms a semisolid amalgam that can be shaped to fill a cavity. On standing, mercury reacts with the other metals to form a hard solid mixture of Ag_5Hg_8 and Sn_7Hg_8 . The mixture expands slightly during reaction, forming a tight fit within the cavity.

As described in Section 7.7, *ionic solids* contain cations and anions held in a three-dimensional lattice by strong coulombic attractions. Thus ionic solids do not dissolve unless considerable solvent-ion interactions exist to counterbalance the energy cost of breaking the ions free from the lattice. There are no ionic liquids at room temperature, so at first we might think there are no solvents suitable for ionic solids. Some ionic solids dissolve in water, however, because water is a *highly polar* liquid in which strong ion-dipole interactions exist between water molecules and ions in aqueous solution. Figure 10-39 illustrates the solvation of Na^+ and Cl^- ions as NaCl dissolves in water.



Zinc metal reacts with aqueous acids.

The mercury atoms in dental fillings are chemically bound and do not dissolve, so they are safe for the wearer, despite the fact that mercury is highly toxic. Dentists who mix the amalgams, however, may be at risk of mercury poisoning. New resin materials are replacing mercury amalgams as the material of choice for dental fillings.

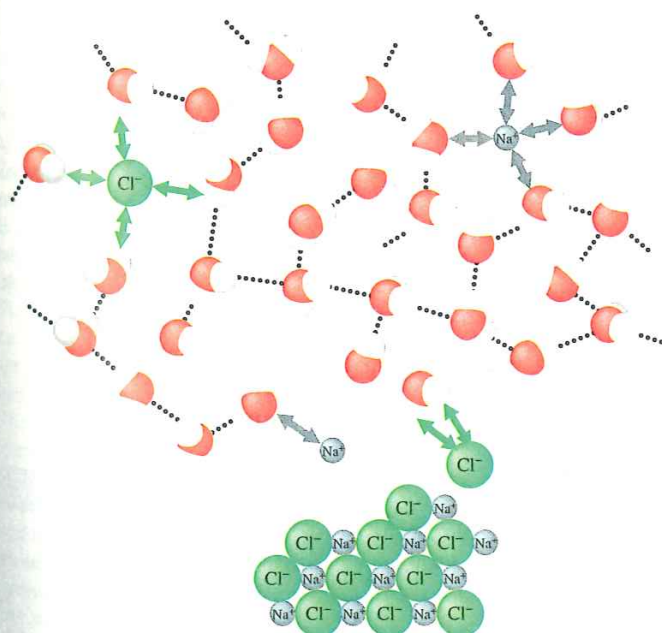
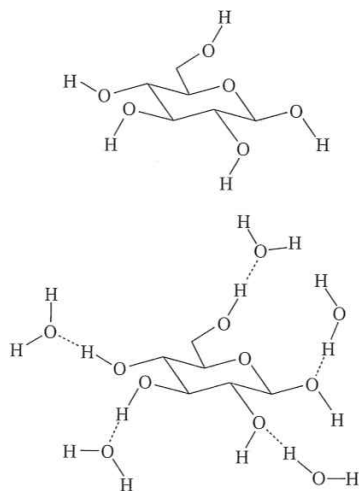


Figure 10-39

A molecular picture showing the ion-dipole interactions that help a solid ionic crystal dissolve in water. The arrows indicate ion-dipole interactions.

**Figure 10-40**

The line structure of glucose (top). All five polar O—H groups can form hydrogen bonds with water molecules (dotted lines, bottom).

► Glucose and other sugars are discussed in more detail in Section 11.5.

Recall that in assessing solubility, three sets of forces must be considered. Strong attractive cation-anion interactions in the ionic solid must be overcome; these impede solubility and make many ionic salts insoluble. Counterbalancing these are attractive forces between water dipoles and solute ions; these enhance solubility and help account for the existence of soluble salts. Hydrogen-bonding interactions in the solvent also have to be taken into account, but ions often are compact enough in size that their presence does not significantly alter the hydrogen-bonding network in water. Besides energetics, order-disorder considerations, which are discussed in Chapter 13, also play a major role in the solubility behavior of ionic solids.

The interplay among these several effects makes the prediction of ionic salt solubility complicated. As a simplifying generalization, the solubility guidelines presented in Chapter 4 categorize ionic solids as soluble or insoluble. For soluble salts the stabilization resulting from ion-dipole interactions compares favorably with the coulombic forces of the ionic solid. For insoluble salts, ion-dipole interactions provide too little stabilization to overcome the forces that hold the ions in the solid lattice.

Molecular solids are held together by dispersion forces, dipole forces, and sometimes, hydrogen bonds. Such solids dissolve readily in solvents with similar types of intermolecular forces. Nonpolar iodine, for instance, is soluble in nonpolar liquids such as carbon tetrachloride (CCl_4). Many organic compounds are molecular solids that dissolve in organic liquids such as cyclohexane and acetone.

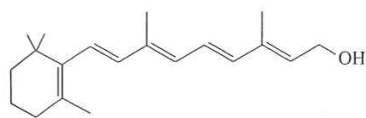
Hydrogen bonding in the aqueous environment allows water to dissolve materials that can form hydrogen bonds. Hydrogen bonding makes sugars such as sucrose and glucose very soluble in water. Glucose, whose structure is shown in Figure 10-40, is an organic molecule with five polar O—H groups, each of which forms hydrogen bonds with water molecules. Thus glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) is quite soluble in water, whereas naphthalene, a solid hydrocarbon limited to dispersion forces, is nearly insoluble in water.

The best solvent for a molecular solid is one whose intermolecular forces match the forces holding the molecules in the crystal. For a solid held together by dispersion forces, good solvents are nonpolar liquids such as CCl_4 and C_6H_{12} . For polar solids a polar solvent such as acetone works well. The best solvent for ionic salts is water. This does not mean, however, that *every* polar solid dissolves in acetone or that *every* ionic salt dissolves in water. A substance dissolves when the balance of coulombic forces favors solubility. We can predict that the balance will be *unfavorable* for a salt in a nonpolar solvent or a nonpolar organic molecule in water, but there is no foolproof method for predicting a *favorable* balance for potentially favorable cases. Solubility guidelines are only guidelines, and they are highly empirical. Sample Problem 10-8 provides some practice in recognizing solubility types. Box 10-2 describes chromatography, a separation technique that exploits solubility differences.

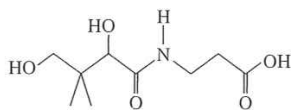
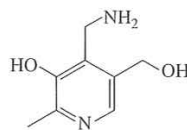
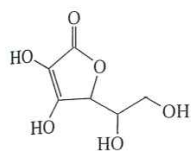
Sample Problem 10-8

Solubilities of Vitamins

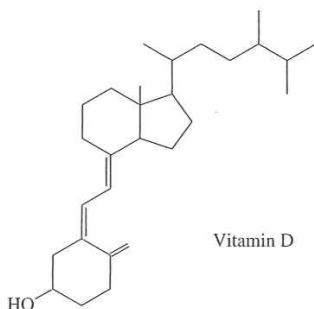
Vitamins, organic molecules required by the body for proper function but not synthesized by the body, must be present in the foods people eat. Vitamins can be grouped into two categories: fat soluble, which dissolve in fatty hydrocarbon-like tissues, and water soluble. The structures of several vitamins follow. Assign each one to the appropriate category.



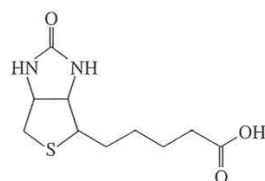
Vitamin A

Pantothenic acid
(Vitamin B₅)Pyridoxamine
(Vitamin B₆)

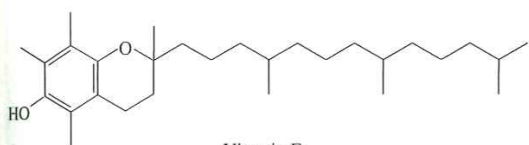
Vitamin C



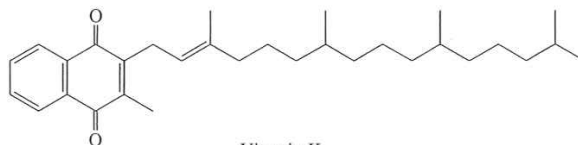
Vitamin D



Biotin



Vitamin E



Vitamin K

Method: At first glance, it may seem that the like-dissolves-like guideline does not apply here. Certainly, none of these complex molecules look like water, and the resemblance to simple hydrocarbons such as cyclohexane is also remote. Keep in mind, however, that the basis for the like-dissolves-like principle is that similar compounds dissolve in each other because they have *common patterns* of intermolecular interactions. Sample Problem 10-7 indicates that alcohols with large nonpolar segments do not dissolve well in water. We can categorize vitamins similarly by the amount of the structure that can be stabilized by hydrogen bonding to water molecules.

A hydrogen-bond donor must have a hydrogen atom bonded to F, O, or N, and a hydrogen-bond acceptor is an electronegative atom with a lone pair of electrons. By these criteria, all the vitamins shown are capable of some hydrogen bonding. However, vitamins A, D, E, and K have large regions containing only nonpolar C—C and C—H bonds. Like the longer alcohols, these molecules have too few hydrogen-bonding sites for them to be soluble in water. As a result, these are fat-soluble vitamins.

The four remaining molecules, vitamin C, biotin, pantothenic acid, and pyridoxamine, have a comparatively large number of O—H and N—H groups. These groups make these vitamins strong hydrogen bonders, so they are all water soluble. (In fact, all the B vitamins are soluble in water.)

The different solubilities of these two kinds of vitamins have important metabolic consequences. Fat-soluble vitamins can be stored in fatty body tissue for a long time because they do not dissolve in aqueous body fluids. As a result, too much of a fat-soluble vitamin can overload the storage capabilities and lead to a toxic reaction. Water-soluble vitamins, on the other hand, cannot be stored, and the body excretes anything more than the amount it can use immediately. People must therefore have a regular supply of water-soluble vitamins in their diets to remain healthy.

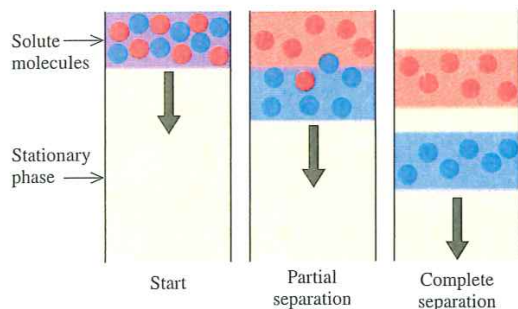
Box 10-2

Chromatography

One of the day-to-day operations that takes place in a laboratory is the separation and purification of chemical substances. Synthesis reactions often produce mixtures of two or more products; biomolecules must be extracted from their natural sources; confiscated substances must be purified and identified by criminologists. Among the various techniques for the purification of chemical compounds, none is as versatile or powerful as **chromatography**. The earliest work in chromatography was the separation of colored plant materials, leading to the name of the technique (which means "color writing").

There are many types of chromatography, but all are based on the same principles. A *mobile phase* carries the compounds to be separated, and an insoluble *stationary phase* binds these compounds through intermolecular forces.

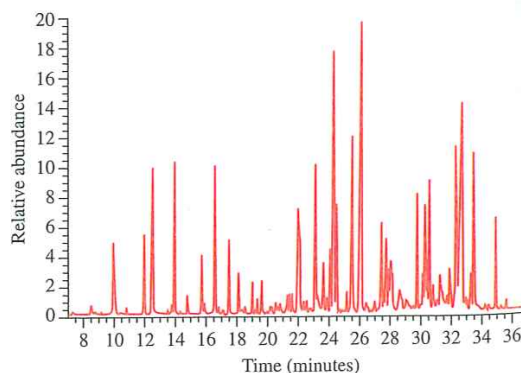
The figure below shows how chromatography separates compounds. The mobile phase dissolves the compounds of interest and carries them over the stationary phase. The rate of movement of compounds depends on how strongly they interact with the stationary phase. Because solutes move only when in the mobile phase, molecules that have a very low affinity for the stationary phase (shown in the figure as *blue circles*) move quickly, whereas those that bind more tightly to the stationary phase (shown in the figure as *red circles*) lag behind. After the materials have traveled a sufficient distance, they become separated into distinct "bands"; each band may contain one pure material. As the mobile phase comes off the lower end of the column, it can be collected in small volumes called *fractions* or *cuts*. When the separations are complete, the various components of the original mixture are found in different fractions.



Chromatography is extremely versatile because the stationary phase and the mobile phase can be varied to match the types of compounds that need to be separated. For example, some stationary phases separate solutes according to their polarity. Polar groups on the stationary phase bind solutes through dipole-dipole or hydrogen-bonding interactions. The binding is reversible, and eventually the solvent washes the solutes off the stationary phase. The more polar the solute, the tighter it binds to the stationary phase. Thus the faster the solutes move through the column, the lower their polarity.

Size-exclusion chromatography uses a stationary phase made up of particles that are perforated with holes or channels, much like a sponge. Large molecules cannot enter the channels, so they move quickly around the particles and through the column. Small molecules can move in and out of the channels, so they travel a more tortuous path and take longer to pass through the column. Thus the largest solute molecules emerge from the chromatography column first, and the smallest molecules emerge last. Pore size in these stationary phases can be controlled to accommodate an enormous range of molecular sizes, from mixtures of small gas molecules to huge biomolecules with molar masses in excess of 100,000 g/mol.

Chromatographic techniques are classified according to the nature of their mobile and stationary phases. Gas chromatography (GC) is used to separate mixtures of gases or volatile liquids. The mixture to be separated is vaporized in an oven, and the gaseous mobile phase passes through a long, narrow column packed with a finely divided solid that may be impregnated with a nonvolatile liquid (stationary phase). As the components of the mixture emerge from the column, their presence is sensed by a detector and displayed as a graph on a computer screen (see graph).



Box 10-2

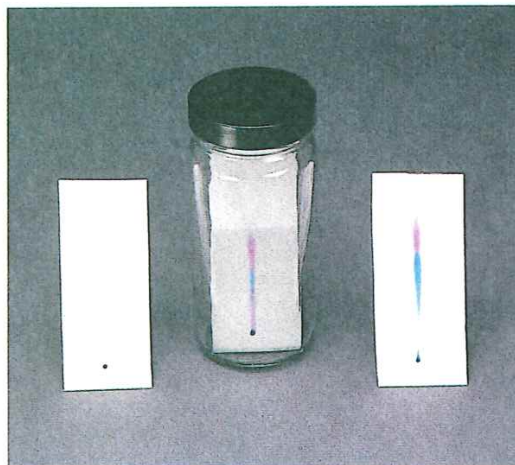
Chromatography — cont'd

The most widespread use of GC is in identifying trace components of a mixture. Among other things, GC is used to test urine for the presence of illegal drugs, identify pollutants and measure their concentrations in groundwater, assay the purity of a volatile compound isolated in the laboratory, and follow the progress of a chemical reaction by monitoring the disappearance of starting materials or the appearance of products.

Liquid chromatography (LC) uses a liquid mobile phase that passes down the stationary phase of a finely divided solid. This technique is widely used to purify chemical substances on a multigram scale.

In thin-layer chromatography (TLC) a minute amount of a mixture is placed as a small spot at the bottom of a plate coated with a thin layer of a solid stationary phase, usually SiO_2 or Al_2O_3 . The plate is placed, with the "spotted" end down, in a chamber containing a small amount of a suitable liquid solvent that acts as the mobile phase. Intermolecular forces carry the solvent and the mixture up the plate, and the dissolved solutes spread out according to their polarity. The plate is removed from the chamber when the solvent nears the top. The plate dries as the solvent evaporates, leaving the nonvolatile components of the mixture as spots located at different positions on the plate.

The TLC shown below reveals that a common blue ink is a mixture of several different colored compounds. TLC is often used to monitor the progress of chemical reactions. It is also used to determine the optimal separation conditions for larger-scale chromatographic techniques such as LC.



Section Exercises

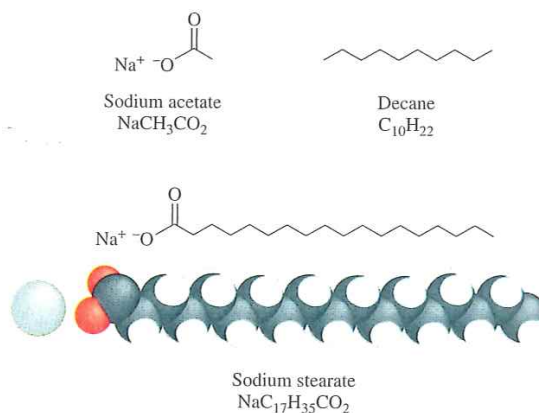
- 10.5.1 Explain in terms of attractive forces why salts containing Zn^{2+} ions are soluble in water but Zn metal is insoluble.
- 10.5.2 List the types of intermolecular interactions that stabilize a solution of acetone in methanol, and draw molecular pictures that illustrate any dipole-dipole and hydrogen-bonding interactions that exist between these substances.
- 10.5.3 On the basis of their molecular structures, predict which of the following silicon-containing materials are water soluble: elemental Si, SiO_2 , Na_4SiO_4 , and $\text{Si}(\text{CH}_3)_4$.

10.6 DUAL-NATURE MOLECULES: SURFACTANTS AND BIOLOGICAL MEMBRANES

Substances that do not dissolve in water, such as organic fats and oils, are called **hydrophobic**. Substances that are miscible with water, such as the organic but hydrogen-bonding molecules methanol and acetone, are called **hydrophilic**. Some molecules contain both hydrophilic and hydrophobic regions. Such a dual-nature molecule may have a polar or ionic "head" that is compatible with water and a

Figure 10-41

Sodium stearate is a typical dual-nature molecule. It has a hydrophilic polar head that resembles sodium acetate and a hydrophobic nonpolar tail that is a hydrocarbon similar to decane.



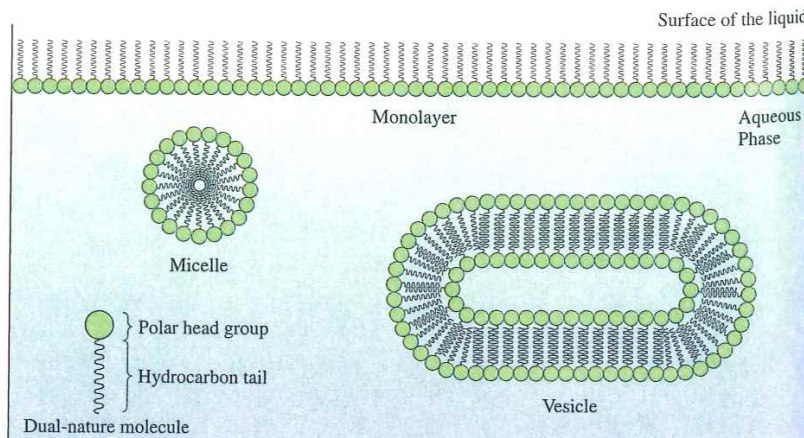
long hydrocarbon “tail” that is incompatible with water. Sodium stearate, whose structure is shown in Figure 10-41, is a dual-nature molecule. The head of the stearate anion resembles the water-soluble acetate anion, and the tail is a hydrocarbon chain containing 17 carbon atoms.

Dual-nature molecules such as sodium stearate can form three different structures when they are placed in water (Figure 10-42). They may form a molecular **monolayer** on the surface, in which the polar head groups are immersed in the water while the nonpolar tails are aggregated together on the surface. Agitating the solution may cause the molecules to arrange into spherical aggregates called **micelles**, in which the hydrophobic tails point inward and the polar heads lie on the outside of the structure, where they interact with the aqueous solvent. Dual-nature molecules may also form enclosed bilayers, called **vesicles**, which have two parallel rows of molecules oriented so that their hydrocarbon tails are clustered.

All these arrangements obey the principle of like dissolving like. The hydrocarbon tails aggregate through dispersion forces because they are incompatible with the aqueous medium. The hydrogen-bonding network of the solvent would be disrupted by incorporating these tails into the solution. The polar heads, on the other hand, interact strongly with water to maximize hydrogen bonding and ion-dipole interactions.

Figure 10-42

Cross-sectional molecular views of the structures that can form when dual-nature molecules are placed in water. The molecules may form a monolayer at the surface, spherical clusters called **micelles**, or bilayer structures called **vesicles**. In all three structures the hydrocarbon tails cluster together to minimize their interactions with water molecules, and the polar head groups are positioned to maximize their interactions with water molecules.



Surfactants

Dual-nature molecules are widely used in industrial chemistry to modify the behavior of aqueous solutions. In this context they are called **surfactants**. Common surfactant head groups include carboxylate ($-\text{CO}_2^-$), sulfonate ($-\text{SO}_3^-$), sulfate ($-\text{OSO}_3^-$), and ammonium ($-\text{NH}_3^+$). The negative charge of an anionic head group usually is neutralized by Na^+ , and the positive charge of ammonium usually is neutralized by Cl^- . These counterions are used because they are nontoxic and their salts are highly soluble.

The most commonly known dual-nature molecules are soaps and detergents. Clothing becomes soiled by a wide variety of substances; some are water soluble, and others are not. A soap or detergent removes water-insoluble grease (for example, butter, fat, and oil) from the clothing surface. Dispersion forces stabilize the attachment of grease particles to the hydrocarbon tails of surfactant molecules, which form aggregates. Agitation removes these aggregates from the fabric, suspending them in solution as a large number of tiny micelles with grease particles trapped inside. The micelles do not redeposit on the fabric because their hydrophilic heads hold them in solution. When water is drained from the washing machine, the grease-containing micelles are swept away, leaving clean clothes behind.

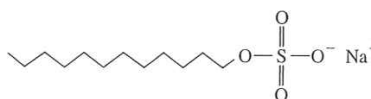
Soaps are derived from natural sources such as animal fats that contain stearic acid and other long-chain organic acids. These carboxylate surfactants form insoluble salts with Ca^{2+} and Mg^{2+} . In regions where water is "hard," these soaps precipitate calcium and magnesium stearate as a "scum" that inhibits cleansing action and is responsible for bathtub rings. Detergents such as sodium lauryl sulfate, on the other hand, are "synthetic" compounds, originally prepared in the laboratory, that contain sulfonate and sulfate head groups. These groups do not form precipitates with divalent cations, but they have a tendency to lather and foam. Foaming is a disadvantage in washing machines but is considered to be an advantage in hair shampoos. The cleaning action of soaps and detergents is similar, but detergents have largely replaced soaps because of their superior behavior in hard water.

Surfactants are used in such a wide variety of ways that billions of dollars are spent on them every year. They appear in many household products, including cleansing agents and shampoos (recall the chapter introduction). Some surfactants are used as emulsifiers in processed foods such as bottled salad dressing. An emulsifier causes normally incompatible liquids such as the oil and water in salad dressing to disperse in each other. Emulsifiers act by forming molecular connections between the liquids: Their hydrophobic tails interact with oil molecules, and their hydrophilic heads interact with water molecules.

Gasoline contains surfactants designed to prevent the accumulation of high-boiling compounds on the surfaces of engine fuel injectors. These deposits interfere with the flow of air and cause rough idling and poor gas mileage. In this case the hydrophilic polar ends interact strongly with the solid metal surface, and the hydrophobic ends are compatible with liquid gasoline. The polar ends adhere to the metal walls of the injection system while their tails extend into the fuel mixture. This creates a thin, nonpolar film that protects the surface from gummy deposits. These same films help prevent the formation of rust by screening the metal surface from water molecules.

Figure 10-43 illustrates that surfactants also decrease the surface tension of water. In the figure, the drop of water that contains a surfactant is flattened and deformed, giving it a larger surface area than the drop of water that contains no surfactant. Surfactant molecules reduce surface tension by forming a monolayer on the aqueous surface. Unlike water molecules at the surface, this monolayer does not experience an attractive force drawing molecules back into the bulk of the liquid. The reduction in surface tension leaves gravity free to "flatten" the drop.

Soap made by boiling animal fat in an alkaline solution obtained from ashes has been known since the time of the ancient Sumerians, 2500 BC.



Sodium lauryl sulfate (common ingredient in shampoo).

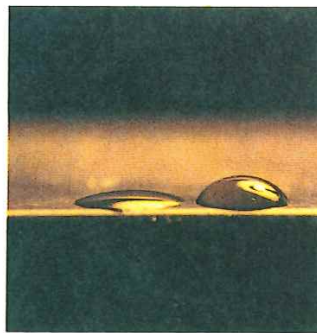


Figure 10-43

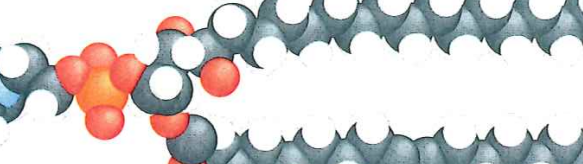
Surfactants reduce surface tension by forming a monolayer at the water-air interface. The water droplet on the left contains a surfactant, making its surface tension lower and causing it to flatten and spread out.

Chemists and engineers in the petroleum industry are studying ways to use surfactants to increase the amount of oil that can be recovered from wells. The goal is to develop inexpensive, environmentally safe surfactants that can be mixed with water and injected into existing oil wells. The surfactant will promote formation of an oil-water emulsion that has a lower viscosity than oil and should be easier to extract from the well.

This is just a sampling of the industrial applications of these versatile materials. A host of other industries use surfactants in significant amounts. Examples include pharmaceuticals, paper, mining, petroleum, tanning, photography, electroplating, and adhesives.

Diagram illustrating the structure of a phospholipid molecule, showing the Hydrophilic head and the Hydrophobic tail.

The Hydrophilic head consists of a phosphate group (P) bonded to a trimethylammonium group ($(\text{H}_3\text{C})_3\text{N}^+$) and a glycerol backbone. The Hydrophobic tail consists of two fatty acid chains: one saturated and one monounsaturated.



Cell Membranes

It may seem like a huge conceptual leap from industrial surfactants to biological cell membranes, but the same principles apply to both sets of substances.

Every biological cell is surrounded by a membrane only a few molecules thick. Among the major components of membranes are molecules called *phospholipids*, which are dual-nature molecules. Although their chemical structures are more complex than simple surfactants such as sodium stearate, phospholipids nevertheless have hydrophilic heads and hydrophobic tails. Figure 10-44 shows the structure of one membrane phospholipid, lecithin. The hydrophilic end of lecithin has a cationic $\text{N}(\text{CH}_3)_3^+$ group and eight oxygen atoms with nonbonding pairs of electrons, all of which form hydrogen bonds with water molecules. The hydrophobic portion of lecithin consists of two hydrocarbon tails.

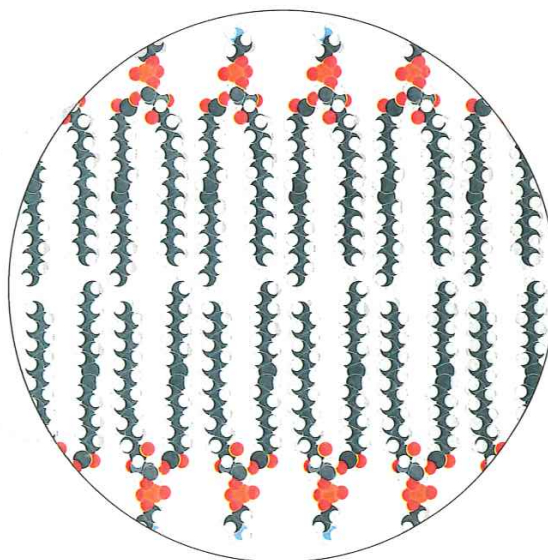
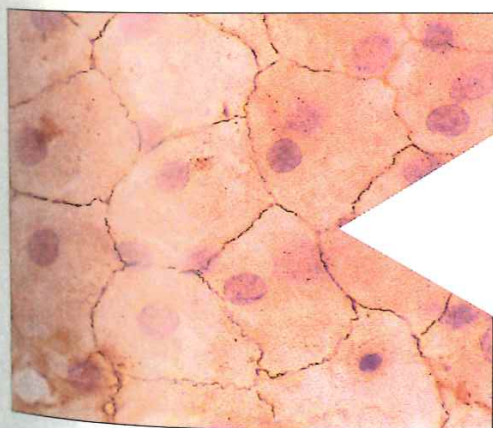
Phospholipids form bilayers in aqueous media. The molecules form two approximately parallel rows with tails aligned on the inside and heads toward the outside, in contact with the solution. This arrangement, shown in Figure 10-45, is analogous to the vesicles in Figure 10-42. The bilayer forms a closed sac that contains the aqueous cytoplasm and all the cellular components. Thus a cell can be viewed as a large and complex vesicle.

One purpose of a cellular lipid bilayer is to control which molecules pass into and out of the cell. Uncharged small molecules such as water, ammonia, and oxygen can diffuse through the membrane. Hydrophobic molecules such as hydrocarbons can also pass through because they are soluble in the overlapping tails that make up the interior of the bilayer. Ions and water-soluble polar molecules such as glucose and urea, on the other hand, cannot get through the membrane.

For cells to carry out their functions, glucose and other nutrients must be brought in, and urea and other waste products must be expelled. This would be an impossible task if cell membranes were composed only of phospholipids. Specific

Figure 10-45

A lipid bilayer contains two layers of dual-nature molecules arranged tail to tail. The polar head groups face outward and are stabilized by dipolar and hydrogen-bonding interactions with water molecules.



Phase Equilibria

The freezing point of pure water is 0°C at a pressure of 1 atm. Below this temperature, liquid water freezes to solid ice; above 0°C , ice melts to give liquid water. At exactly 0°C , solid ice and liquid water can coexist indefinitely in a state of dynamic equilibrium.

The molecular view shown in Figure 10-47, A, reveals that two processes occur in a mixture of ice and water at 0°C . First, liquid water molecules that collide with the ice crystals sometimes are captured and added to the solid phase. At the same time, molecules on the surface of the ice crystals sometimes become detached and enter the surrounding liquid. A state of dynamic equilibrium is reached when equal numbers of molecules move in each direction in any given time. Then there is no net change, even though individual molecules continue to move back and forth between the phases. One proof of this molecular movement comes from radioactivity studies. If radioactive ice is placed in nonradioactive water at 0°C , the water slowly becomes radioactive because of the transfer of radioactive water molecules between phases.

The ice-water equilibrium exists only at 0°C (when the pressure is 1 atm). Lowering the temperature decreases the rate at which molecules escape from the surface of the ice, and the liquid freezes. Raising the temperature increases the rate of escape, and the solid melts.

A similar dynamic equilibrium exists between liquid water and water vapor. When the pressure exerted on the liquid is 1 atm, the temperature at which liquid water is in equilibrium with gaseous water is 100°C (Figure 10-47, B). Some molecules at the liquid surface have sufficient energy to escape into the gas phase, and some molecules in the gas phase are captured when they strike the liquid surface. Under conditions of dynamic equilibrium, equal numbers of molecules move in each direction at any given time. This equilibrium exists only at 100°C (when the pressure is 1 atm). Lowering the temperature reduces the rate at which molecules escape from the liquid phase, and condensation occurs. Raising the temperature increases the rate of escape from the liquid phase, and the liquid boils.

These two equilibria provide the basis for precise definitions of the normal freezing point and the normal boiling point. The **normal freezing point (*fp*)** of a substance is the temperature at which solid and liquid coexist at equilibrium under a pressure of 1 atm. The **normal boiling point (*bp*)** of a liquid is the temperature at which liquid and vapor coexist at equilibrium under a pressure of 1 atm.

Tritium (T) is a radioactive isotope of hydrogen. Radioactive ice can be made by including some molecules of T_2O in a sample of water as it is frozen. Tritium is introduced in Chapter 2, and radioactivity is discussed in Chapter 20.

When water boils in an open container, the steam diffuses into the surrounding atmosphere, leading to a continual escape of molecules. Consequently, the liquid-vapor equilibrium can be observed only when the gas is confined to a closed space.

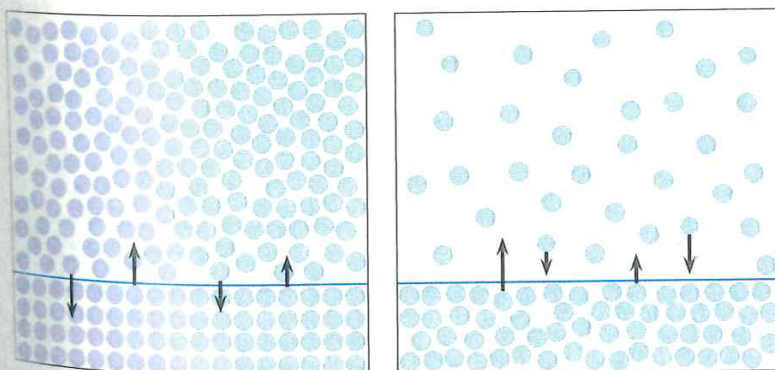


Figure 10-47

Molecular views of the dynamic equilibria between pure phases. A, The equilibrium between liquid and solid. B, The equilibrium between liquid and gas. At the equilibrium temperature, the rate of escape of molecules from the liquid phase equals the rate of capture by the liquid phase. For clarity, the motions of molecules confined within a phase have not been shown, but remember that all molecules are constantly in motion.

Effect of Solutes

Four common properties of solutions, known as **colligative properties**, are modified by the presence of solute molecules. They are freezing point, boiling point, vapor pressure, and osmotic pressure.

The molecular view of freezing and boiling can be used to show how dissolved substances influence melting points and boiling points. In a solution, solute molecules replace some of the solvent molecules, so a given volume of a solution contains a smaller number of solvent molecules than the same volume of pure solvent. Consequently, the presence of solute molecules reduces the rate at which solvent molecules leave the liquid phase. Figure 10-48 shows how this affects a liquid-solid equilibrium: Changing one rate without changing the other rate throws the dynamic equilibrium out of balance.

The addition of solutes *decreases* the freezing point of a solution. In the solution, solvent molecules collide with crystals of solid solvent less frequently than they do in the pure solvent. Consequently, fewer molecules are captured by the solid phase than escape from the solid to the liquid. Cooling the solution restores dynamic equilibrium because it simultaneously reduces the number of molecules that have sufficient energy to break away from the surface of the solid and increases the number of molecules in the liquid with low enough kinetic energy to be captured by the solid.

Experiments show that at low solute concentration the change in freezing point of a solution, ΔT_f , depends on the concentration of the solution:

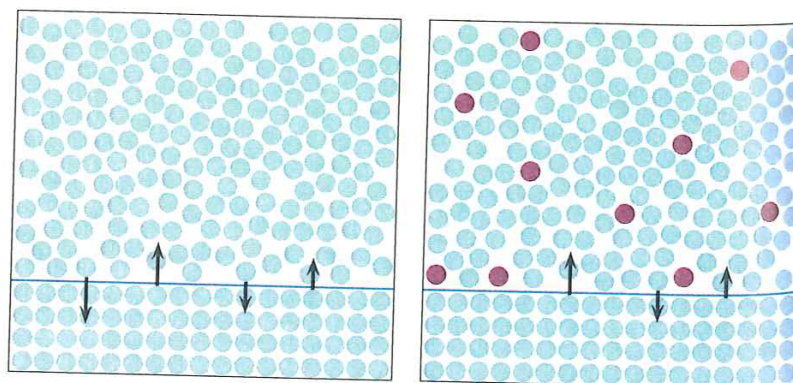
$$\Delta T_f = K_f c_m \quad (10-2)$$

Here, c_m is a new concentration measure, the **molality**, which is defined to be the number of moles of solute divided by the mass of solvent in kilograms. This way of expressing concentration is preferred to molarity (moles of solute divided by volume of solution in liters) because molality, unlike molarity, is independent of temperature. The constant K_f is called the **freezing point depression constant**. The constant is different for different *solvents* but does not depend on the identity of the *solutes*. For water, K_f is 1.858 °C kg/mol. Sample Problem 10-9 illustrates the use of Equation 10-2.

Equation 10-2 can be derived from our simple molecular picture and kinetic molecular theory. The derivation is independent of the nature of solute and solvent, so Equation 10-2 is valid for other solvents besides water, except that K_f has a different value for each solvent.

Figure 10-48

Molecular views of the rates of solid-liquid phase transfer of a pure liquid and a solution at the normal freezing point. The addition of solute does not change the rate of escape from the solid, but it decreases the rate at which the solid captures solvent molecules from the solution. This disrupts the dynamic equilibrium between escape and capture.



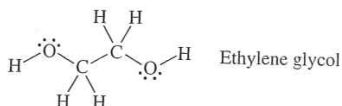
Dynamic equilibrium:
Two solid molecules escape,
two liquid molecules are captured

Solute disrupts equilibrium:
Two solid molecules escape,
one liquid molecule is captured

Sample Problem 10-9

Freezing Point Depression

Ethylene glycol (1,2-ethanediol) is added to automobile radiators to prevent cooling water from freezing. Estimate the freezing point of radiator coolant that contains 2.00 kg of ethylene glycol and 5.00 L of water.



Method: The question asks for the freezing point of a solution. The phrase *to prevent the water from freezing* reveals that we are dealing with the depression of the freezing point of water. Equation 10-2 describes this process for a dilute solution: $\Delta T_f = K_f c_m$. A coolant solution is quite concentrated, so we do not expect the equation to apply exactly, but we can use it to obtain an estimate of the freezing point.

The freezing point depression constant for water is known from experiments and can be found in tables: $K_f = 1.858\text{ }^\circ\text{C kg/mol}$. To calculate the freezing point, we must first determine the molality of the solute in this solution.

Molality is the moles of solute divided by the mass of solvent in kilograms. The number of moles of solute is found from the mole-mass relationship, and the mass of solvent can be found from the density of water. The molar mass (*MM*) of ethylene glycol is obtained from its chemical formula, $\text{C}_2\text{H}_6\text{O}_2$: $MM = 62.07\text{ g/mol}$. Now we find the number of moles:

$$n_{\text{C}_2\text{H}_6\text{O}_2} = \frac{(2.00\text{ kg})(10^3\text{ g/kg})}{62.07\text{ g/mol}} = 32.2\text{ mol}$$

We find the mass of water from its density, $\rho = 1.00\text{ g/mL}$, and then convert to kg:

$$m_{\text{water}} = \rho V = (1.00\text{ g/mL})(5.00\text{ L})(10^3\text{ mL/L})(10^{-3}\text{ kg/g}) = 5.00\text{ kg}$$

$$c_m = \frac{32.2\text{ mol}}{5.00\text{ kg}} = 6.44\text{ mol/kg}$$

Substitute into Equation 10-2 to estimate the difference between the freezing point of the solution and that of pure water:

$$\Delta T_f = K_f c_m = (1.858\text{ }^\circ\text{C kg/mol})(6.44\text{ mol/kg}) = 12\text{ }^\circ\text{C}$$

This is the amount by which the freezing point of the solution *differs* from that of pure water. Because the freezing point of water is $0\text{ }^\circ\text{C}$ and freezing points are depressed by adding solutes, the new freezing point is below $0\text{ }^\circ\text{C}$: $T_f = -12\text{ }^\circ\text{C}$.

The effect of a solute on the boiling point of a solution is opposite to its effect on the freezing point. A boiling point is *increased* by adding a nonvolatile solute. This is because the solute reduces the rate of escape of solvent molecules into the gas phase. To get back to dynamic equilibrium, the solution must be heated so that more molecules acquire sufficient energy to escape from the liquid phase.

Molecular analysis and experimental studies show that the change in the boiling point of a solution obeys the same type of equation as the change in the freezing point:

$$\Delta T_b = K_b c_m \quad (10-3)$$

The result is rounded to two significant figures because the equation is not expected to be accurate at high molality.

A nonvolatile solute is one that has a negligible vapor pressure at the boiling point of the solution.

In Equation 10-3, ΔT_b is the elevation of the boiling point, c_m is the molality of the solute, and K_b is a constant called the **boiling point elevation constant**. The constant depends on the identity of the *solvent* but not on the identities of the non-volatile *solutes*. Thus there is a different boiling point elevation constant for every solvent; for water, $K_b = 0.512^\circ\text{C kg/mol}$. Equation 10-3 is used in the same way as Equation 10-2.

Osmosis

Water molecules can pass through cell membranes, but most solutes cannot. These are **semipermeable membranes**, and the movement of water through them is called **osmosis**.

If a semipermeable membrane separates two identical solutions, solvent molecules move in both directions at the same rate, and there is no net osmosis. The two sides of the membrane are at dynamic equilibrium. The situation changes when the solutions on the two sides of the membrane are different. Consider the membrane in Figure 10-49, which has pure water on one side and a solution of sugar in water on the other. The sugar molecules reduce the concentration of solvent molecules in the solution. Consequently, more solvent molecules pass through the membrane from the pure solvent to the solution than from the solution to the pure solvent. Now water flows from the pure-solvent side to the solution side, and there is a net rate of osmosis.

What can be done to increase the rate of solvent flow from the solution side of the membrane? An increase in pressure on the solution side accomplishes this because it increases the rate of transfer of water molecules from the solution side to the solvent side.

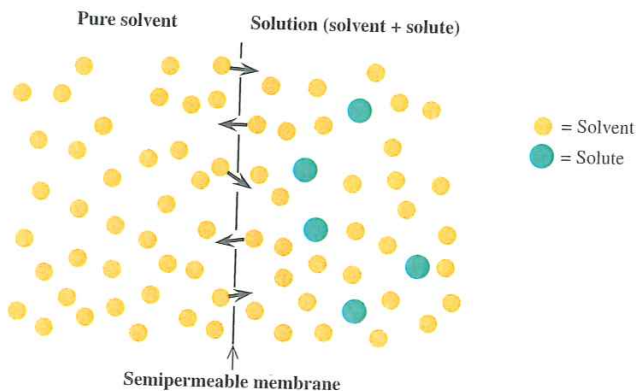
Figure 10-50 shows that increasing the pressure on the solution until the rate of solvent transfer is equal in both directions reestablishes dynamic equilibrium, and net osmosis falls to zero. The pressure increase needed to equalize the transfer rates is called the **osmotic pressure (Π)**. Osmotic pressure is a pressure *difference*. Pressure is exerted on both sides of a semipermeable membrane, and Π is the *extra pressure* that must be exerted on the solution to maintain dynamic equilibrium.

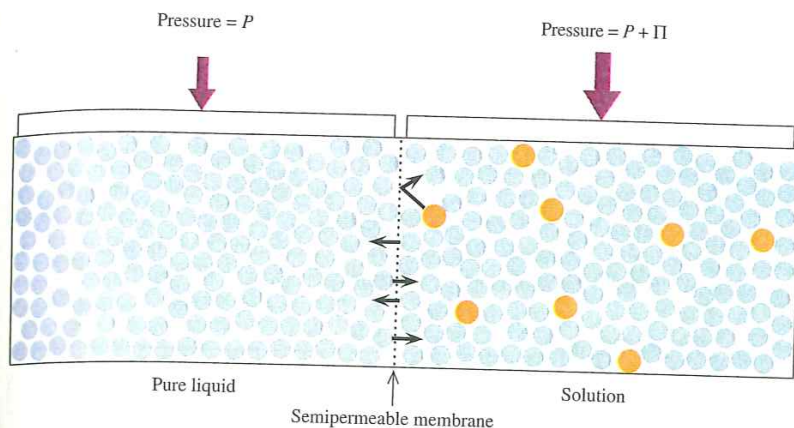
Like freezing point depression and boiling point elevation, osmotic pressure is proportional to the concentration of solute molecules. Experiments show that osmotic pressure is proportional to both concentration (expressed as molarity, M) and temperature:

$$\Pi = MRT \quad (10-4)$$

Figure 10-49

Small solvent molecules can pass back and forth freely through the pores of a semipermeable membrane, but solute molecules cannot. The presence of solute molecules in a solution reduces the concentration of solvent molecules, and this in turn reduces the rate at which solvent molecules pass out of the solution. There is an imbalance in transfer rates, which leads to osmosis.



**Figure 10-50**

To equalize the rates of transfer of solvent molecules from a solution and from pure solvent, an additional osmotic pressure (Π) must be exerted on the solution.

In Equation 10-4, M is the total molarity of all solutes, T is the temperature in kelvins, and R is the gas constant. If osmotic pressure is expressed in atmospheres, the fact that molarity is in moles per liter requires us to use $R = 0.08206 \text{ L atm/mol K}$.

Osmotic pressure effects can be substantial. For example, the waters of the oceans contain dissolved salts at a total ionic molarity of about 1.13 M. The osmotic pressure of ocean water can be calculated:

$$\Pi = MRT = (1.13 \text{ mol/L})(0.08206 \text{ L atm/mol K})(298 \text{ K}) = 27.6 \text{ atm}$$

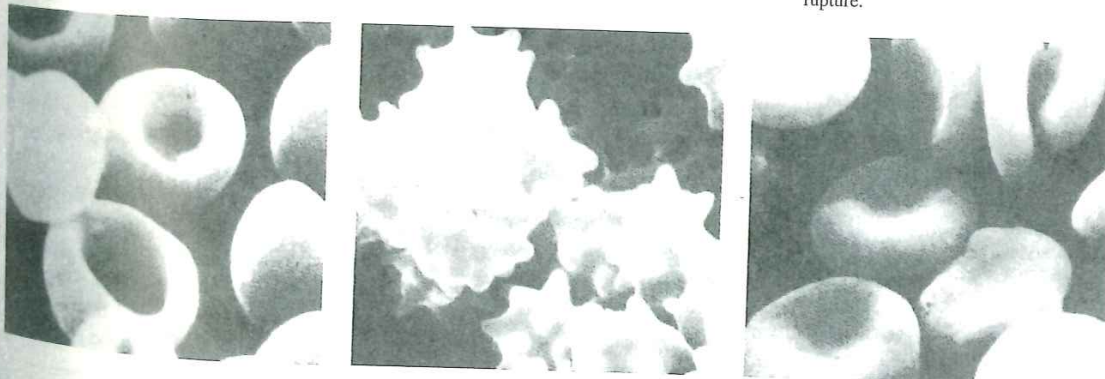
This means that if samples of pure water and ocean water were placed on opposite sides of a semipermeable membrane, an external pressure of 27.6 atm would have to be applied to the ocean water side to prevent osmosis. The osmotic pressure of ocean water is *more than 25 times atmospheric pressure*. By comparison, the freezing point of ocean water is depressed by only about 1% from the freezing point of pure water, from 273 K to about 271 K (-2°C).

Osmotic pressure plays a key role in biological chemistry because the cells of the human body are encased in semipermeable membranes and bathed in body fluids. Under normal physiological conditions the body fluid outside the cells has the same total solute molarity as the fluid inside the cells, and there is no *net* osmosis across cell membranes. Solutions with the same solute molarity are called *isotonic* solutions.

The situation changes if a molarity imbalance is created. Figure 10-51 shows red blood cells immersed in solutions of different molarities. When the fluid outside the cell is at *higher* solute molarity, transport of water across the membrane into the

Figure 10-51

When bathed in isotonic solution (*left*), red blood cells retain their normal shape because there is no net osmosis across their membranes. In a solution at higher concentration (*center*), the osmotic flow removes water from the cell interior, causing cells to shrink and wrinkle. In a solution at lower concentration (*right*), the net osmotic flow pumps water into cells, expanding them until they may rupture.



cell slows. The net result is that water leaves the cell, causing it to shrink. When the fluid outside the cell is at *lower* molarity, movement of water into the cell increases. The extra water in the cell causes an increase in internal pressure. Eventually, the internal pressure of the cell matches the osmotic pressure, and water transport reaches dynamic equilibrium. Unfortunately, osmotic pressures are so large that cells can burst under the increased pressure before they reach equilibrium.

Red blood cells are particularly susceptible to these potentially damaging concentration changes because they are suspended in the aqueous medium of the blood. Consequently, solutions used for intravenous feeding must be isotonic. Sample Problem 10-10 deals with isotonic solutions.

Sample Problem 10-10

Isotonic Solutions

Isotonic intravenous solutions contain 49 g/L of glucose ($C_6H_{12}O_6$). What is the osmotic pressure of blood?

Method: Isotonic solutions, by definition, exert equal osmotic pressures. Therefore Π for blood is the same as Π for the glucose solution. We can calculate Π from Equation 10-4 after converting the concentration into moles per liter:

$$\Pi = MRT \quad \text{and} \quad M = \text{mol/L} = \frac{m/MM}{L}$$

From the formula of glucose, $MM = 180 \text{ g/mol}$. Substitute to find the molarity of the glucose solution:

$$M = \frac{(49 \text{ g})}{(180 \text{ g/mol})(1 \text{ L})} = 0.272 \text{ mol/L}$$

Because the question asks about blood in the human body, T is human body temperature, which is 37°C .

$$T = 37 + 273 = 310 \text{ K} \quad R = 0.08206 \text{ L atm/mol K}$$

$$\Pi = (0.272 \text{ mol/L})(0.08206 \text{ L atm/mol K})(310 \text{ K}) = 6.9 \text{ atm}$$

The result is rounded to two significant figures to match the initial data (49 g/L).

If a sample of red blood cells is added to pure water, osmosis carries water into the cells. This process would continue until the internal pressure of the cell was 6.9 atm higher than the pressure on the outside of the cell. However, 6.9 atm is much more than the cell membrane can tolerate. Consequently, red blood cells burst when immersed in pure water.

When the additional pressure applied to a solution is less than the osmotic pressure, solvent molecules flow from pure solvent into the solution. When the additional pressure equals the osmotic pressure, equilibrium is established, and there is no net flow of solvent molecules. What if we apply an additional pressure that is *greater* than the osmotic pressure? Now the pressure on the solution is sufficient to drive solvent molecules from the solution into the pure solvent. Osmosis now transfers solvent in the opposite direction; **reverse osmosis** occurs.

Reverse osmosis can be used to purify water, because the liquid passing through the semipermeable membrane is pure solvent. A reverse osmosis water purifier requires semipermeable membranes that do not rupture under the high pressures required for reverse osmosis. This presents formidable engineering difficulties. Recall that seawater has an osmotic pressure of nearly 28 atm and that red blood cells rupture by 7 atm. Nevertheless, in recent years, membranes have been developed that make it feasible to purify water using this technique.

Determination of Molar Mass

The magnitude of osmotic pressure is large enough that measurements of Π provide a convenient way to determine the molar mass of a compound. The osmotic pressure equation (Equation 10-4) can be solved for molar mass after molarity is expressed in terms of mass and molar mass:

$$\Pi = MRT \quad \Pi = \frac{mRT}{V(MM)}$$

A simple rearrangement gives an equation for calculating molar mass:

$$MM = \frac{mRT}{\Pi V} \quad (10-5)$$

For determination of the molar mass of an unknown compound, a measured mass of material is dissolved to give a measured volume of solution. The system is held at constant temperature, and the osmotic pressure is determined. Osmotic pressure measurements are particularly useful for determining the molar masses of large molecules such as polymers and biological materials, as Sample Problem 10-11 illustrates.

Sample Problem 10-11

Determining Molar Masses

A 25.00-mL aqueous solution containing 0.420 g of hemoglobin has an osmotic pressure of 4.6 torr at 27 °C. What is the molar mass of hemoglobin?

Method: Equation 10-5, which is used to calculate the molar mass by osmometry, is derived from the osmotic pressure expression, Equation 10-4.

All of the necessary data are given in the problem:

$$m_{\text{solute}} = 0.420 \text{ g} \quad R = 0.08206 \text{ L atm/mol K} \quad T = 27^\circ\text{C} + 273 = 300 \text{ K}$$

$$\Pi = (4.6 \text{ torr})(1 \text{ atm}/760 \text{ torr}) = 6.05 \times 10^{-3} \text{ atm}$$

$$V_{\text{solution}} = (25.00 \text{ mL})(1 \text{ L}/1000 \text{ mL}) = 2.500 \times 10^{-2} \text{ L}$$

$$MM = \frac{mRT}{\Pi V} = \frac{(0.420 \text{ g})(8.206 \times 10^{-2} \text{ L atm/mol K})(300 \text{ K})}{(6.05 \times 10^{-3} \text{ atm})(2.500 \times 10^{-2} \text{ L})}$$

$$MM = 6.8 \times 10^4 \text{ g/mol}$$

As in any calculation, be careful to express all data in appropriate units. The osmotic pressure was measured to two significant figures, so the result has two significant figures.

Section Exercises

- 10.7.1** A water-soluble protein molecule has a molar mass of 985 g/mol. Calculate the freezing point depression, boiling point elevation, and osmotic pressure at 27 °C of an aqueous solution containing 0.750 g/L of this protein. (Assume that the solution has a density of 1.000 g/mL.)
- 10.7.2** Redraw Figure 10-49 using arrows to represent water movement across the membrane during reverse osmosis.
- 10.7.3** In your own words, write a detailed, molecular-level description of how reverse osmosis can be used to desalinate seawater.

CHAPTER REVIEW

Chapter Summary

1. Attractive forces between molecules cause most substances to be liquids or solids under normal conditions, and they lead to nonideal behavior of gases at high pressure and low temperature. Real gases deviate from ideality because of intermolecular attractions and finite molecular sizes.
2. The molecules in liquids cohere but move freely. Liquid droplets tend to form spheres because of surface tension, and liquids resist flow to varying degrees.
3. The strengths of intermolecular interactions determine the boiling point of a substance. These interactions include dispersion, dipolar attraction, and hydrogen bonding. The latter, particularly important in aqueous environments, involves partial sharing of electrons between a fluorine, oxygen, or nitrogen atom and a hydrogen atom in a highly polar bond.
4. Solids are categorized according to the type of forces holding them together. Molecular solids have only dispersion forces, metallic solids have delocalized bonding, network solids have covalent bonding, and ionic solids have ion-ion interactions. Solid properties vary widely because of the variety of these forces.
5. Any crystalline solid is composed of a repeating pattern whose smallest complete part is a unit cell. The simplest of these repeat patterns, adopted by many atomic and metallic solids, are hexagonal close-packed, face-centered cubic, and body-centered cubic structures. Amorphous solids, such as glasses, lack a regular structure. Defects in crystals impart many useful properties.
6. A solution is a homogeneous mixture of varying amounts of solutes contained in a solvent. Substances that are subject to similar intermolecular forces tend to dissolve in each other, leading to the generalization "like dissolves like." Most liquid solutions have an upper limit on the amount of solute they can hold.
7. Surfactants, which are molecules that contain water-compatible and water-incompatible structures, form monolayers, micelles, and vesicles in aqueous media. Similar dual-nature molecules make up cell membranes.
8. Solute depresses the freezing point, raises the boiling point, and generates an osmotic pressure of a solution. The magnitudes of these colligative properties depend only on the concentration of the solute, not on its identity.

Key Terms

adhesive forces
cohesive forces
intermolecular forces
intramolecular forces
normal boiling point (bp)
normal freezing point (fp)
surface tension
van der Waals equation
viscosity

dipolar forces
dispersion forces
hydrogen bond
ionic solid
metallic solid
molecular solid
network solid
polarizability
superconductor

amorphous solid
body-centered cubic structure
close-packed structure
crystalline defect
crystalline solid
cubic close-packed structure
face-centered cubic structure
glass
hexagonal close-packed structure
unit cell

alloy
amalgam
chromatography
miscible
saturated
solubility
solute
solution
solvent

hydrophilic
hydrophobic
micelle
monolayer
surfactant
vesicle

boiling point elevation constant
colligative properties
freezing point depression constant
molality
osmosis
osmotic pressure
reverse osmosis
semipermeable membrane

Skills to Master

- Explaining variations in boiling points
- Identifying hydrogen bonds
- Describing surface tension and viscosity
- Recognizing types of solids
- Depicting simple crystal types
- Drawing molecular pictures of solutions
- Predicting solubility patterns
- Describing surfactant properties
- Calculating colligative properties

Learning Exercises

- Write a chapter summary of two pages or less that summarizes the important ideas and concepts presented in this chapter.
- List all the types of interactions that can act to hold a solid together. Organize the list from strongest to weakest.
- Draw molecular pictures that show every type of hydrogen bond that exists in a solution containing methanol, water, and ammonia.
- Write a paragraph that describes the phenomenon of superconductivity.
- Define and give an example of each of the following: (a) close-packed structure; (b) unit cell; (c) molecular solid; (d) covalent solid; (e) amorphous solid; and (f) surfactant.
- Update your list of memory-bank equations. Be sure to mention how the equations in this chapter are used.
- Write a paragraph that describes the types of substances that form monolayers, micelles, and vesicles in water. Explain the differences among these structures.
- Prepare a list of the terms in Chapter 10 that are new to you. Write a one-sentence definition for each, using your own words. If you need help, consult the glossary.

Problems

The Nature of Intermolecular Forces

- Redraw Figure 10-4 to include a graph showing the intermolecular attractive forces for Cl_2 , whose boiling point of -34°C is intermediate between that of F_2 (-188°C) and Br_2 ($+59^\circ\text{C}$).
- Methane condenses at 121 K, but carbon tetrachloride boils at 350 K. Sketch an energy-distance plot similar to that of Figure 10-4 that shows the behavior of both of these substances.
- Predict whether intermolecular attractions become more or less significant when the following changes are imposed: (a) A gas is expanded to a larger volume at constant temperature. (b) More gas is forced into the same volume at constant temperature. (c) The temperature of the gas is lowered at constant volume.
- Predict whether molecular volume becomes more or less significant when each of the changes in Problem 10.3 is imposed.
- Draw pictures showing the atomic arrangements of samples of $\text{Ag}_{(s)}$, $\text{Ar}_{(g)}$, and $\text{Hg}_{(l)}$.
- Draw pictures showing the atomic arrangements of samples of $\text{Zn}_{(s)}$, $\text{Kr}_{(g)}$, and $\text{Ga}_{(l)}$.
- From the following experimental data, calculate the percent deviation from ideal behavior: 1.00 mol CO_2 in a 1.20 L container at 40.0°C exerts 19.7 atm pressure.
- From the following experimental data, calculate the percent deviation from ideal behavior: 3.000 g H_2 at 0.00°C and 193.5 atm occupies a volume of 189.18 cm^3 .
- Chlorine gas is commercially produced electrochemically from seawater and then stored under pressure in metal tanks. A typical tank has a volume of 15.0 L and contains 1.25 kg of Cl_2 . Use the van der Waals equation to calculate the pressure in this tank if the temperature is 295 K and compare the result with the ideal gas value.
- Chlorine gas used in chemical syntheses is transferred from tanks under high pressure to reactor flasks at considerably lower pressure. If 10.5 g of Cl_2 is introduced into a 5.00-L reaction flask at 145°C , calculate the pressure of Cl_2 gas using the van der Waals equation and using the ideal gas equation.

10.11 Pentane is a C_5 hydrocarbon, gasoline contains mostly C_8 hydrocarbons, and fuel oil contains hydrocarbons in the C_{12} range. List these three hydrocarbons in order of increasing viscosity, and explain what molecular feature accounts for the variation.

10.12 Given that a lubricant must flow easily to perform its function, which grade of motor oil is preferred for winter use, high or low viscosity? Why?

Types of Intermolecular Forces

10.13 Arrange the following in order of ease of liquefaction: CCl_4 , CH_4 , and CF_4 . Explain your ranking.

10.14 Arrange the following in order of increasing boiling point: Ar, He, Ne, and Xe. Explain your ranking.

10.15 Draw molecular pictures of CCl_4 and CH_4 , showing the relative amount of polarizability of each.

10.16 Draw molecular pictures of Ne and Xe, showing the relative amount of polarizability of each.

10.17 List ethanol (C_2H_5OH), propane (C_3H_8), and *n*-pentane (C_5H_{12}) in order of increasing boiling point, and explain what features determine this order.

10.18 List *n*-propanol (C_3H_7OH), dimethyl ether (CH_3OCH_3), and diethyl ether ($C_2H_5OC_2H_5$) in order of increasing boiling point and explain what features determine this order.

10.19 Which of the following will form hydrogen bonds with another molecule of the same substance? (a) CH_2Cl_2 ; (b) H_2SO_4 ; (c) H_3COCH_3 ; and (d) $H_2NCH_2CO_2H$.

10.20 Which of the following can form hydrogen bonds with water? (a) CH_4 ; (b) I_2 ; (c) HF; (d) CH_3-O-CH_3 ; and (e) $(CH_3)_3COH$.

10.21 Draw Lewis structures showing all possible hydrogen-bonding interactions for (a) two NH_3 molecules and (b) an NH_3 molecule and an H_2O molecule.

10.22 Draw Lewis structures that show the hydrogen-bonding interactions for (a) two CH_3OH molecules and (b) an HF molecule and an acetone molecule [$(CH_3)_2C=O$].

Forces in Solids

10.23 Classify each of the following as ionic, network, molecular, or metallic solids: Sn, S_8 , Se, SiO_2 , and Na_2SO_4 .

10.24 Classify each of the following as ionic, network, molecular, or metallic solids: Pt, P_4 , Ge, As_2O_3 , and $(NH_4)_3PO_4$.

10.25 Describe the differences in (a) bonding characteristics and (b) macroscopic properties between metals and network solids.

10.26 Describe the differences in (a) interparticle forces and (b) macroscopic properties between molecular and ionic solids.

10.27 Classify each of the following solids as network, metallic, ionic, or molecular: (a) a solid that conducts electricity; (b) a solid that does not conduct electricity but dissolves in water to give a conducting solution; and (c) a solid that does not conduct electricity and melts below $100^\circ C$ to give a nonconducting liquid.

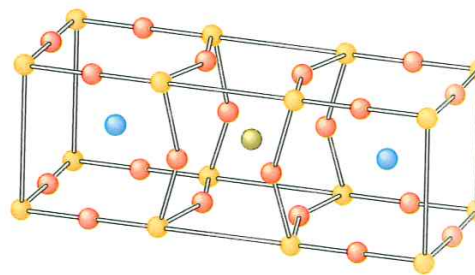
10.28 Indicate what type of solid (ionic, network, metallic, or molecular/atomic) each forms on solidification: (a) HCl; (b) KCl; (c) NH_4NO_3 ; (d) Mn; and (e) Si.

Order in Solids

10.29 The density of graphite is 2260 kg m^{-3} , whereas that of diamond is 3513 kg m^{-3} . Why do these two forms of the same substance have different densities? Draw structural pictures to illustrate your answer.

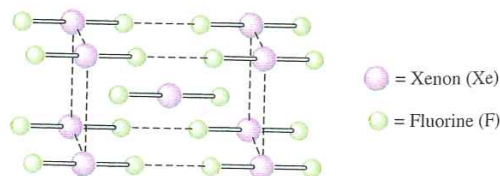
10.30 Amorphous silica has a density of around 2.3 g/cm^3 , whereas crystalline quartz has a density of 2.65 g/cm^3 . Why do these two forms of the same substance have different densities? Draw structural pictures to illustrate your answer.

10.31 Recently, a new group of solids was prepared that can act as superconductors at temperatures near the boiling point of liquid nitrogen. The unit cell of one of these new superconductors follows. Identify the formula of the compound.



● Barium ● Yttrium ● Oxygen ● Copper

10.32 The unit cell of a compound of xenon and fluorine follows. What is the formula of the compound?



● = Xenon (Xe)

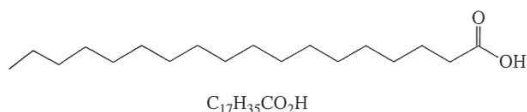
● = Fluorine (F)

10.33 Construct part of the Lewis structure of carborundum, the diamondlike compound of empirical formula SiC .

10.34 Draw the unit cell of the NaCl crystal and determine the number of nearest neighbors of opposite charge for each ion in this unit cell.

The Nature of Solutions

- 10.35 Salad oil (whose major ingredients are long-chain fatty acids such as $C_{17}H_{33}CO_2H$) and vinegar (a dilute aqueous solution of acetic acid, CH_3CO_2H) are not miscible. Explain.

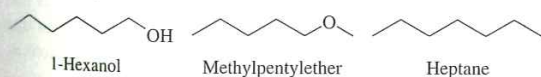


- 10.36 Acetonitrile, CH_3CN , is miscible with both water and cyclohexane (C_6H_{12}), but water and cyclohexane are nearly insoluble in each other. Explain.

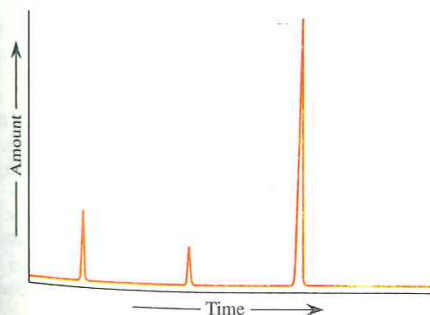


- 10.37 Ammonia can be condensed to a liquid at low temperature. What kinds of solids would you expect to be soluble in liquid ammonia?
- 10.38 Mercury is the only metallic element that is a liquid at room temperature. What kinds of solids would you expect to be soluble in liquid mercury?
- 10.39 How many hydrogen bonds to water molecules can one glycerol molecule ($HOCH_2CHOHCH_2OH$) form? Draw Lewis structures that show the hydrogen bonding of a glycerol molecule dissolved in water.
- 10.40 How many hydrogen bonds to water molecules can be formed by one molecule of glycine in its ionic form ($^+NH_3CH_2CO_2^-$)? Draw Lewis structures that show the hydrogen bonding of a glycine molecule dissolved in water.

- 10.41 A sample for gas chromatography contains the following compounds:

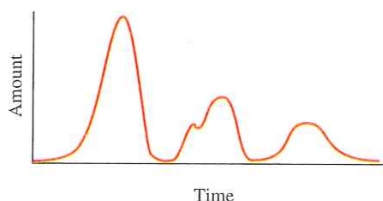


The sample is passed through a gas chromatography column whose condensed phase attracts polar compounds. The chromatograph looks like this:



- (a) Associate each peak with the appropriate compound.
(b) Determine which compound is present in the largest amount and which in the smallest amount.

- 10.42 You have prepared a sample of polymer and have performed liquid chromatography using molecular sieves to determine its molecular size. The chromatogram follows:

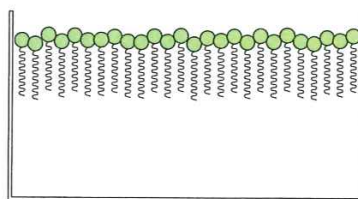
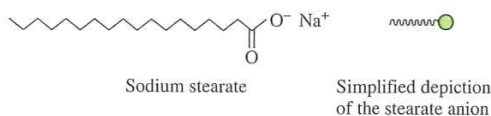


- (a) How many components does your sample contain?
(b) Is there a larger amount of long-, medium-, or short-chain polymer molecules in the sample? Explain.

Dual-Nature Molecules: Surfactants and Biological Membranes

- 10.43 Of the following compounds, which will be the best and which will be the worst surfactant: (a) propionic acid, $H_3CCH_2CO_2H$; (b) sodium lauryl sulfate, $H_3C(CH_2)_{11}OSO_3^-Na^+$; and (c) lauryl alcohol, $H_3C(CH_2)_{11}OH$. Support your choices with molecular pictures.

- 10.44 The figure that follows represents a solution of the surfactant sodium stearate. Decide whether the solvent is polar or nonpolar. Explain your reasoning.



- 10.45 Some surfactants form membranes that span small holes between two aqueous solutions. These membranes are liquid bilayers two molecules thick. Draw a molecular picture of one of these membranes.
- 10.46 Stearic acid forms a monolayer on the surface of gasoline. Draw a molecular picture that shows how stearic acid molecules are arranged in this monolayer.

Properties of Aqueous Solutions

- 10.47 Compute the freezing point of a wine that is 12% by mass ethanol. (Ignore all other solutes.)

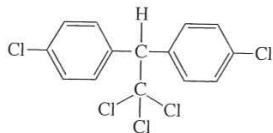
- 10.48** Calculate the freezing point of a solution that contains 12.50 g sucrose ($C_{12}H_{22}O_{11}$) in 155 mL of water.
- 10.49** Do you have enough information to calculate the boiling point of the wine in Problem 10.47? If so, calculate it. If not, explain what feature of wine prevents you from doing this calculation.
- 10.50** Do you have enough information to calculate the boiling point of the solution in Problem 10.48? If so, calculate it. If not, explain what feature of the solution prevents you from doing this calculation.
- 10.51** An aqueous solution contains 1.00 g/L of a derivative of the detergent lauryl alcohol. The osmotic pressure of this

solution at 25.0 °C is measured to be 64.8 torr. (a) What is the molar mass of the detergent? (b) The hydrocarbon portion of the molecule is an 11-carbon chain. What is the molar mass of the polar portion?

- 10.52** Polystyrene is a plastic that dissolves in benzene. When a benzene solution ($\rho = 0.88 \text{ g mL}^{-1}$) containing 8.5 g/L of polystyrene is placed in an osmometer at 25 °C, the solution reaches equilibrium when the height of liquid inside the osmometer is 10.9 cm higher than outside. Calculate the molar mass of the polystyrene. (HINT: Begin by converting the height difference into millimeters of mercury using density differences.)

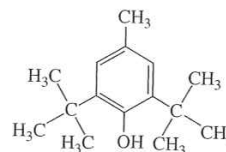
Additional Paired Problems

- 10.53** You have been hired by the local utility company as a quality control chemist. They ask you to analyze samples of their natural gas, which they buy from several sources. What technique would you recommend? Describe how this technique works.
- 10.54** You have prepared a new, highly colored solid compound and want to determine whether your product is pure or contains several components. What technique would provide this information most conveniently? Describe how the technique works.
- 10.55** An aqueous solution containing 1.00 g of a sugar in $1.00 \times 10^2 \text{ mL}$ of solution has an osmotic pressure of 1.36 atm at 25 °C. What is the molar mass of this sugar?
- 10.56** Compute the molar mass of vitamin C, if a solution containing 22.0 g in $1.00 \times 10^2 \text{ g}$ of water freezes at -2.33 °C .
- 10.57** Rank the following substances in order of increasing solubility in water, and state the reasons for your rankings: C_6H_6 (benzene), $HOCH_2CH(OH)CH(OH)CH_2OH$ (erythritol), and $C_5H_{11}OH$ (pentanol).
- 10.58** Rank the following substances in order of increasing solubility in cyclohexane (C_6H_{12}) and explain the order of your list: KCl, C_2H_5OH , and C_3H_8 .
- 10.59** Dichlorodiphenyltrichloroethane (DDT) has the following structure:



Is this compound hydrophilic or hydrophobic? Is it readily excreted by animals, or will it concentrate in fatty tissues? Does your answer explain why DDT has been banned as a pesticide?

- 10.60** Butylated hydroxytoluene (BHT) is used as a food preservative. It has the following molecular structure:

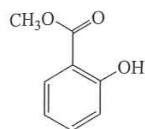


Would you expect to find this compound to be excreted in urine or stored in body fat? BHT is nontoxic to humans.

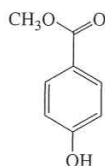
- 10.61** Water and carbon tetrachloride are not miscible. When mixed together, they form two layers, like water and oil. If an aqueous solution of I_2 is shaken with CCl_4 , the iodine is "extracted" into the CCl_4 layer. Explain this behavior on the basis of your knowledge of intermolecular forces.
- 10.62** If some benzene is shaken with a mixture of water and carbon tetrachloride, the resulting mixture contains two layers. Which layer contains the benzene? Explain this behavior on the basis of your knowledge of intermolecular forces.
- 10.63** List all of the different kinds of forces that must be overcome to convert each of the following from a liquid to a gas: (a) NH_3 ; (b) $CHCl_3$; (c) CCl_4 ; and (d) CO_2 .
- 10.64** List all the intermolecular forces that stabilize the liquid phase of each of the following compounds: (a) Xe; (b) SF_4 ; (c) CF_4 ; and (d) CH_3CO_2H (acetic acid).
- 10.65** For each of the following pairs, identify which has the higher boiling point, and identify the type of force that is responsible: (a) CH_3OCH_3 and CH_3OH ; (b) SO_2 and SiO_2 ; (c) HF and HCl; and (d) Br_2 and I_2 .
- 10.66** The boiling points of the Group 16 binary hydrides are as follows: H_2O , 100 °C; H_2S , -60 °C ; and H_2Se , -41 °C . Explain why H_2S has a lower boiling point than both H_2O and H_2Se .

10.67 The compound 1,2-dichloroethylene (ClCHCHCl) exists as *cis* and *trans* isomers. One isomer boils at 47°C , the other at 60°C . Draw Lewis structures of the two isomers. Use dipole moments and symmetry arguments to assign the boiling points to the isomers.

10.68 Why do the two isomers shown have very different melting points?



$\text{C}_8\text{H}_8\text{O}_3$
Methyl-2-hydroxybenzoate
(oil of wintergreen)
mp = -8°C



$\text{C}_8\text{H}_8\text{O}_3$
Methyl-4-hydroxybenzoate
mp = 127°C

Additional Unpaired Problems

10.71 Brackish water, with a salt content around 0.5% by mass, is found in semiarid regions such as the American Southwest. Assuming that brackish water has the same density as pure water and contains only sodium chloride, estimate the osmotic pressure of brackish water at 298 K. (HINT: The total molarity is the sum of the molarities of Na^+ and Cl^- .)

10.72 Some chemists interpret the boiling point of HCl as evidence for hydrogen bonding in this compound. How does the location of HCl on the graph in Figure 10-19 suggest that it may form hydrogen bonds? Draw a molecular picture that shows the possible hydrogen bonds between HCl molecules.

10.73 Identify two elements that form molecular solids, two that form metallic solids, and two that form network solids. Identify regions of the periodic table where elements of these three kinds are located.

10.74 One of the earliest methods of preserving fish was by salting. Explain what happens when fish is placed in concentrated salt solution.

10.75 Would water dissolve salts as well as it does if it had a linear structure (such as CO_2) instead of a bent one? Explain.

10.76 When an aqueous solution is cooled to a low temperature, part of the water freezes as pure ice. What happens to the freezing point of the remaining solution when this occurs? A glass of wine placed in a freezer at -10°C for a very long time forms some ice crystals but does not completely freeze. Compute the molality of ethanol in the remaining liquid phase.

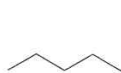
10.69 To make a good solder joint, the liquid metal solder must adhere well to the metal surfaces being joined. "Flux" is used to clean the metal surfaces. What types of substances must flux remove?

10.70 A pipet is considered to be "dirty" when water forms beads on its walls rather than forming a thin film that drains well. Which of the following on the surface of a pipet wall will make it "dirty": (a) grease; (b) Mg^{2+} ions; (c) acetone; and (d) SiO_2 . In each case, explain the intermolecular forces underlying your classification.

10.77 Molecular hydrogen and atomic helium have two electrons, but He boils at 4.2 K, whereas H_2 boils at 20 K. Neon boils at 27.1 K, whereas methane, which has the same number of electrons, boils at 114 K. Explain why molecular substances boil at a higher temperature than atomic substances with the same number of electrons.

10.78 Describe the similarities and differences between hexagonal close-packed and body-centered cubic structures.

10.79 The structures and boiling points of *n*-pentane and 2,2-dimethylpropane follow:



Pentane
 C_5H_{12}
bp = 36°C



2,2-Dimethylpropane
 C_5H_{12}
bp = -10°C

Use the boiling point data along with molecular drawings to explain how shape affects the magnitude of dispersion forces. (See Figures 10-12 and 10-13.)

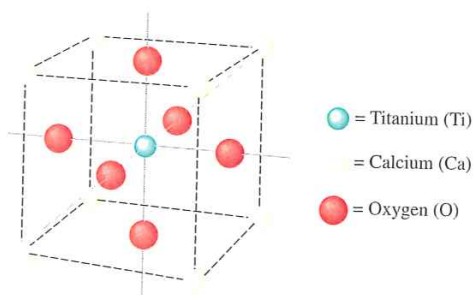
10.80 Quartz and glass are both forms of silicon dioxide. A piece of quartz breaks into a collection of smaller regular crystals with smooth faces. A piece of glass breaks into irregular shards. Use molecular structures to explain why the two solids break so differently.

10.81 Drinking seawater can be dangerous because it is more concentrated than a person's body fluids. Discuss the consequences, at both the cellular and the molecular levels, of drinking too much seawater.

- 10.82** The thin-layer chromatograph of black ink follows. Rank the colored dyes in the ink from most polar to least polar.

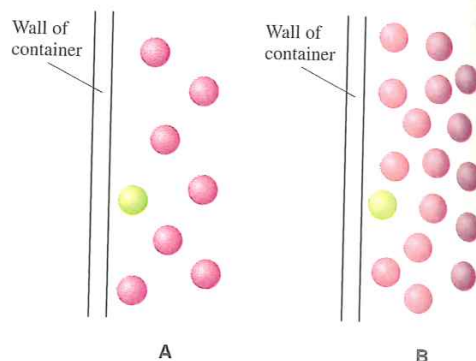


- 10.83** The unit cell of the mineral perovskite follows. What is the formula of perovskite?



- 10.84** Fish have blood that is isotonic with seawater, which freezes at -2.30°C . What is the osmotic pressure of fish blood at 15°C ?
- 10.85** Do you expect water to dissolve gasoline? Knowing that gasoline is less dense than water, would you use water to fight a gasoline fire? Explain.
- 10.86** What molality of ethanol is required to protect the water in an automobile cooling system from freezing at -20°C ?
- 10.87** For each of the following pairs of gases, which one will deviate more from ideal PV/nRT behavior? (a) F_2 and Cl_2 and (b) CH_4 and SnH_4 .

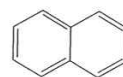
- 10.88** In the two figures shown, the green molecule is about to strike the wall of its container. Assuming all other conditions are identical, which collision will exert greater force on the wall? Explain in terms of intermolecular interactions.



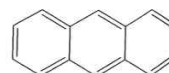
- 10.89** Which has a higher boiling point, CH_3F or CH_3OH ? Why? Illustrate your answer with a molecular picture.
- 10.90** Arrange the following liquids in order of increasing viscosity, and state the factors that determine the ranking: butanol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$; *n*-pentane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$; propane-1,3-diol, $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{OH}$; 2,2-dimethylpropane, $(\text{CH}_3)_4\text{C}$.
- 10.91** Benzene (C_6H_6), naphthalene (C_{10}H_8), and anthracene ($\text{C}_{14}\text{H}_{10}$) are three aromatic hydrocarbons with similar molecular structures. One is a liquid, another is a relatively volatile solid, and the third is a less volatile solid. Which is which? Explain your assignments.



Benzene
 C_6H_6



Napthalene
 C_{10}H_8



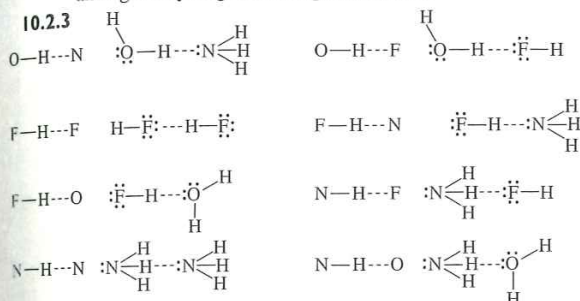
Anthracene
 $\text{C}_{14}\text{H}_{10}$

Answers to Section Exercises

- 10.1.1** At_2 is a solid, with stronger intermolecular forces than either F_2 or Br_2 . Continuing the trends shown in Figure 10-4, the At_2 curve should have a deeper well and a longer internuclear distance than bromine, and its "average kinetic energy line" should appear even deeper in the well.
- 10.1.2** Intermolecular forces cause pV/nRT to be smaller than 1.0. Fluorine reaches the smallest value, so it has the largest intermolecular forces. Helium never dips below 1.0, indicating very small intermolecular forces.
- 10.1.3** (a) Ar boils at a higher temperature than He, indicating that boiling point increases moving down Group 18. Thus Xe boils at a higher temperature than Ar. (b) The lower the boiling point of the element, the smaller its intermolecular forces. The order is $\text{H}_2 < \text{N}_2 < \text{F}_2 < \text{Cl}_2$. (c) Group 18, which has the lowest boiling points, has the smallest intermolecular forces.

10.2.1 (a) Propane has larger polarizability because its electrons are spread over a larger volume than those in krypton. (b) CCl_4 has a larger polarizability because it has more valence electrons and because of the larger size of chlorine's $n = 3$ valence orbitals. (c) CO has a dipole moment, generating dipole-dipole attractions not present in N_2 .

10.2.2 Acetone has dispersion forces and dipole-dipole forces. Methanol has dispersion forces, dipole-dipole forces, and hydrogen bonding forces. Their boiling points are similar because the dipolar and dispersion forces in acetone are larger than the analogous forces in methanol, counterbalancing the hydrogen bonding in methanol.



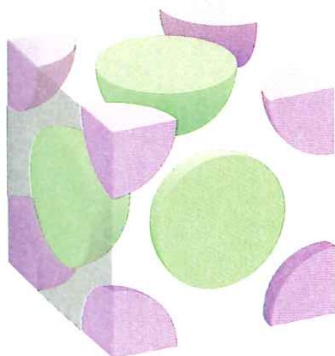
10.3.1 (a) CO_2 is a molecular solid, with dispersion forces between the molecules. (b) S_8 is another molecular solid, with dispersion forces between the molecules. (c) Tin is a metal, with delocalized metallic bonding holding the atoms together. (d) Li_2O is ionic, with coulombic attractions between Li^+ cations and O^{2-} anions.

10.3.2 The order of melting points is $\text{F}_2 < \text{K} < \text{Co} < \text{C}$ (diamond). F_2 is molecular, with dispersion forces only. K and Co are metals, but Co has more valence electrons, resulting in stronger bonds. Diamond is a network solid with strong covalent bonds.

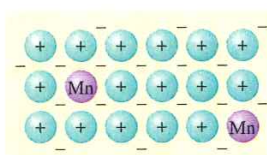
10.3.3 (a) $\text{Mg}_3(\text{PO}_4)_2$; (b) $\text{LiAlSi}_2\text{O}_6$; (c) $\text{Bi}_2\text{Sr}_2\text{CuO}_6$.

10.4.1 All angles in a hexagonal crystal are multiples of 60 degrees, so we expect angles of 60 degrees, 120 degrees, and so on. A cubic close-packed crystal also has right angles, so we expect 90-degree angles as well.

10.4.2 An eighth of each corner atom and half of each face atom is in the unit cell.

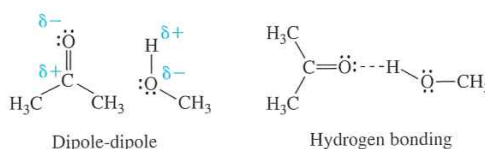


10.4.3



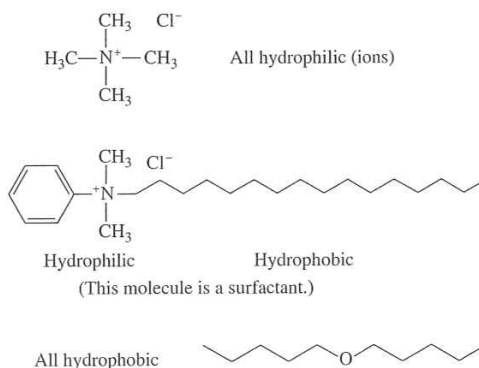
10.5.1 Zn^{2+} is soluble because the solution is stabilized by ion-dipole interactions between partially negative O atoms in water molecules and the Zn^{2+} cations, which replace ion-ion interactions in a zinc salt. Zn metal is insoluble because the cations in the metal are strongly bound by the "sea" of electrons in delocalized orbitals.

10.5.2 Intermolecular interactions are dispersion, dipole-dipole, and hydrogen bonding.



10.5.3 Only Na_4SiO_4 , which is an ionic solid, is water soluble.

10.6.1



10.6.2 Because they are large, they cannot slip easily between the molecules of a lipid bilayer membrane. Because they are hydrophilic, they do not dissolve in the bilayer.

10.7.1 Freezing point depression = $1.44 \times 10^{-3} \text{ }^\circ\text{C}$; boiling point elevation = $3.96 \times 10^{-4} \text{ }^\circ\text{C}$; and osmotic pressure = $1.87 \times 10^{-2} \text{ atm} = 14.2 \text{ torr}$.

10.7.2 The figure should look the same, except there should be more arrows moving from right to left than from left to right.

10.7.3 Your description should include the features shown in your figure for 10.7.2 and the prevention of ion passage through the pores of the semipermeable membrane.