

10 Liquids and Solids

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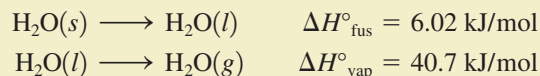
Karst formation in Phang Nga Bay, Thailand at sunset. The Karst is limestone that has eroded into these formations rising out of the sea.

You have only to think about water to appreciate how different the three states of matter are. Flying, swimming, and ice skating are all done in contact with water in its various forms. Clearly, the arrangements of the water molecules must be significantly different in its gas, liquid, and solid forms.

In Chapter 5 we saw that a gas can be pictured as a substance whose component particles are far apart, are in rapid random motion, and exert relatively small forces on each other. The kinetic molecular model was constructed to account for the ideal behavior that most gases approach at high temperatures and low pressures.

Solids are obviously very different from gases. A gas has low density and high compressibility and completely fills its container. Solids have much greater densities, are compressible only to a very slight extent, and are rigid—a solid maintains its shape irrespective of its container. These properties indicate that the components of a solid are close together and exert large attractive forces on each other.

The properties of liquids lie somewhere between those of solids and gases but not midway between, as can be seen from some of the properties of the three states of water. For example, compare the enthalpy change for the melting of ice at 0°C (the heat of fusion) with that for vaporizing liquid water at 100°C (the heat of vaporization):



These values show a much greater change in structure in going from the liquid to the gaseous state than in going from the solid to the liquid state. This suggests that there are extensive attractive forces among the molecules in liquid water, similar to but not as strong as those in the solid state.

The relative similarity of the liquid and solid states also can be seen in the densities of the three states of water. As shown in Table 10.1, the densities for liquid and solid water are quite close.* Compressibilities also can be used to explore the relationship among water's states. At 25°C, the density of liquid water changes from 0.99707 g/cm³ at a pressure of 1 atm to 1.046 g/cm³ at 1065 atm. Given the large change in pressure, this is a very small variation in the density. Ice also shows little variation in density with increased pressure. On the other hand, at 400°C, the density of gaseous water changes from 3.26 × 10⁻⁴ g/cm³ at 1 atm pressure to 0.157 g/cm³ at 242 atm—a huge variation.

The conclusion is clear. The liquid and solid states show many similarities and are strikingly different from the gaseous state, as shown schematically in Fig. 10.1. We must bear this in mind as we develop models for the structures of solids and liquids.

We will proceed in our study of liquids and solids by first considering the properties and structures of liquids and solids. Then we will consider the changes in state that occur between solid and liquid, liquid and gas, and solid and gas.

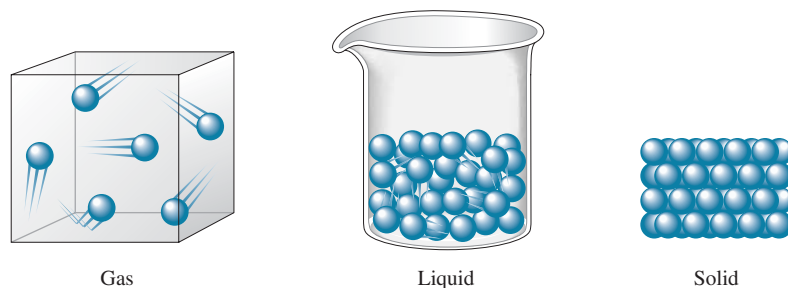


Visualization: Intermolecular Forces: London Dispersion Forces

*Although the densities of solid and liquid water are quite similar, as is typical for most substances, water is quite unusual in that the density of its solid state is slightly less than that of its liquid state. For most substances, the density of the solid state is slightly greater than that of the liquid state.

TABLE 10.1 Densities of the Three States of Water

State	Density (g/cm ³)
Solid (0°C, 1 atm)	0.9168
Liquid (25°C, 1 atm)	0.9971
Gas (400°C, 1 atm)	3.26×10^{-4}

**FIGURE 10.1** Schematic representations of the three states of matter.

10.1 Intermolecular Forces

In Chapters 8 and 9 we saw that atoms can form stable units called *molecules* by sharing electrons. This is called *intramolecular* (within the molecule) *bonding*. In this chapter we consider the properties of the **condensed states** of matter (liquids and solids) and the forces that cause the aggregation of the components of a substance to form a liquid or a solid. These forces may involve covalent or ionic bonding, or they may involve weaker interactions usually called **intermolecular forces** (because they occur between, rather than within, molecules).

It is important to recognize that when a substance such as water changes from solid to liquid to gas, *the molecules remain intact*. The changes in states are due to changes in the forces *among* the molecules rather than in those *within* the molecules. In ice, as we will see later in this chapter, the molecules are virtually locked in place, although they can vibrate about their positions. If energy is added, the motions of the molecules increase, and they eventually achieve the greater movement and disorder characteristic of liquid water. The ice has melted. As more energy is added, the gaseous state is eventually reached, with the individual molecules far apart and interacting relatively little. However, the gas still consists of water molecules. It would take much energy to overcome the covalent bonds and decompose the water molecules into their component atoms. This can be seen by comparing the energy needed to vaporize 1 mole of liquid water (40.7 kJ) with that needed to break the O—H bonds in 1 mole of water molecules (934 kJ).

Intermolecular forces were introduced in Chapter 5 to explain nonideal gas behavior.

Remember that temperature is a measure of the random motions of the particles in a substance.

Dipole–dipole forces are forces that act between polar molecules.

Dipole–Dipole Forces

As we saw in Section 8.3, molecules with polar bonds often behave in an electric field as if they had a center of positive charge and a center of negative charge. That is, they exhibit a dipole moment. Molecules with dipole moments can attract each other electrostatically by lining up so that the positive and negative ends are close to each other, as shown in Fig. 10.2(a). This is called a **dipole–dipole attraction**. In a condensed state such as a liquid, where many molecules are in close proximity, the dipoles find the best compromise between attraction and repulsion. That is, the molecules orient themselves to maximize the $\oplus\text{---}\ominus$ interactions and to minimize $\oplus\text{---}\oplus$ and $\ominus\text{---}\ominus$ interactions, as represented in Fig. 10.2(b).

Dipole–dipole forces are typically only about 1% as strong as covalent or ionic bonds, and they rapidly become weaker as the distance between the dipoles increases. At low pressures in the gas phase, where the molecules are far apart, these forces are relatively unimportant.

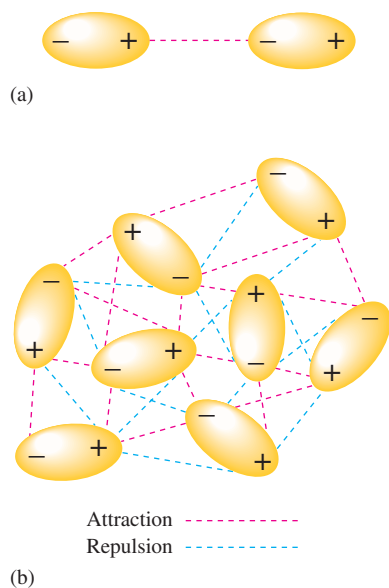
Particularly strong dipole–dipole forces, however, are seen among molecules in which hydrogen is bound to a highly electronegative atom, such as nitrogen, oxygen, or fluorine. Two factors account for the strengths of these interactions: the great polarity of the bond and the close approach of the dipoles, allowed by the very small size of the hydrogen atom. Because dipole–dipole attractions of this type are so unusually strong, they are given a special name—**hydrogen bonding**. Figure 10.3 shows hydrogen bonding among water



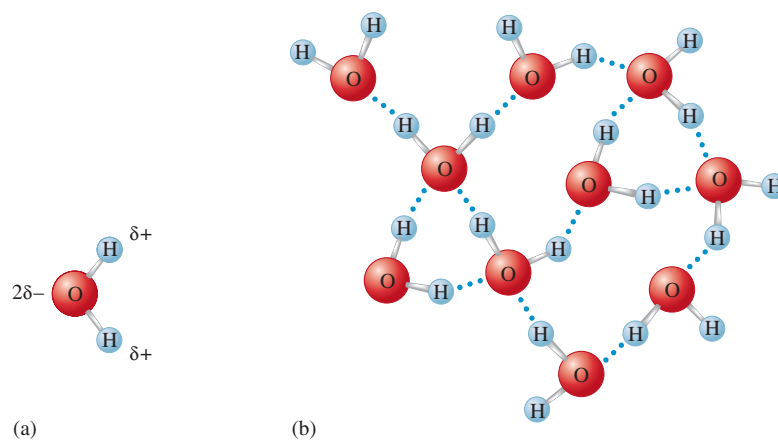
Visualization: Intermolecular Forces: Dipole–Dipole Forces



Visualization: Intermolecular Forces: Hydrogen Bonding Forces

**FIGURE 10.2**

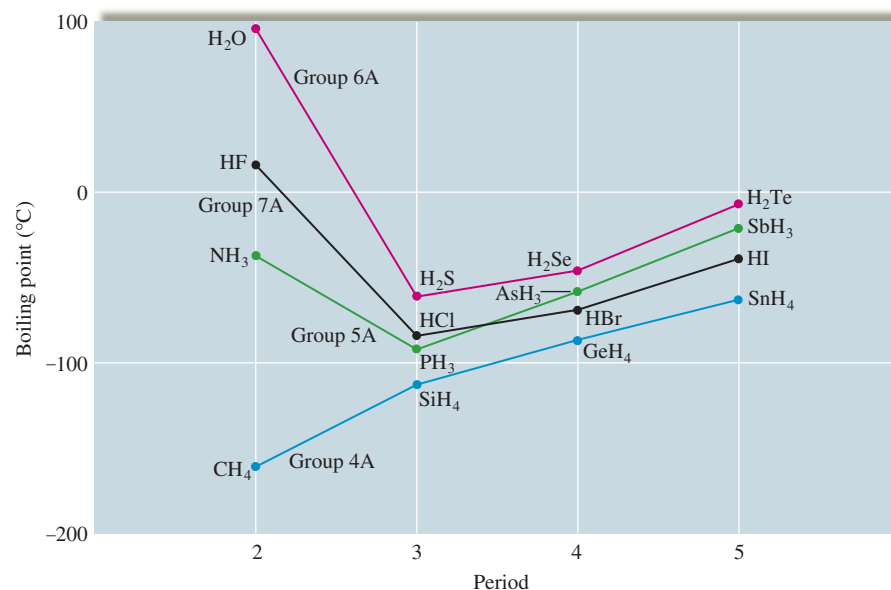
(a) The electrostatic interaction of two polar molecules. (b) The interaction of many dipoles in a condensed state.

**FIGURE 10.3**

(a) The polar water molecule. (b) Hydrogen bonding among water molecules. Note that the small size of the hydrogen atom allows for close interactions.

molecules, which occurs between the partially positive H atoms and the lone pairs on adjacent water molecules.

Hydrogen bonding has a very important effect on physical properties. For example, the boiling points for the covalent hydrides of the elements in Groups 4A, 5A, 6A, and 7A are given in Fig. 10.4. Note that the nonpolar tetrahedral hydrides of Group 4A show a steady increase in boiling point with molar mass (that is, in going down the group), whereas, for the other groups, the lightest member has an unexpectedly high boiling point. Why? The answer lies in the especially large hydrogen bonding interactions that exist among the smallest molecules with the most polar X—H bonds. These unusually strong hydrogen bonding forces are due primarily to two factors. One factor is the relatively large electronegativity values of the lightest elements in each group, which leads to especially polar X—H bonds. The second factor is the small size of the first element of each group, which allows for the close approach of the dipoles, further strengthening the intermolecular forces. Because the interactions among the molecules containing the lightest elements in Groups 5A and 6A are so strong, an unusually large quantity of energy must be supplied

**FIGURE 10.4**

The boiling points of the covalent hydrides of the elements in Groups 4A, 5A, 6A, and 7A.

Boiling point will be defined precisely in Section 10.8.

to overcome these interactions and separate the molecules to produce the gaseous state. These molecules will remain together in the liquid state even at high temperatures—hence the very high boiling points.

Hydrogen bonding is also important in organic molecules (molecules with a carbon chain backbone). For example, the alcohols methanol (CH_3OH) and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) have much higher boiling points than would be expected from their molar masses because of the polar O—H bonds in these molecules, which produce hydrogen bonding.

London Dispersion Forces

Even molecules without dipole moments must exert forces on each other. We know this because all substances—even the noble gases—exist in the liquid and solid states under certain conditions. The forces that exist among noble gas atoms and nonpolar molecules are called **London dispersion forces**. To understand the origin of these forces, let's consider a pair of noble gas atoms. Although we usually assume that the electrons of an atom are uniformly distributed about the nucleus, this is apparently not true at every instant. As the electrons move about the nucleus, a momentary nonsymmetrical electron distribution can develop that produces a temporary dipolar arrangement of charge. The formation of this temporary dipole can, in turn, affect the electron distribution of a neighboring atom. That is, this *instantaneous dipole* that occurs accidentally in a given atom can then *induce* a similar dipole in a neighboring atom, as represented in Fig. 10.5(a). This phenomenon leads to an interatomic attraction that is relatively weak and short-lived but that can be very significant especially for large atoms (see below). For these interactions to become strong enough to produce a solid, the motions of the atoms must be greatly slowed down. This explains, for instance, why the noble gas elements have such low freezing points (see Table 10.2).

Note from Table 10.2 that the freezing point rises going down the group. The principal cause for this trend is that as the atomic number increases, the number of electrons increases, and there is an increased chance of the occurrence of momentary dipole interactions. We describe this phenomenon using the term *polarizability*, which indicates the

TABLE 10.2 The Freezing Points of the Group 8A Elements

Element	Freezing Point ($^{\circ}\text{C}$)
Helium*	-269.7
Neon	-248.6
Argon	-189.4
Krypton	-157.3
Xenon	-111.9

*Helium is the only element that will not freeze by lowering its temperature at 1 atm. Pressure must be applied to freeze helium.

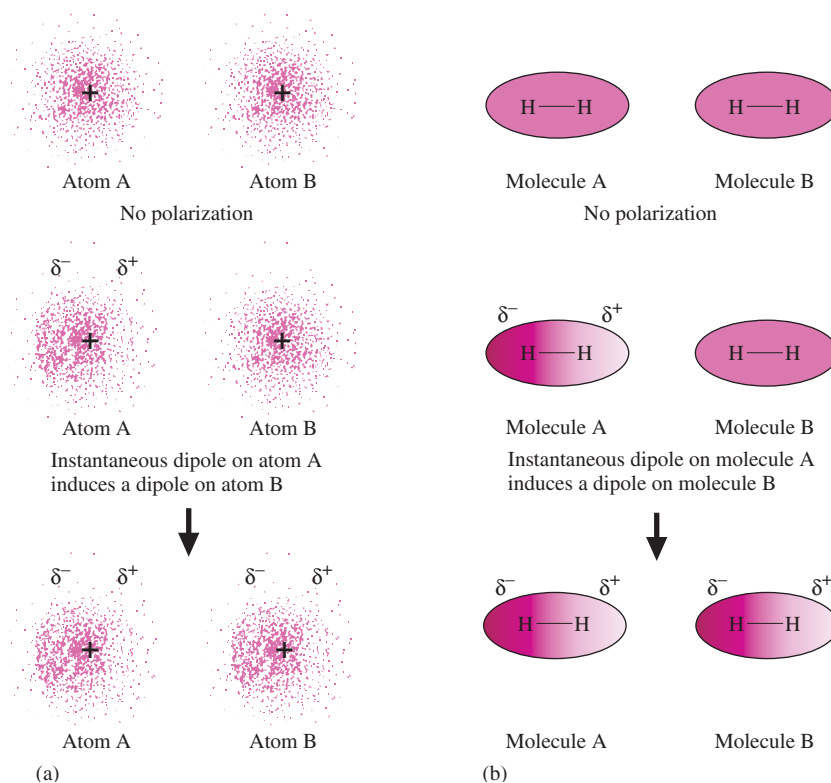


FIGURE 10.5

(a) An instantaneous polarization can occur on atom A, creating an instantaneous dipole. This dipole creates an induced dipole on neighboring atom B. (b) Nonpolar molecules such as H_2 also can develop instantaneous and induced dipoles.

The dispersion forces in molecules with large atoms are quite significant and are often actually more important than dipole–dipole forces.

For a given volume, a sphere has a smaller surface area than any other shape.

Surface tension: The resistance of a liquid to an increase in its surface area.

The composition of glass is discussed in Section 10.5.

Viscosity: A measure of a liquid's resistance to flow.

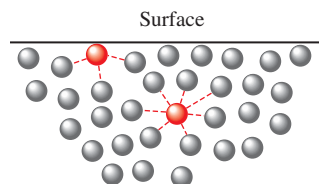


FIGURE 10.6

A molecule in the interior of a liquid is attracted by the molecules surrounding it, whereas a molecule at the surface of a liquid is attracted only by molecules below it and on each side.

ease with which the electron “cloud” of an atom can be distorted to give a dipolar charge distribution. Thus we say that large atoms with many electrons exhibit a higher polarizability than small atoms. This means that the importance of London dispersion forces increases greatly as the size of the atom increases.

These same ideas also apply to nonpolar molecules such as H_2 , CH_4 , CCl_4 , and CO_2 [see Fig. 10.5(b)]. Since none of these molecules has a permanent dipole moment, their principal means of attracting each other is through London dispersion forces.

10.2 The Liquid State

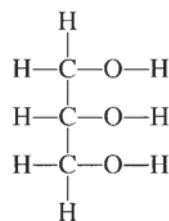
Liquids and liquid solutions are vital to our lives. Of course, water is the most important liquid. Besides being essential to life, water provides a medium for food preparation, for transportation, for cooling in many types of machines and industrial processes, for recreation, for cleaning, and for a myriad of other uses.

Liquids exhibit many characteristics that help us understand their nature. We have already mentioned their low compressibility, lack of rigidity, and high density compared with gases. Many of the properties of liquids give us direct information about the forces that exist among the particles. For example, when a liquid is poured onto a solid surface, it tends to bead as droplets, a phenomenon that depends on the intermolecular forces. Although molecules in the interior of the liquid are completely surrounded by other molecules, those at the liquid surface are subject to attractions only from the side and from below (Fig. 10.6). The effect of this uneven pull on the surface molecules tends to draw them into the body of the liquid and causes a droplet of liquid to assume the shape that has the minimum surface area—a sphere.

To increase a liquid's surface area, molecules must move from the interior of the liquid to the surface. This requires energy, since some intermolecular forces must be overcome. The resistance of a liquid to an increase in its surface area is called the **surface tension** of the liquid. As we would expect, liquids with relatively large intermolecular forces, such as those with polar molecules, tend to have relatively high surface tensions.

Polar liquids typically exhibit **capillary action**, the spontaneous rising of a liquid in a narrow tube. Two different types of forces are responsible for this property: *cohesive forces*, the intermolecular forces among the molecules of the liquid, and *adhesive forces*, the forces between the liquid molecules and their container. We have already seen how cohesive forces operate among polar molecules. Adhesive forces occur when a container is made of a substance that has polar bonds. For example, a glass surface contains many oxygen atoms with partial negative charges that are attractive to the positive end of a polar molecule such as water. This ability of water to “wet” glass makes it creep up the walls of the tube where the water surface touches the glass. This, however, tends to increase the surface area of the water, which is opposed by the cohesive forces that try to minimize the surface. Thus, because water has both strong cohesive (intermolecular) forces and strong adhesive forces to glass, it “pulls itself” up a glass capillary tube (a tube with a small diameter) to a height where the weight of the column of water just balances the water's tendency to be attracted to the glass surface. The concave shape of the meniscus (see Fig. 10.7) shows that water's adhesive forces toward the glass are stronger than its cohesive forces. A nonpolar liquid such as mercury (see Fig. 10.7) shows a convex meniscus. This behavior is characteristic of a liquid in which the cohesive forces are stronger than the adhesive forces toward glass.

Another property of liquids strongly dependent on intermolecular forces is **viscosity**, a measure of a liquid's resistance to flow. As might be expected, liquids with large intermolecular forces tend to be highly viscous. For example, glycerol, whose structure is



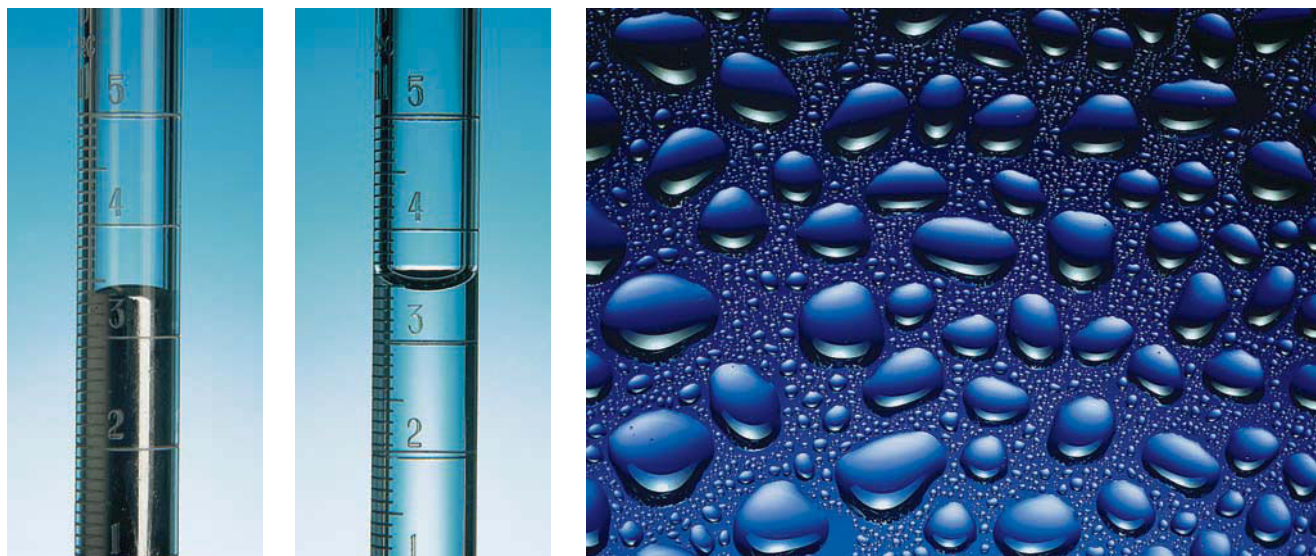
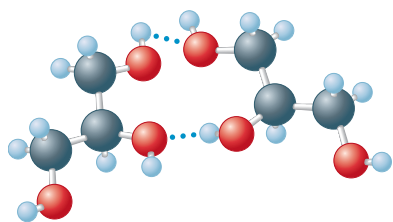


FIGURE 10.7
Nonpolar liquid mercury forms a convex meniscus in a glass tube, whereas polar water forms a concave meniscus.

Beads of water on a waxed car finish. The nonpolar component of the wax causes the water to form approximately spherical droplets.



Glycerol

has an unusually high viscosity due mainly to its high capacity to form hydrogen bonds using its O—H groups (see margin).

Molecular complexity also leads to higher viscosity because very large molecules can become entangled with each other. For example, gasoline, a nonviscous liquid, contains hydrocarbon molecules of the type $\text{CH}_3-(\text{CH}_2)_n-\text{CH}_3$, where n varies from about 3 to 8. However, grease, which is very viscous, contains much larger hydrocarbon molecules in which n varies from 20 to 25.

Structural Model for Liquids

In many respects, the development of a structural model for liquids presents greater challenges than the development of such a model for the other two states of matter. In the gaseous state the particles are so far apart and are moving so rapidly that intermolecular forces are negligible under most circumstances. This means that we can use a relatively simple model for gases. In the solid state, although the intermolecular forces are large, the molecular motions are minimal, and fairly simple models are again possible. The liquid state, however, has both strong intermolecular forces *and* significant molecular motions. Such a situation precludes the use of really simple models for liquids. Recent advances in *spectroscopy*, the study of the manner in which substances interact with electromagnetic radiation, make it possible to follow the very rapid changes that occur in liquids. As a result, our models of liquids are becoming more accurate. As a starting point, a typical liquid might best be viewed as containing a large number of regions where the arrangements of the components are similar to those found in the solid, but with more disorder, and a smaller number of regions where holes are present. The situation is highly dynamic, with rapid fluctuations occurring in both types of regions.

10.3 An Introduction to Structures and Types of Solids

There are many ways to classify solids, but the broadest categories are **crystalline solids**, those with a highly regular arrangement of their components, and **amorphous solids**, those with considerable disorder in their structures.

**FIGURE 10.8**

Two crystalline solids: pyrite (left), amethyst (right).

The regular arrangement of the components of a crystalline solid at the microscopic level produces the beautiful, characteristic shapes of crystals, such as those shown in Fig. 10.8. The positions of the components in a crystalline solid are usually represented by a **lattice**, a three-dimensional system of points designating the positions of the components (atoms, ions, or molecules) that make up the substance. The *smallest repeating unit* of the lattice is called the **unit cell**. Thus a particular lattice can be generated by repeating the unit cell in all three dimensions to form the extended structure. Three common unit cells and their lattices are shown in Fig. 10.9. Note from Fig. 10.9 that the extended structure in each case can be viewed as a series of repeating unit cells that share common faces in the interior of the solid.

Although we will concentrate on crystalline solids in this book, there are many important noncrystalline (amorphous) materials. An example is common glass, which is best pictured as a solution in which the components are “frozen in place” before they can achieve an ordered arrangement. Although glass is a solid (it has a rigid shape), a great deal of disorder exists in its structure.

X-Ray Analysis of Solids

The structures of crystalline solids are most commonly determined by **X-ray diffraction**. Diffraction occurs when beams of light are scattered from a regular array of points in which the spacings between the components are comparable with the wavelength of the light. Diffraction is due to constructive interference when the waves of parallel beams are in phase and to destructive interference when the waves are out of phase.

When X rays of a single wavelength are directed at a crystal, a diffraction pattern is obtained, as we saw in Fig. 7.5. The light and dark areas on the photographic plate occur because the waves scattered from various atoms may reinforce or cancel each other (see Fig. 10.10). The key to whether the waves reinforce or cancel is the difference in distance traveled by the waves after they strike the atoms. The waves are in phase before they are reflected, so if the difference in distance traveled is an *integral number of wavelengths*, the waves will still be in phase.

Since the distance traveled depends on the distance between the atoms, the diffraction pattern can be used to determine the interatomic spacings. The exact relationship can be worked out using the diagram in Fig. 10.11, which shows two in-phase waves being reflected by atoms in two different layers in a crystal. The extra distance traveled by the lower wave is the sum of the distances xy and yz , and the waves will be in phase after reflection if

$$xy + yz = n\lambda \quad (10.1)$$

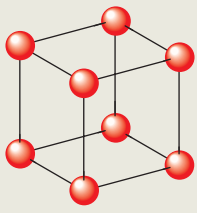
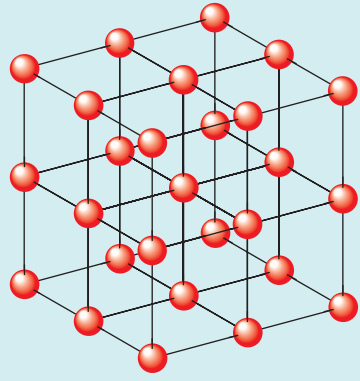
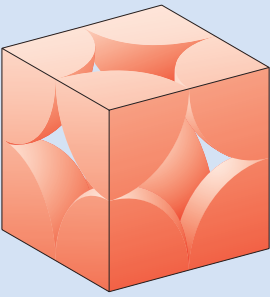
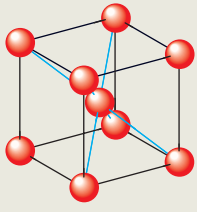
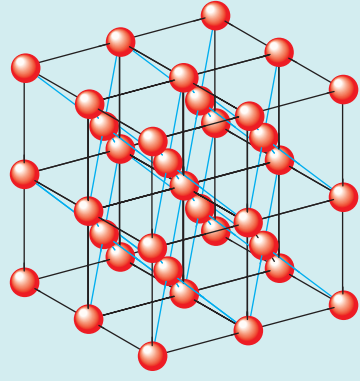
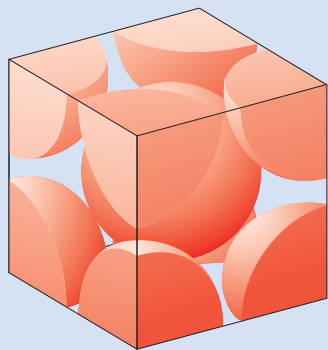
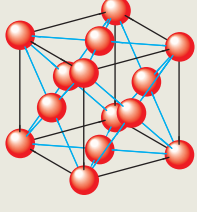
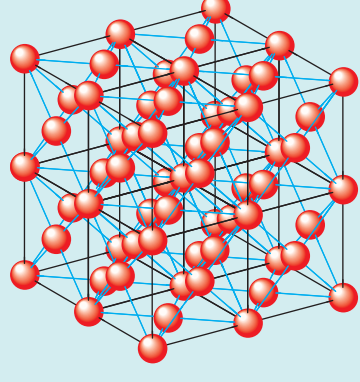
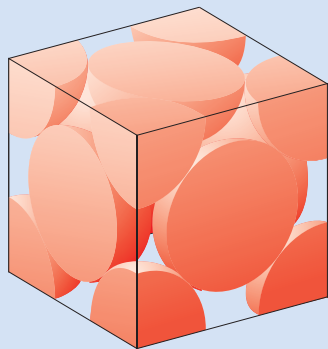
	Unit cell	Lattice	Space-filling unit cell	Example
(a)	 <p>Simple cubic</p>			Polonium metal
(b)	 <p>Body-centered cubic</p>			Uranium metal
(c)	 <p>Face-centered cubic</p>			Gold metal

FIGURE 10.9 Three cubic unit cells and the corresponding lattices. Note that only parts of spheres on the corners and faces of the unit cells reside inside the unit cell, as shown by the “cutoff” versions.

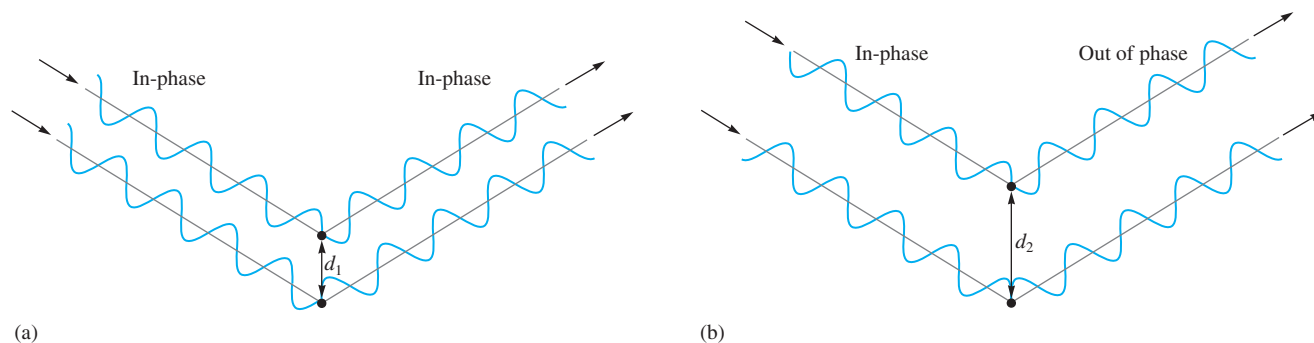
where n is an integer and λ is the wavelength of the X rays. Using trigonometry (see Fig. 10.11), we can show that

$$xy + yz = 2d \sin \theta \quad (10.2)$$

where d is the distance between the atoms and θ is the angle of incidence and reflection. Combining Equation (10.1) and Equation (10.2) gives

$$n\lambda = 2d \sin \theta \quad (10.3)$$

Equation (10.3) is called the *Bragg equation* after William Henry Bragg (1862–1942) and his son William Lawrence Bragg (1890–1972), who shared the Nobel Prize in physics in 1915 for their pioneering work in X-ray crystallography.

**FIGURE 10.10**

X rays scattered from two different atoms may reinforce (constructive interference) or cancel (destructive interference) one another. (a) Both the incident rays and the reflected rays are also in phase. In this case, d_1 is such that the difference in the distances traveled by the two rays is a whole number of wavelengths. (b) The incident rays are in phase but the reflected rays are exactly out of phase. In this case d_2 is such that the difference in distances traveled by the two rays is an odd number of half wavelengths.

A diffractometer is a computer-controlled instrument used for carrying out the X-ray analysis of crystals. It rotates the crystal with respect to the X-ray beam and collects the data produced by the scattering of the X rays from the various planes of atoms in the crystal. The results are then analyzed by computer.

The techniques for crystal structure analysis have reached a level of sophistication that allows the determination of very complex structures, such as those important in biological systems. For example, the structures of several enzymes have been determined, thus enabling biochemists to understand how they perform their functions. We will explore this topic further in Chapter 12. Using X-ray diffraction, we can gather data on bond lengths and angles and in so doing can test the predictions of our models of molecular geometry.

Sample Exercise 10.1

Using the Bragg Equation



Graduate student Maria Zhuravlera operating an X-ray diffractometer at Michigan State University.

X rays of wavelength 1.54 \AA were used to analyze an aluminum crystal. A reflection was produced at $\theta = 19.3$ degrees. Assuming $n = 1$, calculate the distance d between the planes of atoms producing this reflection.

Solution

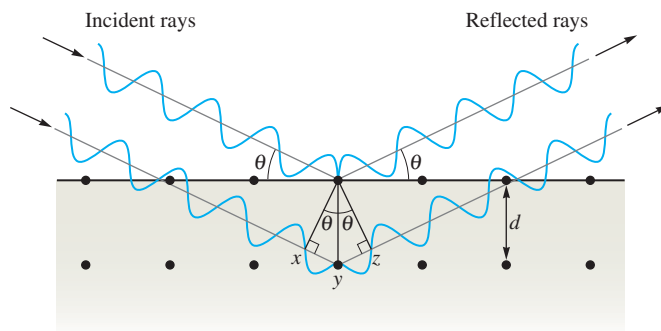
To determine the distance between the planes, we use Equation (10.3) with $n = 1$, $\lambda = 1.54 \text{ \AA}$, and $\theta = 19.3$ degrees. Since $2d \sin \theta = n\lambda$,

$$d = \frac{n\lambda}{2 \sin \theta} = \frac{(1)(1.54 \text{ \AA})}{(2)(0.3305)} = 2.33 \text{ \AA} = 233 \text{ pm}$$

See Exercises 10.41 through 10.44.

FIGURE 10.11

Reflection of X rays of wavelength λ from a pair of atoms in two different layers of a crystal. The lower wave travels an extra distance equal to the sum of xy and yz . If this distance is an integral number of wavelengths ($n = 1, 2, 3, \dots$), the waves will reinforce each other when they exit the crystal.



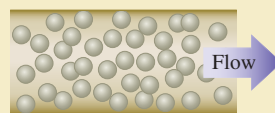
CHEMICAL IMPACT

Smart Fluids

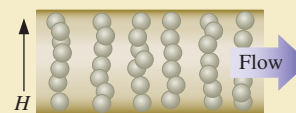
Matter seems to be getting smarter these days. Increasingly, we have discovered materials that can remember their initial shape after being deformed or can sense and respond to their environment. In particular, valuable new materials have been formulated whose properties can be changed instantly by applying a magnetic or electric field.

One example of such a substance is a fluid whose flow characteristics (rheology) can be changed from free flowing to almost solid in about 0.01 second by the application of an electromagnetic field. This “magnetorheological” (MR) fluid was developed by Lord Corporation. Working in collaboration with Delphi Corporation, the company is applying the fluid in suspension control of General Motors automobiles such as Cadillacs and Corvettes. The so-called Magneride system has sensors that monitor the road surface and provide information about what suspension damping is needed. In response, a message is instantly sent to an electromagnetic coil in the shock absorbers, which adjusts the viscosity of the MR fluid to provide continuously variable damping. The result: an amazingly smooth ride and unerring road-holding ability.

The MR fluid is composed of a synthetic oil in which particles of an iron-containing compound are suspended. When



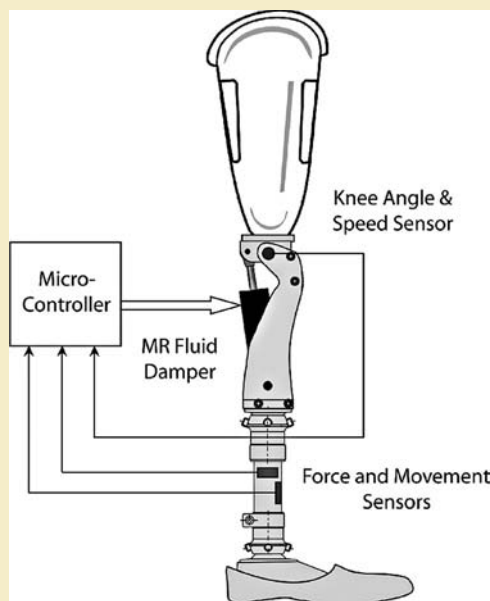
Magnetic field off
Magnetic particles flow randomly



Magnetic field on
Applied field (H) creates structure that increases viscosity

the magnetic field is turned off, these particles flow freely in all directions (see the figure above). When the field is turned on, the particles aggregate into chains that line up perpendicular to the flow of the fluid, thereby increasing its viscosity in proportion to the strength of the applied field.

Many other applications of MR fluids besides auto suspensions are under development. For example, this technology is being used in a prosthesis (see below) for above-the-knee amputees, which gives them a more natural gait and improves stair climbing. One very large-scale application is in Japan’s National Museum of Emerging Science and Innovation, where an MR fluid is being used in dampers to protect the building against earthquake damage. Large MR-fluid dampers are also being used for stabilizing bridges such as the Dong Ting Lake Bridge in China’s Hunan province to steady it in high winds.



This High Intelligence Prosthesis for the knee uses an MR fluid damper to provide motion that closely duplicates the natural movement of the knee joint.

Types of Crystalline Solids

There are many different types of crystalline solids. For example, although both sugar and salt dissolve readily in water, the properties of the resulting solutions are quite different. The salt solution readily conducts an electric current, whereas the sugar solution does not. This behavior arises from the nature of the components in these two solids. Common salt (NaCl) is an ionic solid; it contains Na^+ and Cl^- ions. When solid sodium chloride dissolves in the polar water, sodium and chloride ions are distributed throughout the resulting solution and are free to conduct electric current. Table sugar (sucrose), on the other hand, is composed of neutral molecules that are dispersed throughout the water when the solid dissolves. No ions are present, and the resulting solution does not conduct electricity. These examples illustrate two important types of solids: **ionic solids**, represented by sodium chloride, and **molecular solids**, represented by sucrose. Ionic solids have ions at the points of the lattice that describes the structure of the solid. A molecular solid, on the other hand, has discrete covalently bonded molecules at each of its lattice points. Ice is a molecular solid that has an H_2O molecule at each point (see Fig. 10.12).

Buckminsterfullerene, C_{60} , is a particular member of the fullerene family.

A third type of solid is represented by elements such as carbon (which exists in the forms graphite, diamond, and the fullerenes), boron, silicon, and all metals. These substances all have atoms at the lattice points that describe the structure of the solid. Therefore, we call solids of this type **atomic solids**. Examples of these three types of solids are shown in Fig. 10.12.

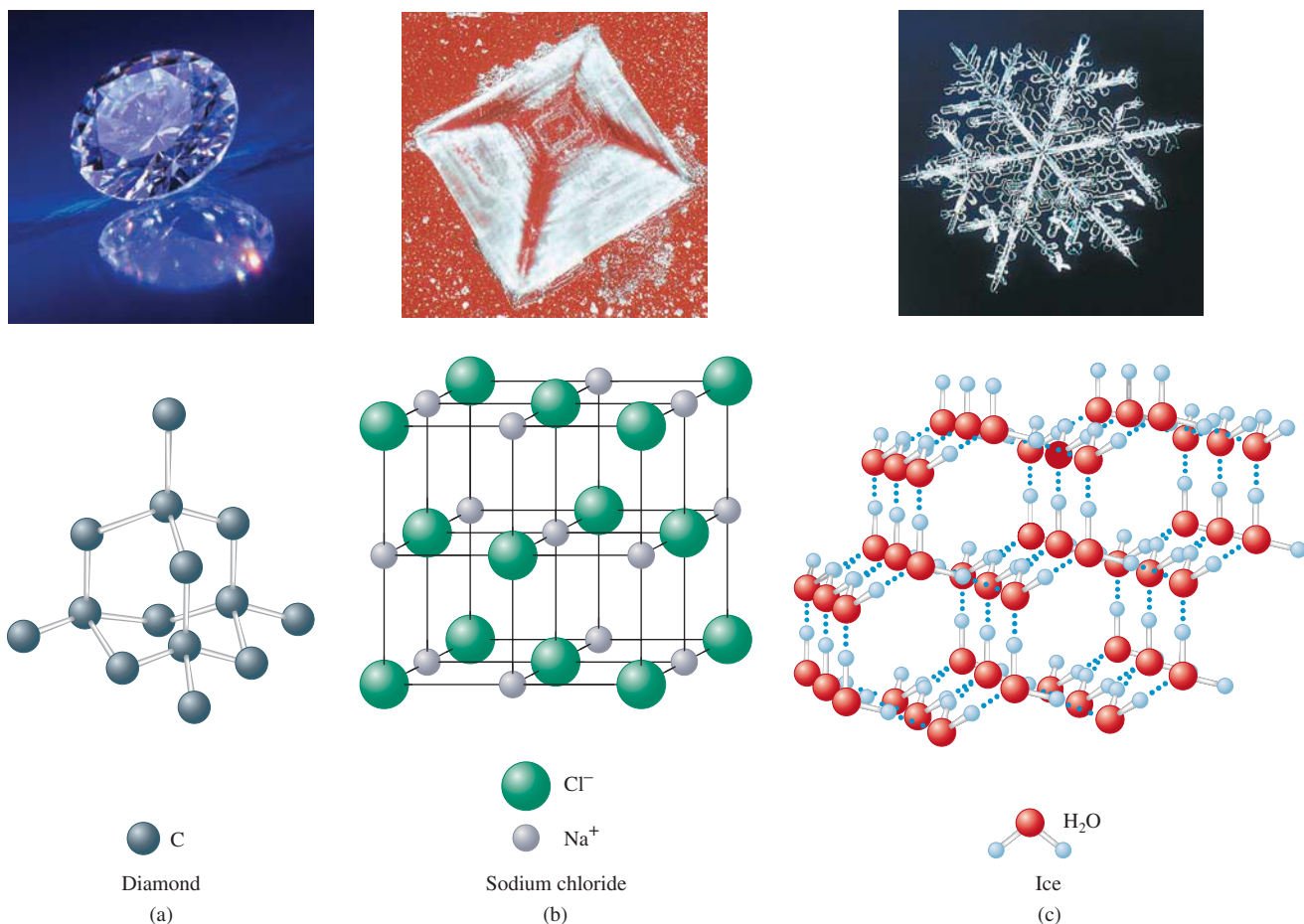


FIGURE 10.12

Examples of three types of crystalline solids. Only part of the structure is shown in each case. (a) An atomic solid. (b) An ionic solid. (c) A molecular solid. The dotted lines show the hydrogen bonding interactions among the polar water molecules.

TABLE 10.3 Classification of Solids

	Atomic Solids				
	<i>Metallic</i>	<i>Network</i>	<i>Group 8A</i>	<i>Molecular Solids</i>	<i>Ionic Solids</i>
Components That Occupy the Lattice Points:	Metal atoms	Nonmetal atoms	Group 8A atoms	Discrete molecules	Ions
Bonding:	Delocalized covalent	Directional covalent (leading to giant molecules)	London dispersion forces	Dipole–dipole and/or London dispersion forces	Ionic

To summarize, we find it convenient to classify solids according to what type of component occupies the lattice points. This leads to the classifications *atomic solids* (atoms at the lattice points), *molecular solids* (discrete, relatively small molecules at the lattice points), and *ionic solids* (ions at the lattice points). In addition, atomic solids are placed into the following subgroups based on the bonding that exists among the atoms in the solid: *metallic solids*, *network solids*, and *Group 8A solids*. In metallic solids, a special type of delocalized nondirectional covalent bonding occurs. In network solids, the atoms bond to each other with strong directional covalent bonds that lead to giant molecules, or networks, of atoms. In the Group 8A solids, the noble gas elements are attracted to each other with London dispersion forces. The classification of solids is summarized in Table 10.3.

The markedly different bonding present in the various atomic solids leads to dramatically different properties for the resulting solids. For example, although argon, copper, and diamond all are atomic solids, they have strikingly different properties. Argon (a Group 8A solid) has a very low melting point (-189°C), whereas diamond (a network solid) and copper (a metallic solid) melt at high temperatures (about 3500 and 1083°C , respectively). Copper is an excellent conductor of electricity, whereas argon and diamond are both insulators. Copper can be easily changed in shape; it is both malleable (can be formed into thin sheets) and ductile (can be pulled into a wire). Diamond, on the other hand, is the hardest natural substance known. We will explore the structure and bonding of atomic solids in the next two sections.

10.4 Structure and Bonding in Metals

Metals are characterized by high thermal and electrical conductivity, malleability, and ductility. As we will see, these properties can be traced to the nondirectional covalent bonding found in metallic crystals.

A metallic crystal can be pictured as containing spherical atoms packed together and bonded to each other equally in all directions. We can model such a structure by packing uniform, hard spheres in a manner that most efficiently uses the available space. Such an arrangement is called **closest packing**. The spheres are packed in layers, as shown in Fig. 10.13, in which each sphere is surrounded by six others. In the second layer the spheres do not lie directly over those in the first layer. Instead, each one occupies an indentation (or dimple) formed by three spheres in the first layer. In the third layer the spheres can occupy the dimples of the second layer in two possible ways: They can occupy positions so that each sphere in the third layer lies directly over a sphere in the first layer (the *aba* arrangement; Fig. 10.13a), or they can occupy positions so that no sphere in the third layer lies over one in the first layer (the *abc* arrangement; Fig. 10.13b).

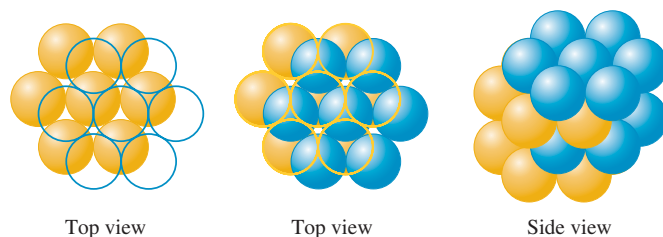
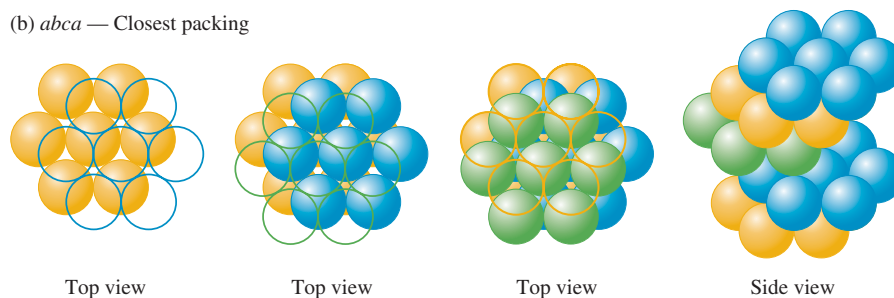
The *aba* arrangement has the *hexagonal* unit cell shown in Fig. 10.14, and the resulting structure is called the **hexagonal closest packed (hcp) structure**. The *abc* arrangement has a *face-centered cubic* unit cell, as shown in Fig. 10.15, and the resulting structure is

The internal forces in a solid determine the properties of the solid.

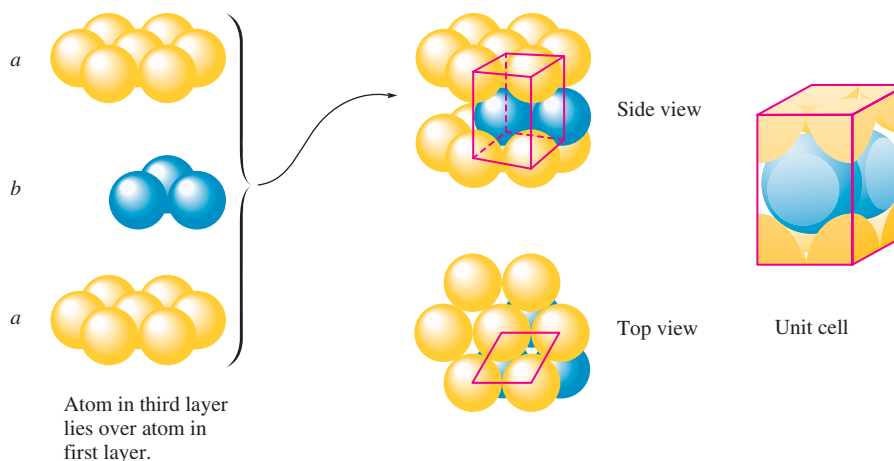
The closest packing model for metallic crystals assumes that metal atoms are uniform, hard spheres.



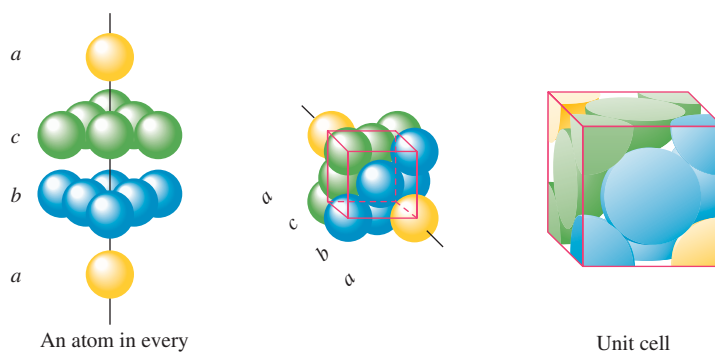
Visualization: Electron Sea Model

(a) *abab* — Closest packing(b) *abca* — Closest packing**FIGURE 10.13**

The closest packing arrangement of uniform spheres. In each layer a given sphere is surrounded by six others, creating six dimples, only three of which can be occupied in the next layer. (a) *aba* packing: The second layer is like the first, but it is displaced so that each sphere in the second layer occupies a dimple in the first layer. The spheres in the third layer occupy dimples in the second layer so that the spheres in the third layer lie directly over those in the first layer (*aba*). (b) *abc* packing: The spheres in the third layer occupy dimples in the second layer so that no spheres in the third layer lie above any in the first layer (*abc*). The fourth layer is like the first.

**FIGURE 10.14**

When spheres are closest packed so that the spheres in the third layer are directly over those in the first layer (*aba*), the unit cell is the hexagonal prism illustrated here in red.

**FIGURE 10.15**

When spheres are packed in the *abc* arrangement, the unit cell is face-centered cubic. To make the cubic arrangement easier to see, the vertical axis has been tilted as shown.

An atom in every fourth layer lies over an atom in the first layer.



CHEMICAL IMPACT

Seething Surfaces

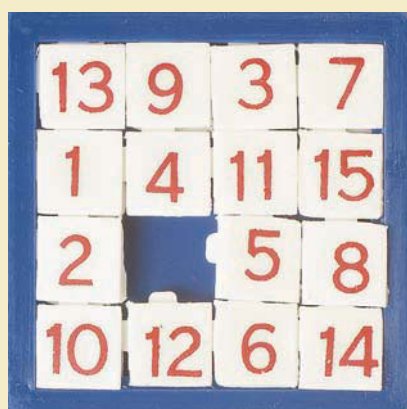
When we picture a solid, we think of the particles as being packed closely together with relatively little motion. The particles are thought to vibrate randomly about their positions but stay in nearly the same place. Recent research, however, indicates surface particles are a great deal more mobile than was previously thought. Independent teams of scientists from the University of Leiden in the Netherlands and Sandia National Laboratory in New Mexico have found a surprising amount of atom-swapping occurring on the surface of a copper crystal.

The Dutch scientist Raoul van Gastel and his colleagues used a scanning tunneling microscope (STM) to study the surface of a copper crystal containing indium atom impurities. They noted that a given patch of surface would stay the same for several scans and then, suddenly, the indium atoms would appear at different places. Surprisingly, the indium atoms seemed to make “long jumps,” moving as many as five atom positions between scans. The most likely explanation for these movements is a “hole” created by a copper atom escaping the surface. This hole moves around as other atoms shift to fill it in succession (see accompanying figure). The best analogy to the movement of the hole is the toy slide puzzle with 15 numbered pieces and one missing

piece in a 4×4 array. The object of the game is to slide a piece into the hole and then repeat the process until the numbers appear in order.

The hole on the copper surface moves very fast—up to 100 million times per second—shuffling copper atoms and allowing the indium atoms to change positions. Van Gastel believes that all of the observed motion results from just a few fast-moving holes. In fact, he suggests that just one in 6 billion copper atoms is missing at a given time, analogous to one person in the entire earth’s population. Its absence causes a given atom on the surface to move every 30 or 40 seconds. Brian Swartzentruber of Sandia National Laboratories came to similar conclusions using an STM to track the movement of palladium atoms on a copper surface.

These results have important implications. For example, metal surfaces are often used to speed up particular reactions. The motions on the metal surface could significantly influence the way that reactants interact with the surface. Also, a lot of effort is now being expended to construct tiny “machines” (called nanoscale devices) by assembling individual atoms on a solid surface. These devices could be literally torn apart by excess surface motions.



A toy slide puzzle.

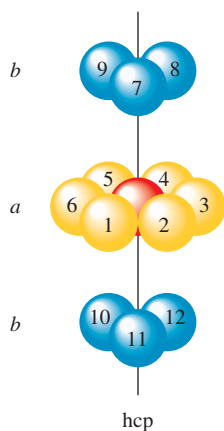


FIGURE 10.16
The indicated sphere has 12 nearest neighbors.

called the **cubic closest packed (ccp) structure**. Note that in the hcp structure the spheres in every other layer occupy the same vertical position (*ababab · · ·*), whereas in the ccp structure the spheres in every fourth layer occupy the same vertical position (*abcabca · · ·*). A characteristic of both structures is that each sphere has 12 equivalent nearest neighbors: 6 in the same layer, 3 in the layer above, and 3 in the layer below (that form the dimples). This is illustrated for the hcp structure in Fig. 10.16.

Knowing the *net* number of spheres (atoms) in a particular unit cell is important for many applications involving solids. To illustrate how to find the net number of spheres in a unit cell, we will consider a face-centered cubic unit cell (Fig. 10.17). Note that this unit cell is defined by the *centers* of the spheres on the cube's corners. Thus 8 cubes share a given sphere, so $\frac{1}{8}$ of this sphere lies inside each unit cell. Since a cube has 8 corners, there are $8 \times \frac{1}{8}$ pieces, or enough to put together 1 whole sphere. The spheres at the center of each face are shared by 2 unit cells, so $\frac{1}{2}$ of each lies inside a particular unit cell. Since the cube has 6 faces, we have $6 \times \frac{1}{2}$ pieces, or enough to construct 3 whole spheres. Thus the net number of spheres in a face-centered cubic unit cell is

$$\left(8 \times \frac{1}{8}\right) + \left(6 \times \frac{1}{2}\right) = 4$$

Sample Exercise 10.2

Calculating the Density of a Closest Packed Solid

Silver crystallizes in a cubic closest packed structure. The radius of a silver atom is 144 pm. Calculate the density of solid silver.

Solution

Density is mass per unit volume. Thus we need to know how many silver atoms occupy a given volume in the crystal. The structure is cubic closest packed, which means the unit cell is face-centered cubic, as shown in the accompanying figure.

We must find the volume of this unit cell for silver and the net number of atoms it contains. Note that in this structure the atoms touch along the diagonals for each

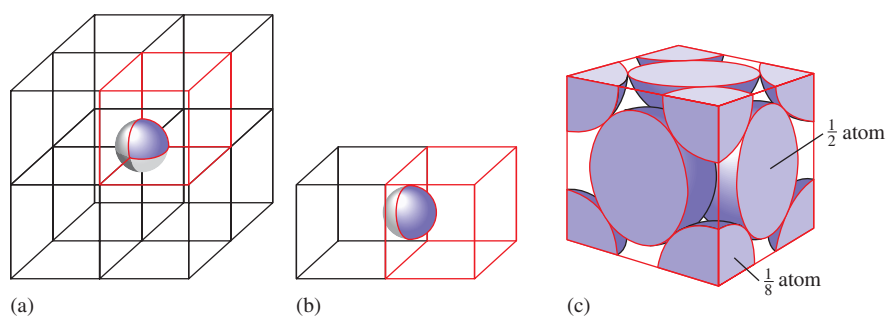
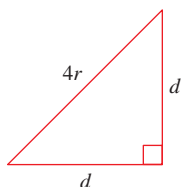
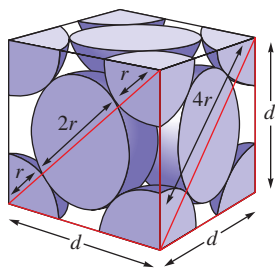


FIGURE 10.17

The net number of spheres in a face-centered cubic unit cell. (a) Note that the sphere on a corner of the colored cell is shared with 7 other unit cells (a total of 8). Thus $\frac{1}{8}$ of such a sphere lies within a given unit cell. Since there are 8 corners in a cube, there are 8 of these $\frac{1}{8}$ pieces, or 1 net sphere. (b) The sphere on the center of each face is shared by 2 unit cells, and thus each unit cell has $\frac{1}{2}$ of each of these types of spheres. There are 6 of these $\frac{1}{2}$ spheres to give 3 net spheres. (c) Thus the face-centered cubic unit cell contains 4 net spheres (all of the pieces can be assembled to give 4 spheres).



Crystalline silver contains cubic closest packed silver atoms.

Malleable: Can be pounded into thin sheets.

Ductile: Can be drawn to form a wire.

face and not along the edges of the cube. Thus the length of the diagonal is $r + 2r + r$, or $4r$. We use this fact to find the length of the edge of the cube by the Pythagorean theorem:

$$\begin{aligned}d^2 + d^2 &= (4r)^2 \\2d^2 &= 16r^2 \\d^2 &= 8r^2 \\d &= \sqrt{8r^2} = r\sqrt{8}\end{aligned}$$

Since $r = 144$ pm for a silver atom,

$$d = (144 \text{ pm})(\sqrt{8}) = 407 \text{ pm}$$

The volume of the unit cell is d^3 , which is $(407 \text{ pm})^3$, or $6.74 \times 10^7 \text{ pm}^3$. We convert this to cubic centimeters as follows:

$$6.74 \times 10^7 \text{ pm}^3 \times \left(\frac{1.00 \times 10^{-10} \text{ cm}}{\text{pm}}\right)^3 = 6.74 \times 10^{-23} \text{ cm}^3$$

Since we know that the net number of atoms in the face-centered cubic unit cell is 4, we have 4 silver atoms contained in a volume of $6.74 \times 10^{-23} \text{ cm}^3$. The density is therefore

$$\begin{aligned}\text{Density} &= \frac{\text{mass}}{\text{volume}} = \frac{(4 \text{ atoms})(107.9 \text{ g/mol})(1 \text{ mol}/6.022 \times 10^{23} \text{ atoms})}{6.74 \times 10^{-23} \text{ cm}^3} \\&= 10.6 \text{ g/cm}^3\end{aligned}$$

See Exercises 10.45 through 10.48.

Examples of metals that form cubic closest packed solids are aluminum, iron, copper, cobalt, and nickel. Magnesium and zinc are hexagonal closest packed. Calcium and certain other metals can crystallize in either of these structures. Some metals, however, assume structures that are not closest packed. For example, the alkali metals have structures characterized by a *body-centered cubic (bcc) unit cell* (see Fig. 10.9), where the spheres touch along the body diagonal of the cube. In this structure, each sphere has 8 nearest neighbors (count the number of atoms around the atom at the center of the unit cell), as compared with 12 in the closest packed structures. Why a particular metal adopts the structure it does is not well understood.

Bonding Models for Metals

Any successful bonding model for metals must account for the typical physical properties of metals: malleability, ductility, and the efficient and uniform conduction of heat and electricity in all directions. Although the shapes of most pure metals can be changed relatively easily, most metals are durable and have high melting points. These facts indicate that the bonding in most metals is both *strong* and *nondirectional*. That is, although it is difficult to separate metal atoms, it is relatively easy to move them, provided the atoms stay in contact with each other.

The simplest picture that explains these observations is the *electron sea model*, which envisions a regular array of metal cations in a “sea” of valence electrons (see Fig. 10.18). The mobile electrons can conduct heat and electricity, and the metal ions can be easily moved around as the metal is hammered into a sheet or pulled into a wire.



CHEMICAL IMPACT

Closest Packing of M & Ms

Although we usually think of scientists as dealing with esoteric and often toxic materials, sometimes they surprise us. For example, scientists at several prestigious universities have lately shown a lot of interest in M & M candies.

To appreciate the scientists' interest in M & Ms, we must consider the importance of packing atoms, molecules, or microcrystals in understanding the structures of solids. The most efficient use of space is the closest packing of uniform spheres, where 74% of the space is occupied by the spheres and 26% of space is left unoccupied. Although the structures of most pure metals can be explained in terms of closest packing, most other substances—such as many alloys and ceramics—consist of random arrays of microscopic particles. For this reason, it is of interest to study how such objects pack in a random way.

When uniform spheres, such as marbles, are poured into a large container, the resulting random packing of the spheres results in only 64% of the space being occupied by the spheres. Thus it was very surprising when Princeton University chemist Salvatore Torquato and his colleagues at Cornell and North Carolina Central Universities discovered that, when the ellipsoidal-shaped M & Ms are poured into a large container, the candies occupy 73.5% of the available space. In other words, the randomly packed M & Ms occupy space with almost the same efficiency as closest packed spheres do.

Why do randomly packed ellipsoids occupy space so much more efficiently than randomly packed spheres? The

scientists speculate that because the ellipsoids can tip and rotate in ways that spheres cannot, they can pack more closely to their neighbors.

According to Torquato, these results are important because they will help us better understand the properties of disordered materials ranging from powders to glassy solids. He also says that M & Ms make ideal test objects because they are inexpensive and uniform and “you can eat the experiment afterward.”



A related model that gives a more detailed view of the electron energies and motions is the **band model**, or **molecular orbital (MO) model**, for metals. In this model, the electrons are assumed to travel around the metal crystal in molecular orbitals formed from the valence atomic orbitals of the metal atoms (Fig. 10.19).

Recall that in the MO model for the gaseous Li_2 molecule (Section 9.3), two widely spaced molecular orbital energy levels (bonding and antibonding) result when two identical atomic orbitals interact. However, when many metal atoms interact,

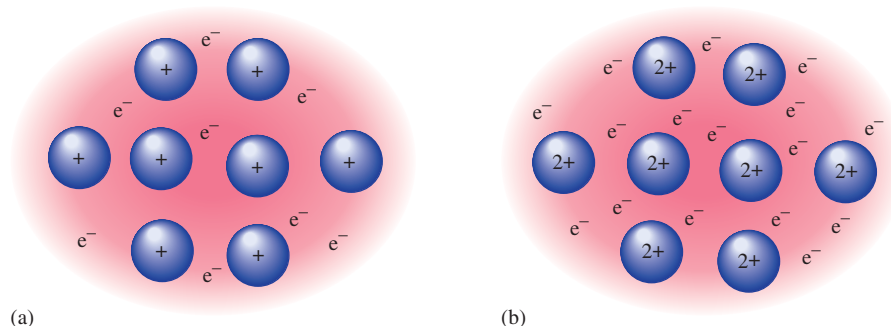
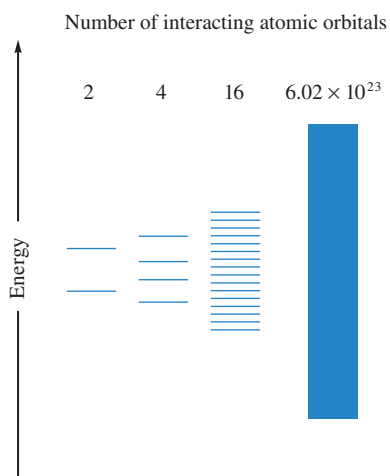


FIGURE 10.18

The electron sea model for metals postulates a regular array of cations in a “sea” of valence electrons. (a) Representation of an alkali metal (Group 1A) with one valence electron. (b) Representation of an alkaline earth metal (Group 2A) with two valence electrons.

**FIGURE 10.19**

The molecular orbital energy levels produced when various numbers of atomic orbitals interact. Note that for two atomic orbitals two rather widely spaced energy levels result. (Recall the description of H_2 in Section 9.2.) As more atomic orbitals are available to form molecular orbitals, the resulting energy levels are more closely spaced, finally producing a band of very closely spaced orbitals.

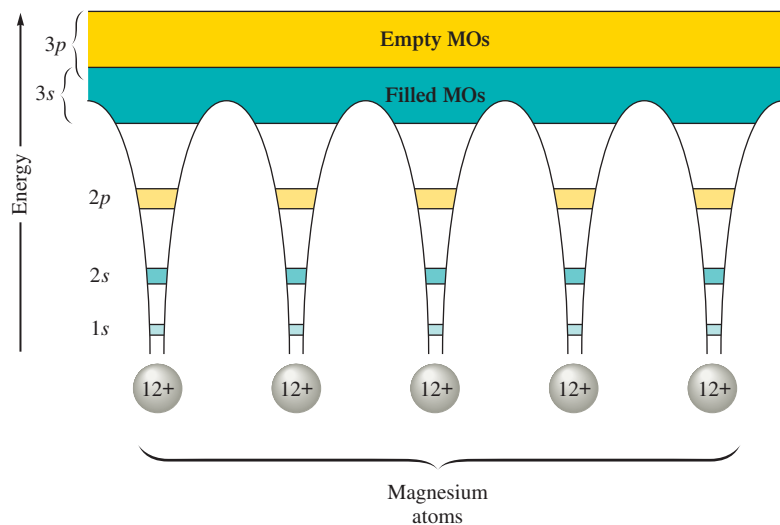
as in a metal crystal, the large number of resulting molecular orbitals become more closely spaced and finally form a virtual continuum of levels, called *bands*, as shown in Fig. 10.19.

As an illustration, picture a magnesium metal crystal, which has an hcp structure. Since each magnesium atom has one $3s$ and three $3p$ valence atomic orbitals, a crystal with n magnesium atoms has available $n(3s)$ and $3n(3p)$ orbitals to form the molecular orbitals, as illustrated in Fig. 10.20. Note that the core electrons are localized, as shown by their presence in the energy “well” around each magnesium atom. However, the valence electrons occupy closely spaced molecular orbitals, which are only partially filled.

The existence of empty molecular orbitals close in energy to filled molecular orbitals explains the thermal and electrical conductivity of metal crystals. Metals conduct electricity and heat very efficiently because of the availability of highly mobile electrons. For example, when an electric potential is placed across a strip of metal, for current to flow, electrons must be free to move. In the band model for metals, the electrons in partially filled bands are mobile. These conduction electrons are free to travel throughout the metal crystal as dictated by the potential imposed on the metal. The molecular orbitals occupied by these conducting electrons are called *conduction bands*. These mobile electrons also account for the efficiency of the conduction of heat through metals. When one end of a metal rod is heated, the mobile electrons can rapidly transmit the thermal energy to the other end.

Metal Alloys

Because of the nature of the structure and bonding of metals, other elements can be introduced into a metallic crystal relatively easily to produce substances called alloys. An **alloy** is best defined as *a substance that contains a mixture of elements and has metallic properties*. Alloys can be conveniently classified into two types.

**FIGURE 10.20**

(left) A representation of the energy levels (bands) in a magnesium crystal. The electrons in the $1s$, $2s$, and $2p$ orbitals are close to the nuclei and thus are localized on each magnesium atom as shown. However, the $3s$ and $3p$ valence orbitals overlap and mix to form molecular orbitals. Electrons in these energy levels can travel throughout the crystal. (right) Crystals of magnesium grown from a vapor.



CHEMICAL IMPACT

What Sank the Titanic?

On April 12, 1912, the steamship *Titanic* struck an iceberg in the North Atlantic approximately 100 miles south of the Grand Banks of Newfoundland and within 3 hours was resting on the bottom of the ocean. Of her more than 2300 passengers and crew, over 1500 lost their lives. While the tragic story of the *Titanic* has never faded from the minds and imaginations of the generations that followed, the 1985 discovery of the wreck by a joint Franco-American expedition at a depth of 12,612 feet rekindled the world's interest in the “greatest oceangoing vessel” ever built. The discovery also would reveal important scientific clues as to why and how the *Titanic* sank so quickly in the frigid waters of the North Atlantic.

The *Titanic* was designed to be virtually “unsinkable,” and even in the worst-case scenario, a head-on collision with another ocean liner, the ship was engineered to take from one to three days to sink. Thus its quick trip to the bottom has puzzled scientists for years. In 1991, Steve Blasco, an ocean-floor geologist for the Canadian Department of Natural Resources, led a scientific expedition to the wreck. On one of 17 dives to the site, Blasco's team recovered a piece of steel that appeared to be a part of the *Titanic*'s hull. Unlike modern steel, which would have shown evidence of bending in a collision, the steel recovered from the *Titanic* appeared to have shattered on impact with the iceberg. This suggested that the metal might not have been as ductile (*ductility* is the ability to stretch without breaking) as it should have been. In 1994, tests were conducted on small pieces of metal, called *coupons*, cut from the recovered piece of hull. These samples shattered without bending. Further analysis showed that the steel used to construct the hull of the *Titanic* was high in sulfur content, and it is known that sulfur

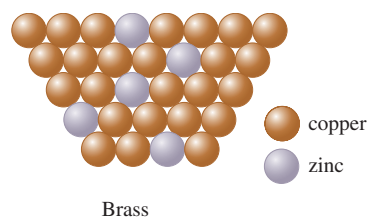
occlusions tend to make steel more brittle. This evidence suggests that the quality of the steel used to make the hull of the *Titanic* may very well have been an important factor that led to the rapid sinking of the ship.

But—not so fast. The *Titanic* continues to provoke controversy. A team of naval engineers and scientists recently have concluded that it was not brittle steel but faulty rivets that doomed the *Titanic*. During expeditions in 1996 and 1998 conducted by RMS Titanic, Inc., more samples of *Titanic*'s steel and rivets were obtained for further study. Analysis of these samples by a team headed by Tim Foecke of the National Institute of Standards and Technology (NIST) shows that the rivets contain three times the expected amount of silicate slag. Foecke and his colleagues argue that the high slag content resulted in weak rivets that snapped in large numbers when the collision occurred, mortally wounding the ship.

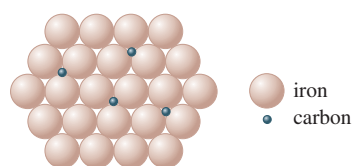
What sank the *Titanic*? It hit an iceberg. The details remain to be figured out.



Bow of the *Titanic* under $2\frac{1}{2}$ miles of water.



(a)

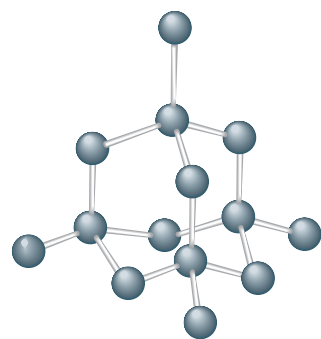


(b)

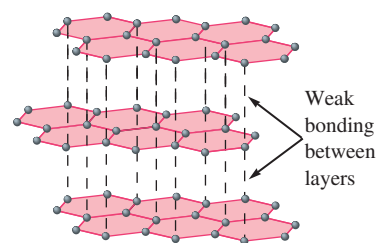
FIGURE 10.21
Two types of alloys.



Visualization: Homogeneous
Mixtures: Air and Brass



(a)



(b)

FIGURE 10.22
The structures of diamond and graphite. In each case only a small part of the entire structure is shown.

TABLE 10.4 The Composition of the Two Brands of Steel Tubing Commonly Used to Make Lightweight Racing Bicycles

Brand of Tubing	% C	% Si	% Mn	% Mo	% Cr
Reynolds	0.25	0.25	1.3	0.20	—
Columbus	0.25	0.30	0.65	0.20	1.0

In a **substitutional alloy** some of the host metal atoms are *replaced* by other metal atoms of similar size. For example, in brass, approximately one-third of the atoms in the host copper metal have been replaced by zinc atoms, as shown in Fig. 10.21(a). Sterling silver (93% silver and 7% copper), pewter (85% tin, 7% copper, 6% bismuth, and 2% antimony), and plumber's solder (95% tin and 5% antimony) are other examples of substitutional alloys.

An **interstitial alloy** is formed when some of the interstices (holes) in the closest packed metal structure are occupied by small atoms, as shown in Fig. 10.21(b). Steel, the best-known interstitial alloy, contains carbon atoms in the holes of an iron crystal. The presence of the interstitial atoms changes the properties of the host metal. Pure iron is relatively soft, ductile, and malleable due to the absence of directional bonding. The spherical metal atoms can be rather easily moved with respect to each other. However, when carbon, which forms strong directional bonds, is introduced into an iron crystal, the presence of the directional carbon–iron bonds makes the resulting alloy harder, stronger, and less ductile than pure iron. The amount of carbon directly affects the properties of steel. *Mild steels*, containing less than 0.2% carbon, are ductile and malleable and are used for nails, cables, and chains. *Medium steels*, containing 0.2 to 0.6% carbon, are harder than mild steels and are used in rails and structural steel beams. *High-carbon steels*, containing 0.6 to 1.5% carbon, are tough and hard and are used for springs, tools, and cutlery.

Many types of steel also contain elements in addition to iron and carbon. Such steels are often called *alloy steels*, and they can be viewed as being mixed interstitial (carbon) and substitutional (other metals) alloys. Bicycle frames, for example, are constructed from a wide variety of alloy steels. The compositions of the two brands of steel tubing most commonly used in expensive racing bicycles are given in Table 10.4.

10.5 Carbon and Silicon: Network Atomic Solids

Many atomic solids contain strong directional covalent bonds to form a solid that might best be viewed as a “giant molecule.” We call these substances **network solids**. In contrast to metals, these materials are typically brittle and do not efficiently conduct heat or electricity. To illustrate network solids, in this section we will discuss two very important elements, carbon and silicon, and some of their compounds.

The two most common forms of carbon, diamond and graphite, are typical network solids. In diamond, the hardest naturally occurring substance, each carbon atom is surrounded by a tetrahedral arrangement of other carbon atoms to form a huge molecule [see Fig. 10.22(a)]. This structure is stabilized by covalent bonds, which, in terms of the localized electron model, are formed by the overlap of sp^3 hybridized carbon atomic orbitals.

It is also useful to consider the bonding among the carbon atoms in diamond in terms of the molecular orbital model. Energy-level diagrams for diamond and a typical metal are given in Fig. 10.23. Recall that the conductivity of metals can be explained by

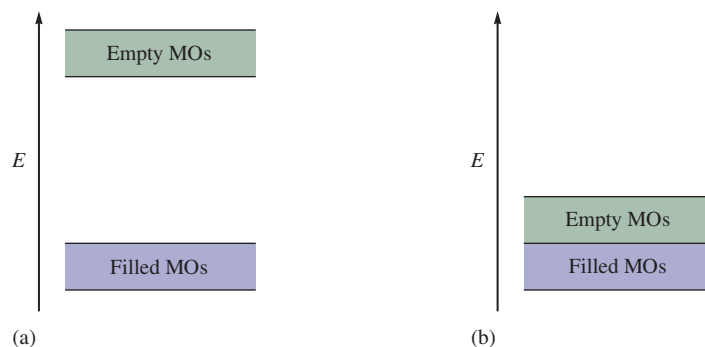


FIGURE 10.23

Partial representation of the molecular orbital energies in (a) diamond and (b) a typical metal.



Visualization: Network Solids



Graphite and diamond, two forms of carbon.

postulating that electrons are excited from filled levels into the very near empty levels, or conduction bands. However, note that in the energy-level diagram for diamond there is a *large gap between the filled and the empty levels*. This means that electrons cannot be transferred easily to the empty conduction bands. As a result, diamond is not expected to be a good electrical conductor. In fact, this prediction of the model agrees exactly with the observed behavior of diamond, which is known to be an electrical insulator—it does not conduct an electric current.

Graphite is very different from diamond. While diamond is hard, basically colorless, and an insulator, graphite is slippery, black, and a conductor. These differences, of course, arise from the differences in bonding in the two types of solids. In contrast to the tetrahedral arrangement of carbon atoms in diamond, the structure of graphite is based on layers of carbon atoms arranged in fused six-membered rings, as shown in Fig. 10.22(b). Each carbon atom in a particular layer of graphite is surrounded by the three other carbon atoms in a trigonal planar arrangement with 120-degree bond angles. The localized electron model predicts sp^2 hybridization in this case. The three sp^2 orbitals on each carbon are used to form σ bonds with three other carbon atoms. One $2p$ orbital remains unhybridized on each carbon and is perpendicular to the plane of carbon atoms, as shown in Fig. 10.24.

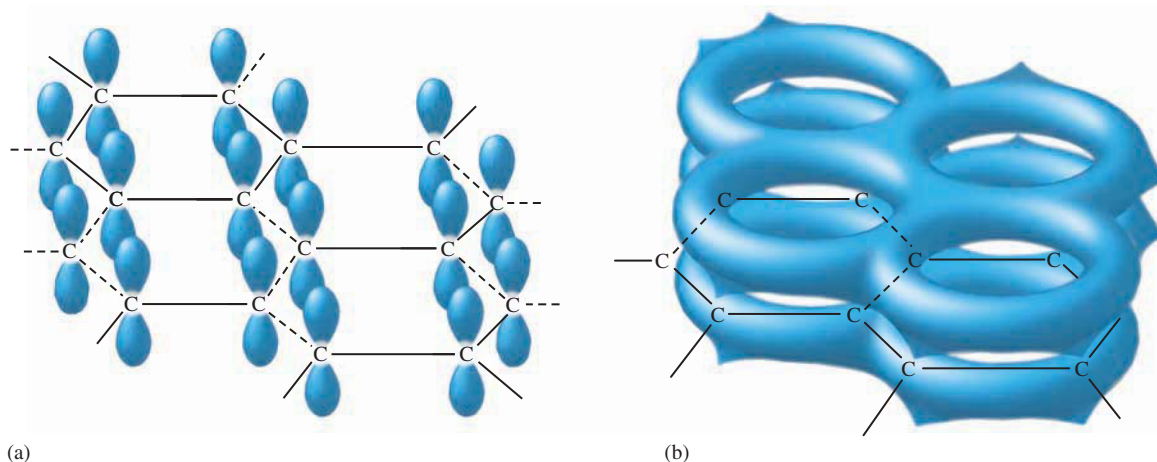


FIGURE 10.24

The p orbitals (a) perpendicular to the plane of the carbon ring system in graphite can combine to form (b) an extensive π -bonding network.

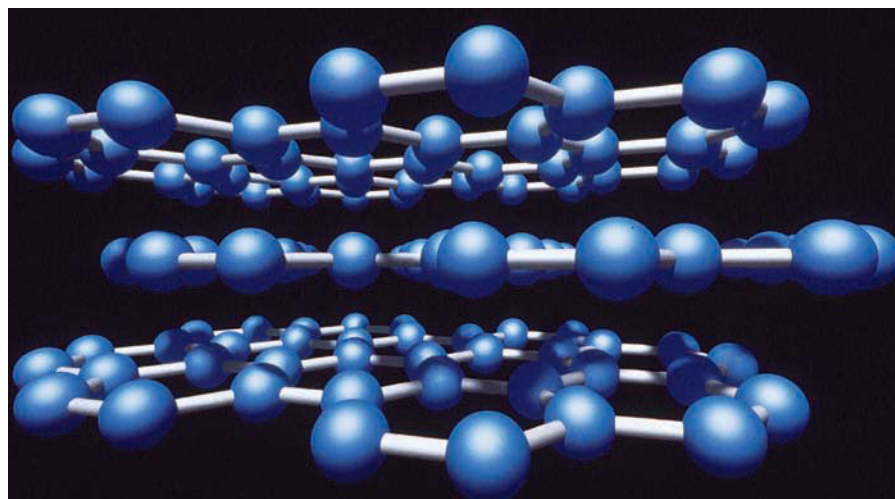


FIGURE 10.25
Graphite consists of layers of carbon atoms.

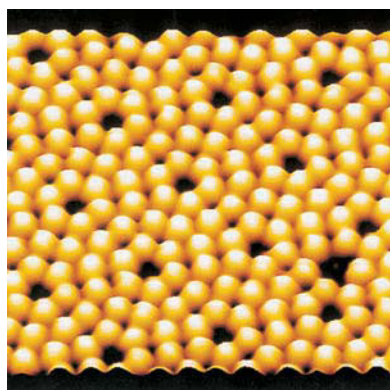
These orbitals combine to form a group of closely spaced π molecular orbitals that are important in two ways. First, they contribute significantly to the stability of the graphite layers because of the π bond formation. Second, the π molecular orbitals with their delocalized electrons account for the electrical conductivity of graphite. These closely spaced orbitals are exactly analogous to the conduction bands found in metal crystals.

Graphite is often used as a lubricant in locks (where oil is undesirable because it collects dirt). The slipperiness that is characteristic of graphite can be explained by noting that graphite has very strong bonding *within* the layers of carbon atoms but little bonding *between* the layers (the valence electrons are all used to form σ and π bonds among carbons within the layers). This arrangement allows the layers to slide past one another quite readily. Graphite's layered structure is shown in Fig. 10.25. This is in contrast to diamond, which has uniform bonding in all directions in the crystal.

Because of their extreme hardness, diamonds are used extensively in industrial cutting implements. Thus it is desirable to convert cheaper graphite to diamond. As we might expect from the higher density of diamond (3.5 g/cm^3) compared with that of graphite (2.2 g/cm^3), this transformation can be accomplished by applying very high pressures to graphite. The application of 150,000 atm of pressure at 2800°C converts graphite virtually completely to diamond. The high temperature is required to break the strong bonds in graphite so the rearrangement can occur.

Silicon is an important constituent of the compounds that make up the earth's crust. In fact, silicon is to geology as carbon is to biology. Just as carbon compounds are the basis for most biologically significant systems, silicon compounds are fundamental to most of the rocks, sands, and soils found in the earth's crust. However, although carbon and silicon are next to each other in Group 4A of the periodic table, the carbon-based compounds of biology and the silicon-based compounds of geology have markedly different structures. Carbon compounds typically contain long strings of carbon-carbon bonds, whereas the most stable silicon compounds involve chains with silicon-oxygen bonds.

The fundamental silicon-oxygen compound is **silica**, which has the empirical formula SiO_2 . Knowing the properties of the similar compound carbon dioxide, one might expect silica to be a gas that contains discrete SiO_2 molecules. In fact, nothing could be further from the truth—quartz and some types of sand are typical of the materials composed of silica. What accounts for this difference? The answer lies in the bonding.



Computer-generated model of silica.

The bonding in the CO_2 molecule was described in Section 9.1.

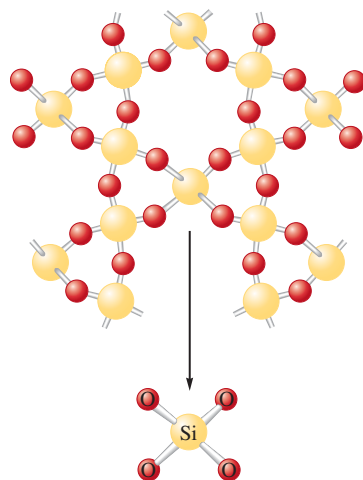
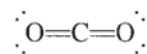


FIGURE 10.26 (top) The structure of quartz (empirical formula SiO_2). Quartz contains chains of SiO_4 tetrahedra (bottom) that share oxygen atoms.

Recall that the Lewis structure of CO_2 is



and that each $\text{C}=\text{O}$ bond can be viewed as a combination of a σ bond involving a carbon sp hybrid orbital and a π bond involving a carbon $2p$ orbital. On the contrary, silicon cannot use its valence $3p$ orbitals to form strong π bonds with oxygen, mainly because of the larger size of the silicon atom and its orbitals, which results in less effective overlap with the smaller oxygen orbitals. Therefore, instead of forming π bonds, the silicon atom satisfies the octet rule by forming single bonds with four oxygen atoms, as shown in the representation of the structure of quartz in Fig. 10.26. Note that each silicon atom is at the center of a tetrahedral arrangement of oxygen atoms, which are shared with other silicon atoms. Although the empirical formula for quartz is SiO_2 , the structure is based on a *network* of SiO_4 tetrahedra with shared oxygen atoms rather than discrete SiO_2 molecules. It is obvious that the differing abilities of carbon and silicon to form π bonds with oxygen have profound effects on the structures and properties of CO_2 and SiO_2 .

Compounds closely related to silica and found in most rocks, soils, and clays are the **silicates**. Like silica, the silicates are based on interconnected SiO_4 tetrahedra. However, in contrast to silica, where the O/Si ratio is 2:1, silicates have O/Si ratios greater than 2:1 and contain silicon–oxygen *anions*. This means that to form the neutral solid silicates, cations are needed to balance the excess negative charge. In other words, silicates are salts containing metal cations and polyatomic silicon–oxygen anions. Examples of important silicate anions are shown in Fig. 10.27.

When silica is heated above its melting point (about 1600°C) and cooled rapidly, an amorphous solid called a **glass** results (see Fig. 10.28). Note that a glass contains

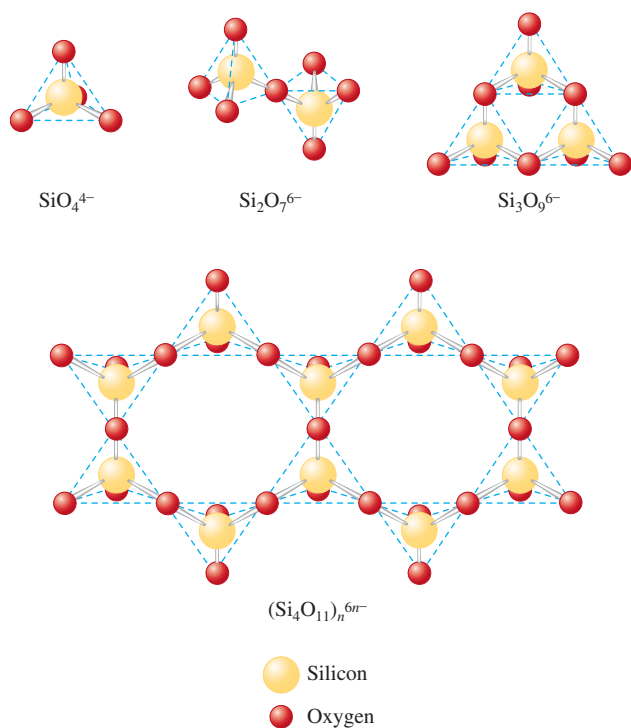


FIGURE 10.27 Examples of silicate anions, all of which are based on SiO_4^{4-} tetrahedra.

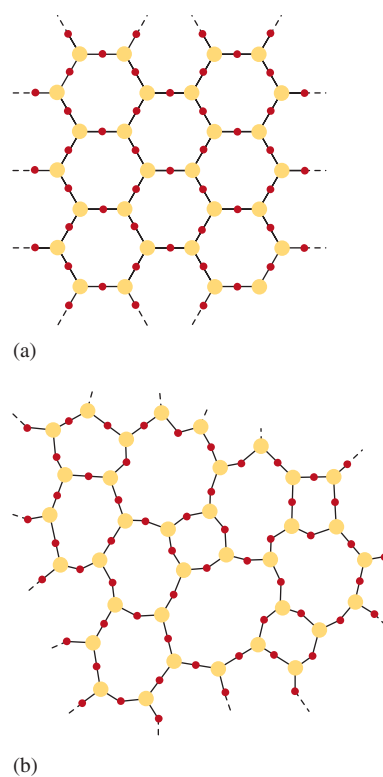


FIGURE 10.28 Two-dimensional representations of (a) a quartz crystal and (b) a quartz glass.

TABLE 10.5 Compositions of Some Common Types of Glass

Type of Glass	Percentages of Various Components						
	SiO ₂	CaO	Na ₂ O	B ₂ O ₃	Al ₂ O ₃	K ₂ O	MgO
Window (soda-lime glass)	72	11	13	—	0.3	3.8	—
Cookware (aluminosilicate glass)	55	15	—	—	20	—	10
Heat-resistant (borosilicate glass)	76	3	5	13	2	0.5	—
Optical	69	12	6	0.3	—	12	—



A glass pitcher being manufactured.

a good deal of disorder, in contrast to the crystalline nature of quartz. Glass more closely resembles a very viscous solution than it does a crystalline solid. Common glass results when substances such as Na₂CO₃ are added to the silica melt, which is then cooled. The properties of glass can be varied greatly by varying the additives. For example, addition of B₂O₃ produces a glass (called *borosilicate glass*) that expands and contracts little under large temperature changes. Thus it is useful for labware and cooking utensils. The most common brand name for this glass is Pyrex. The addition of K₂O produces an especially hard glass that can be ground to the precise shapes needed for eyeglass and contact lenses. The compositions of several types of glass are shown in Table 10.5.

Ceramics

Ceramics are typically made from clays (which contain silicates) and hardened by firing at high temperatures. Ceramics are nonmetallic materials that are strong, brittle, and resistant to heat and attack by chemicals.

Like glass, ceramics are based on silicates, but with that the resemblance ends. Glass can be melted and remelted as often as desired, but once a ceramic has been hardened, it is resistant to extremely high temperatures. This behavior results from the very different structures of glasses and ceramics. A glass is a *homogeneous*, noncrystalline “frozen solution,” and a ceramic is *heterogeneous*. A ceramic contains two phases: minute crystals of silicates that are suspended in a glassy cement.

To understand how ceramics harden, it is necessary to know something about the structure of clays. Clays are formed by the weathering action of water and carbon dioxide on the mineral feldspar, which is a mixture of silicates with empirical formulas such as K₂O · Al₂O₃ · 6SiO₂ and Na₂O · Al₂O₃ · 6SiO₂. Feldspar is really an *aluminosilicate* in which aluminum as well as silicon atoms are part of the oxygen-bridged polyanion. The weathering of feldspar produces kaolinite, consisting of tiny thin platelets with the empirical formula Al₂Si₂O₅(OH)₄. When dry, the platelets cling together; when water is present, they can slide over one another, giving clay its plasticity. As clay dries, the platelets begin to interlock again. When the remaining water is driven off during firing, the silicates and cations form a glass that binds the tiny crystals of kaolinite.

Ceramics have a very long history. Rocks, which are natural ceramic materials, served as the earliest tools. Later, clay vessels dried in the sun or baked in fires served as containers for food and water. These early vessels were no doubt crude and quite porous. With the discovery of glazing, which probably occurred about 3000 B.C. in Egypt, pottery became more serviceable as well as more beautiful. Prized porcelain is essentially the same material as crude earthenware, but specially selected clays and glazings are used for porcelain and the clay object is fired at a very high temperature.



An artist paints a ceramic vase before glazing.



CHEMICAL IMPACT

Golfing with Glass

You probably can guess what material traditionally was used to construct the “woods” used in golf. Modern technology has changed things. Like the bats used in college baseball, most “woods” are now made of metal. While bats are made of aluminum, golf club heads are often made of stainless steel or titanium.

Metals and their alloys usually form crystals that contain highly ordered arrangements of atoms. However, a company called Liquidmetal Golf of Laguna Niguel, California, has begun producing golf clubs containing glass—metallic glass. The company has found that when molten mixtures of titanium, zirconium, nickel, beryllium, and copper are cooled, they solidify, forming a glass. Unlike crystalline materials that contain a regular array of atoms, glasses are amorphous—the atoms are randomly scattered throughout the solid.

These golf clubs with metallic glass inserts have some unusual characteristics. Golfers who have tried the clubs say they combine hardness with a “soft feel.” Studies show that the glass transfers more of the energy of the golf swing to the ball with less impact to the golfer’s hands than with regular metal woods.

One of the fortunate properties of this five-component metallic glass (invented in 1992 by William L. Johnson and Atakan Peker at the California Institute of Technology) is that it can be cooled relatively slowly to form the glass. This allows manufacture of relatively large glass objects such as inserts for golf club heads. Most mixtures of metals that form glasses must be cooled very rapidly to obtain the glass, which results in tiny particles of glass leading to powders.



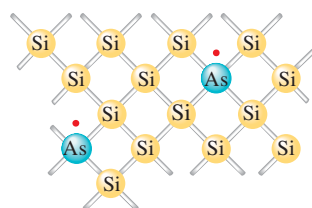
Golf clubs with a titanium shell and metallic glass inserts.

David S. Lee, head of manufacturing at Liquidmetal Golf, says that golf clubs were an obvious first application for this five-component glass because golfers are used to paying high prices for clubs that employ new technology. Liquidmetal Golf is now looking for other applications of this new glass. How about glass bicycle frames?

Although ceramics have been known since antiquity, they are not obsolete materials. On the contrary, ceramics constitute one of the most important classes of “high-tech” materials. Because of their stability at high temperatures and resistance to corrosion, ceramics seem an obvious choice for constructing jet and automobile engines in which the greatest fuel efficiencies are possible at very high temperatures. But ceramics are brittle—they break rather than bend—which limits their usefulness. However, more flexible ceramics can be obtained by adding small amounts of organic polymers. Taking their cue from natural “organoceramics” such as teeth and shells of sea creatures that contain small amounts of organic polymers, materials scientists have found that incorporating tiny amounts of long organic molecules into ceramics as they form produces materials that are much less subject to fracture. These materials should be useful for lighter, more durable engine parts, as well as for flexible superconducting wire and microelectronic devices. In addition, these organoceramics hold great promise for prosthetic devices such as artificial bones.

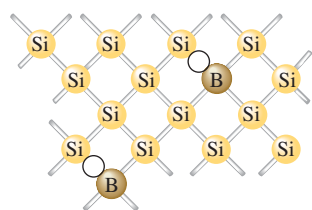


Visualization: Magnetic Levitation by a Superconductor



n-type semiconductor

(a)



p-type semiconductor

(b)

FIGURE 10.29

(a) A silicon crystal doped with arsenic, which has one more valence electron than silicon. (b) A silicon crystal doped with boron, which has one less electron than silicon.

Electrons must be in singly occupied molecular orbitals to conduct a current.

Semiconductors

Elemental silicon has the same structure as diamond, as might be expected from its position in the periodic table (in Group 4A directly under carbon). Recall that in diamond there is a large energy gap between the filled and empty molecular orbitals (see Fig. 10.23). This gap prevents excitation of electrons to the empty molecular orbitals (conduction bands) and makes diamond an insulator. In silicon the situation is similar, but the energy gap is smaller. A few electrons can cross the gap at 25°C, making silicon a **semiconducting element**, or **semiconductor**. In addition, at higher temperatures, where more energy is available to excite electrons into the conduction bands, the conductivity of silicon increases. This is typical behavior for a semiconducting element and is in contrast to that of metals, whose conductivity decreases with increasing temperature.

The small conductivity of silicon can be enhanced at normal temperatures if the silicon crystal is *doped* with certain other elements. For example, when a small fraction of silicon atoms is replaced by arsenic atoms, each having *one more* valence electron than silicon, extra electrons become available for conduction, as shown in Fig. 10.29(a). This produces an **n-type semiconductor**, a substance whose conductivity is increased by doping it with atoms having more valence electrons than the atoms in the host crystal. These extra electrons lie close in energy to the conduction bands and can be easily excited into these levels, where they can conduct an electric current [see Fig. 10.30(a)].

We also can enhance the conductivity of silicon by doping the crystal with an element such as boron, which has only three valence electrons, *one less* than silicon. Because boron has one less electron than is required to form the bonds with the surrounding silicon atoms, an electron vacancy, or *hole*, is created, as shown in Fig. 10.29(b). As an electron fills this hole, it leaves a new hole, and this process can be repeated. Thus the hole advances through the crystal in a direction opposite to movement of the electrons jumping to fill the hole. Another way of thinking about this phenomenon is that in pure silicon each atom has four valence electrons and the low-energy molecular orbitals are exactly filled. Replacing silicon atoms with boron atoms leaves vacancies in these molecular orbitals, as shown in Fig. 10.30(b). This means that there is only one electron in some of the molecular orbitals, and these unpaired electrons can function as conducting electrons. Thus the substance becomes a better conductor. When semiconductors are doped with atoms having fewer valence electrons than the atoms of the host crystal, they are called **p-type semiconductors**, so named because the positive holes can be viewed as the charge carriers.

Most important applications of semiconductors involve connection of a p-type and an n-type to form a **p-n junction**. Figure 10.31(a) shows a typical junction; the red dots

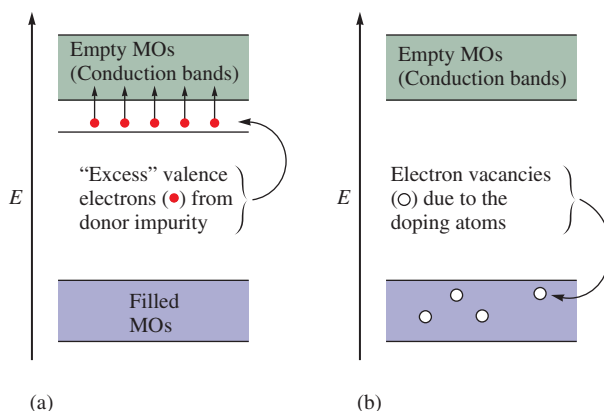
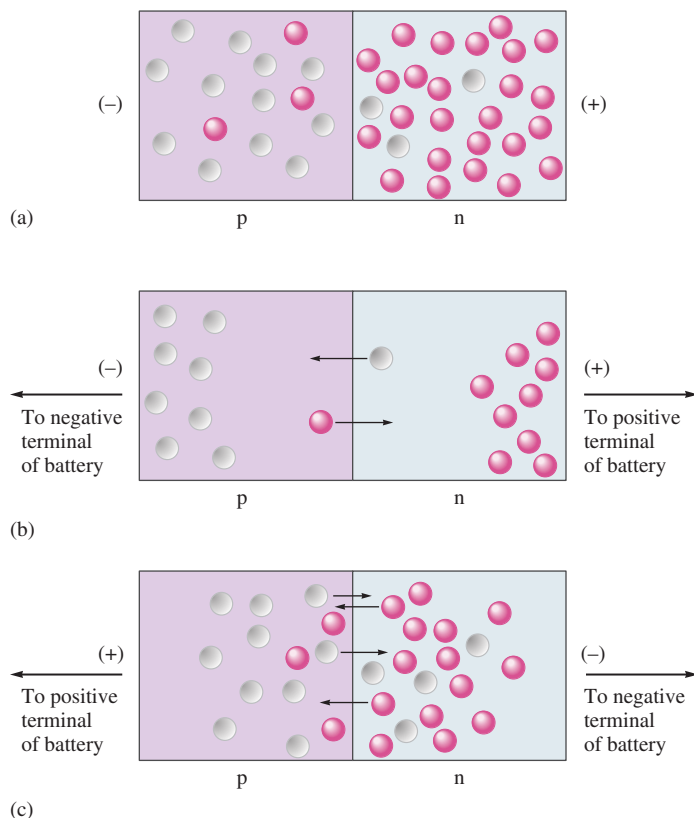


FIGURE 10.30

Energy-level diagrams for (a) an n-type semiconductor and (b) a p-type semiconductor.

**FIGURE 10.31**

The p–n junction involves the contact of a p-type and an n-type semiconductor. (a) The charge carriers of the p-type region are holes (○). In the n-type region the charge carriers are electrons (●). (b) No current flows (reverse bias). (c) Current readily flows (forward bias). Note that each electron that crosses the boundary leaves a hole behind. Thus the electrons and the holes move in opposite directions.

represent excess electrons in the n-type semiconductor, and the white circles represent holes (electron vacancies) in the p-type semiconductor. At the junction, a small number of electrons migrate from the n-type region into the p-type region, where there are vacancies in the low-energy molecular orbitals. The effect of these migrations is to place a negative charge on the p-type region (since it now has a surplus of electrons) and a positive charge on the n-type region (since it has lost electrons, leaving holes in its low-energy molecular orbitals). This charge buildup, called the *contact potential*, or *junction potential*, prevents further migration of electrons.

Now suppose an external electric potential is applied by connecting the negative terminal of a battery to the p-type region and the positive terminal to the n-type region. The situation represented in Fig. 10.31(b) results. Electrons are drawn toward the positive terminal, and the resulting holes move toward the negative terminal—exactly opposite to the natural flow of electrons at the p–n junction. The junction resists the imposed current flow in this direction and is said to be under *reverse bias*. No current flows through the system.

On the other hand, if the battery is connected so that the negative terminal is connected to the n-type region and the positive terminal is connected to the p-type region [Fig. 10.31(c)], the movement of electrons (and holes) is in the favored direction. The junction has low resistance, and a current flows easily. The junction is said to be under *forward bias*.

A p–n junction makes an excellent *rectifier*, a device that produces a pulsating direct current (flows in one direction) from alternating current (flows in both directions alternately). When placed in a circuit where the potential is constantly reversing, a p–n junction transmits current only under forward bias, thus converting the alternating current to direct current. Radios, computers, and other electronic devices formerly



CHEMICAL IMPACT

Transistors and Printed Circuits

Transistors have had an immense impact on the technology of electronic devices for which signal amplification is needed, such as communications equipment and computers. Before the invention of the transistor at Bell Laboratories in 1947, amplification was provided exclusively by vacuum tubes, which were both bulky and unreliable. The first electronic digital computer, ENIAC, built at the University of Pennsylvania, had 19,000 vacuum tubes and consumed 150,000 watts of electricity. Because of the discovery and development of the transistor and the printed circuit, a handheld calculator run by a small battery now has the same computing power as ENIAC.

A *junction transistor* is made by joining n-type and p-type semiconductors so as to form an n–p–n or a p–n–p junction. The former type is shown in Fig. 10.32. In this diagram the input signal (to be amplified) occurs in circuit 1, which has a small resistance and a forward-biased n–p junction (junction 1). As the voltage of the input signal to this circuit varies, the current in the circuit varies, which means there is a change in the number of electrons crossing the n–p junction. Circuit 2 has a relatively large resistance and is under reverse bias. The key to operation of the transistor is that current only flows in circuit 2 when electrons crossing junction 1 also cross junction 2 and travel to the positive terminal. Since the current in circuit 1 determines the number of electrons crossing junction 1, the number of electrons available to cross junction 2 is also directly proportional to the current in circuit 1. The current in circuit 2 therefore varies depending on the current in circuit 1.

The voltage V , current I , and resistance R in a circuit are related by the equation

$$V = IR$$

Since circuit 2 has a large resistance, a given current in circuit 2 produces a larger voltage than the same current in circuit 1, which has a small resistance. Thus a signal or variable voltage in circuit 1, such as might be produced by a human voice on a telephone, is reproduced in circuit 2, but with much greater voltage changes. That is, the input signal has been *amplified* by the junction transistor. This device, which has replaced the large vacuum tube, is a tiny component of a printed circuit on a silicon chip.

Silicon chips are really “planar” transistors constructed from thin layers of n-type and p-type regions connected by conductors. A chip less than 1 cm wide can contain hundreds of printed circuits and be used in computers, radios, and televisions.

A printed circuit has many n–p–n junction transistors. Fig. 10.33 illustrates the formation of one transistor area. The chip begins as a thin wafer of silicon that has been doped with an n-type impurity. A protective layer of silicon dioxide is then produced on the wafer by exposing it in a furnace to an oxidizing atmosphere. The next step is to produce a p-type semiconductor. To do this, the surface of the oxide is covered by a polymeric photoresist, as shown in Fig. 10.33(a). A template that only allows light to shine through in selected areas is then placed on top [Fig. 10.33(b)], and light is shown on the chip. The photoresist

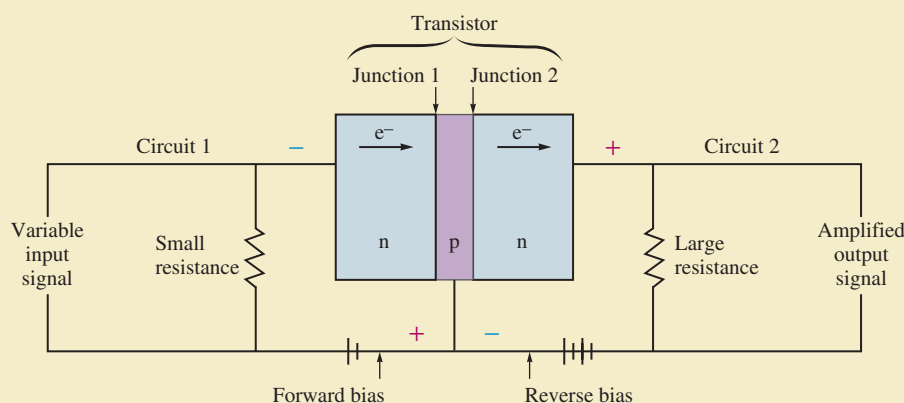


FIGURE 10.32

A schematic of two circuits connected by a transistor. The signal in circuit 1 is amplified in circuit 2.

that has been exposed to light undergoes a chemical change that causes its solubility to be different from the unexposed photoresist. The exposed photoresist is dissolved using selective solvents [Fig. 10.33(c)], and the exposed area is treated with an etching solution to dissolve the oxide coating [Fig. 10.33(d)]. When the remaining photoresist is dissolved, the silicon wafer has its oxide coating intact except at the one spot (of diameter x), as shown in Fig. 10.33(d).

Exposing the wafer to a p-type impurity such as boron at about 1000°C causes a p-type semiconductor area to be formed in the exposed spot as the boron atoms diffuse into the silicon crystal [Fig. 10.33(e)]. Next, to form a small n-type area in the center of the p-type region, the wafer is again placed in the oxidizing furnace to be recoated over its entire surface with oxide. Then a new photoresist covering is applied, which is illuminated through a template with a transparent area indicated by y [Fig. 10.33(f)]. The photoresist and oxide are then removed from the illuminated area, and the wafer is exposed to an n-type impurity to form a small n-type region as shown in Fig. 10.33(g). Next, conductors are layered onto the chip giving the finished transistor [Fig. 10.33(h)], which has two circuits connected through an n-p-n junction (see Fig. 10.32). This transistor then becomes a part of a large circuit layered onto the chip and interconnected by conductors.

The method given here for producing a printed circuit does not represent the latest technology in this field. The manufacture of printed circuits is a highly competitive business, and changes in methodology occur almost daily.

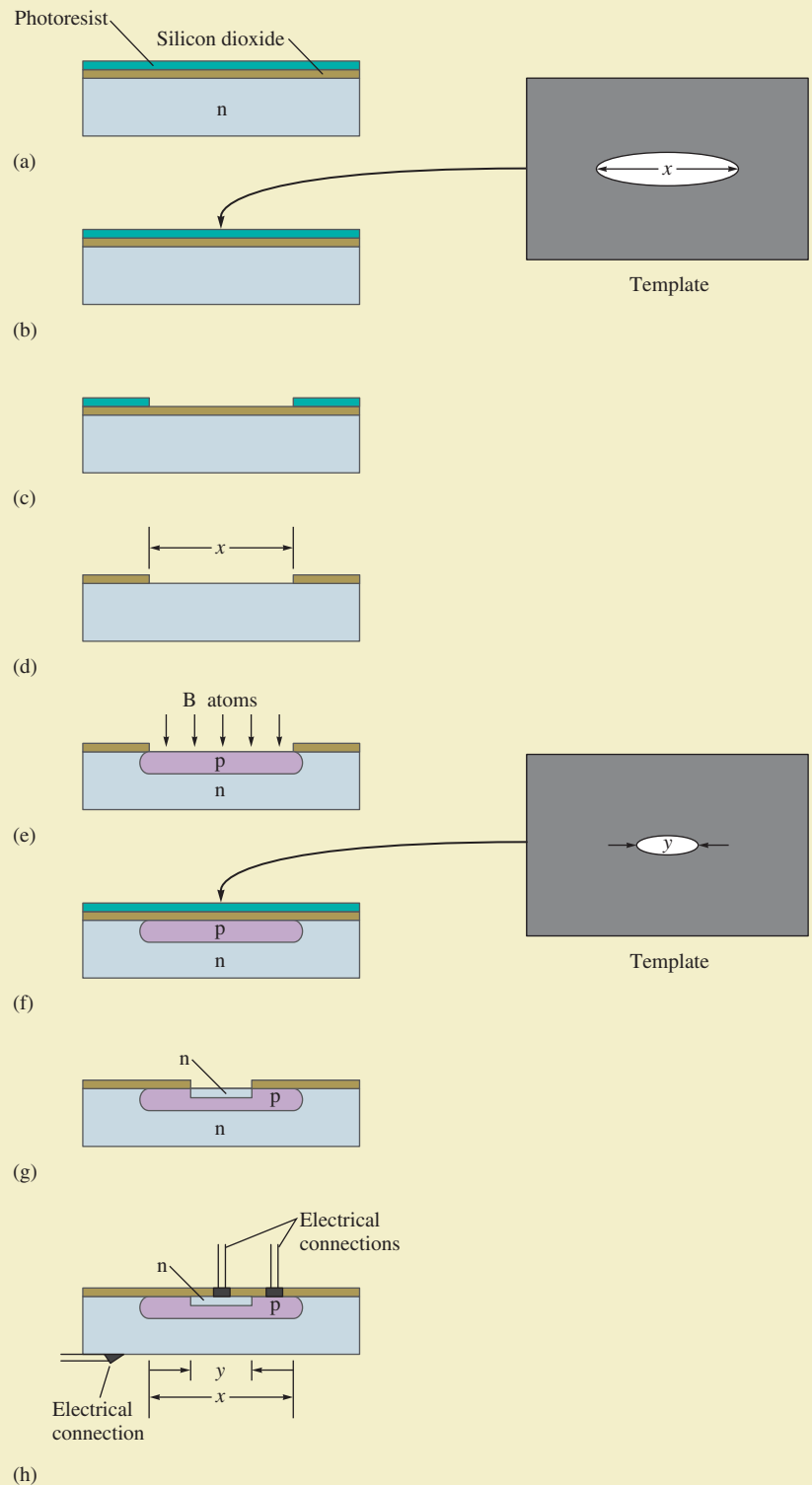


FIGURE 10.33

The steps for forming a transistor in a crystal of initially pure silicon.

used bulky, unreliable vacuum tubes as rectifiers. The p–n junction has revolutionized electronics; modern solid-state components contain p–n junctions in printed circuits.

10.6 Molecular Solids



A “steaming” piece of dry ice.

So far we have considered solids in which atoms occupy the lattice positions. In some of these substances (network solids), the solid can be considered to be one giant molecule. In addition, there are many types of solids that contain discrete molecular units at each lattice position. A common example is ice, where the lattice positions are occupied by water molecules [see Fig. 10.12(c)]. Other examples are dry ice (solid carbon dioxide), some forms of sulfur that contain S_8 molecules [Fig. 10.34(a)], and certain forms of phosphorus that contain P_4 molecules [Fig. 10.34(b)]. These substances are characterized by strong covalent bonding *within* the molecules but relatively weak forces *between* the molecules. For example, it takes only 6 kJ of energy to melt 1 mole of solid water (ice) because only intermolecular (H_2O-H_2O) interactions must be overcome. However, 470 kJ of energy is required to break 1 mole of covalent O–H bonds. The differences between the covalent bonds within the molecules and the forces between the molecules are apparent from the comparison of the interatomic and intermolecular distances in solids shown in Table 10.6.

The forces that exist among the molecules in a molecular solid depend on the nature of the molecules. Many molecules such as CO_2 , I_2 , P_4 , and S_8 have no dipole moment, and the intermolecular forces are London dispersion forces. Because these forces are often relatively small, we might expect all these substances to be gaseous at $25^\circ C$, as is the case for carbon dioxide. However, as the size of the molecules increases, the London forces become quite large, causing many of these substances to be solids at $25^\circ C$.

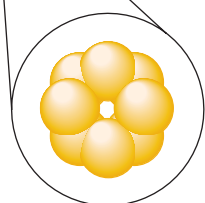
When molecules do have dipole moments, their intermolecular forces are significantly greater, especially when hydrogen bonding is possible. Water molecules are particularly well suited to interact with each other because each molecule has two polar O–H bonds and two lone pairs on the oxygen atom. This can lead to the association



Visualization: Molecular Solids



(a)



(b)

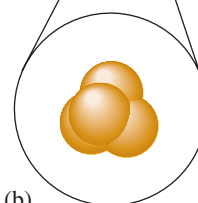


FIGURE 10.34

(a) Sulfur crystals (yellow) contain S_8 molecules. (b) White phosphorus (containing P_4 molecules) is so reactive with the oxygen in air that it must be stored under water.



CHEMICAL IMPACT

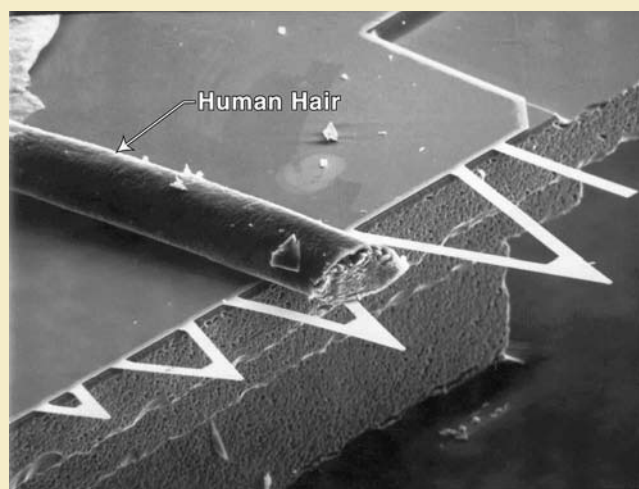
Explosive Sniffer

These days security is at the top of everyone's list of important concerns, especially for those people who are responsible for the safety of our transportation systems. In particular, airports need speedy and sensitive detectors for explosives. Plastic explosives are especially tricky to detect because they do not respond to metal detectors, and they can be shaped into innocent-looking objects to avoid X-ray detection. However, a team of scientists at Oak Ridge National Laboratory led by Thomas Thundat has just published a description of an inexpensive device that is extremely sensitive to two N-containing compounds found in plastic explosives. The key part of this detection device is a tiny (180-micrometer), V-shaped cantilever made of silicon. The cantilever is shown in the accompanying photo next to a human hair for size comparison.

The upper surface of the cantilever was first coated with a layer of gold and then a one-molecule-thick layer of an acid that binds to each of the two N-containing molecules to be detected: pentaerythritol tetranitrate (PETN) and hexahydro-1,3,5-triazine (RDX). When a stream of air containing tiny amounts of PETN or RDX passes over the cantilever, these molecules bind to the cantilever, causing it to bend "like a diving board." This bending is not due to the added mass of the attached PETN and RDX. Rather, the deformation occurs because the area of the cantilever surface where binding takes place stretches relative to the unbound areas. A laser pointed at the cantilever detects the bending motion when PETN or RDX (or both) is present. The device's sensitivity is quite remarkable: 14 parts per trillion of PETN and 30 parts per trillion of RDX.

All in all, this device appears very promising for detecting plastic explosives in luggage. The cantilevers are inexpensive to construct (approximately \$1), and the entire device is about the size of a shoe box. Also, the Oak Ridge team can fabricate thousands of cantilevers in one device. By putting different coatings on the cantilever arms, it should be possible to detect many other types of chemicals and possible biological agents.

This detector looks like a very promising addition to our arsenal of security devices.



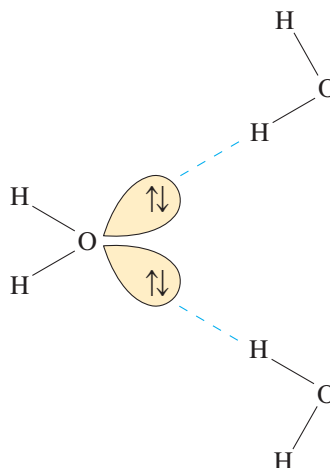
When explosive compounds bind to these V-shaped cantilevers, the microscopic structures, which are about the width of a hair, bend and produce a signal.

TABLE 10.6 Comparison of Atomic Separations Within Molecules (Covalent Bonds) and Between Molecules (Intermolecular Interactions)

Solid	Distance Between Atoms in Molecule*	Closest Distance Between Molecules in the Solid
P ₄	220 pm	380 pm
S ₈	206 pm	370 pm
Cl ₂	199 pm	360 pm

*The shorter distances within the molecules indicate stronger bonding.

of four hydrogen atoms with each oxygen: two by covalent bonds and two by dipole forces:



Note the two relatively short covalent oxygen–hydrogen bonds and the two longer oxygen–hydrogen dipole interactions that can be seen in the ice structure in Fig. 10.12(c).

10.7 Ionic Solids

Ionic solids are stable, high-melting substances held together by the strong electrostatic forces that exist between oppositely charged ions. The principles governing the structures of ionic solids were introduced in Section 8.5. In this section we will review and extend these principles.

The structures of most binary ionic solids, such as sodium chloride, can be explained by the closest packing of spheres. Typically, the larger ions, usually the anions, are packed in one of the closest packing arrangements (hcp or ccp), and the smaller cations fit into holes among the closest packed anions. The packing is done in a way that maximizes the electrostatic attractions among oppositely charged ions and minimizes the repulsions among ions with like charges.

There are three types of holes in closest packed structures:

1. Trigonal holes are formed by three spheres in the same layer [Fig. 10.35(a)].
2. Tetrahedral holes are formed when a sphere sits in the dimple of three spheres in an adjacent layer [Fig. 10.35(b)].
3. Octahedral holes are formed between two sets of three spheres in adjoining layers of the closest packed structures [Fig. 10.35(c)].

For spheres of a given diameter, the holes increase in size in the order

$$\text{trigonal} < \text{tetrahedral} < \text{octahedral}$$

In fact, trigonal holes are so small that they are never occupied in binary ionic compounds. Whether the tetrahedral or octahedral holes in a given binary ionic solid are occupied depends mainly on the *relative* sizes of the anion and cation. For example, in zinc sulfide the S^{2-} ions (ionic radius = 180 pm) are arranged in a cubic closest packed structure with the smaller Zn^{2+} ions (ionic radius = 70 pm) in the tetrahedral holes. The locations of the tetrahedral holes in the face-centered cubic unit cell of the ccp structure are shown in Fig. 10.36(a). Note from this figure that there are eight tetrahedral holes in the unit cell. Also recall from the discussion in Section 10.4 that there are four net spheres in the

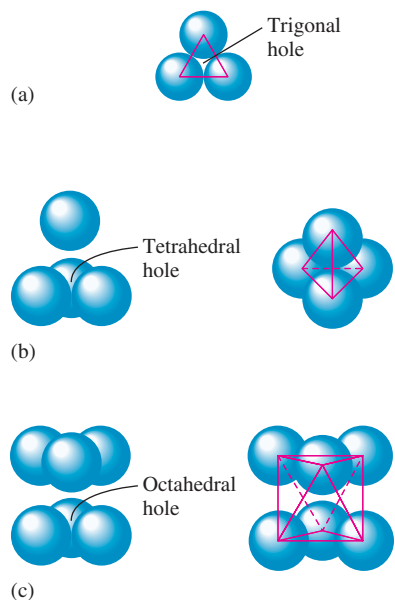
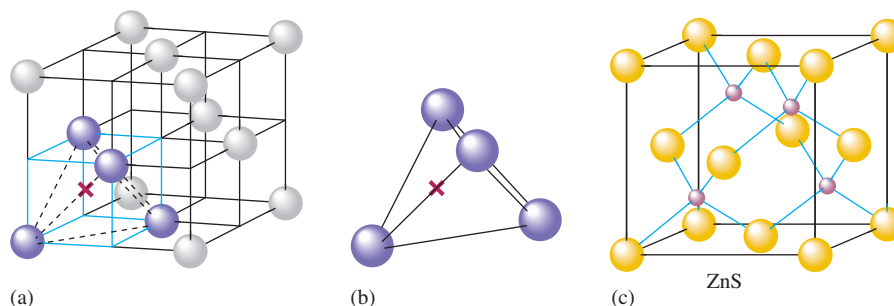


FIGURE 10.35

The holes that exist among closest packed uniform spheres. (a) The trigonal hole formed by three spheres in a given plane. (b) The tetrahedral hole formed when a sphere occupies a dimple formed by three spheres in an adjacent layer. (c) The octahedral hole formed by six spheres in two adjacent layers.

FIGURE 10.36

(a) The location (X) of a tetrahedral hole in the face-centered cubic unit cell. (b) One of the tetrahedral holes. (c) The unit cell for ZnS where the S^{2-} ions (yellow) are closest packed with the Zn^{2+} ions (red) in alternating tetrahedral holes.



face-centered cubic unit cell. Thus there are *twice as many tetrahedral holes as packed anions* in the closest packed structure. Zinc sulfide must have the same number of S^{2-} ions and Zn^{2+} ions to achieve electrical neutrality. Thus in the zinc sulfide structure only *half* the tetrahedral holes contain Zn^{2+} ions, as shown in Fig. 10.36(c).

The structure of sodium chloride can be described in terms of a cubic closest packed array of Cl^- ions with Na^+ ions in all the octahedral holes. The locations of the octahedral holes in the face-centered cubic unit cell are shown in Fig. 10.37(a). The easiest octahedral hole to find in this structure is the one at the center of the cube. Note that this hole is surrounded by six spheres, as is required to form an octahedron. The remaining octahedral holes are shared with other unit cells and are more difficult to visualize. However, it can be shown that the number of octahedral holes in the ccp structure is the *same* as the number of packed anions. Figure 10.37(b) shows the structure for sodium chloride that results from Na^+ ions filling all the octahedral holes in a ccp array of Cl^- ions.

A great variety of ionic solids exists. Our purpose in this section is not to give an exhaustive treatment of ionic solids, but to emphasize the fundamental principles governing their structures. As we have seen, the most useful model for explaining the structures of these solids regards the ions as hard spheres that are packed to maximize attractions and minimize repulsions.

Closest packed structures contain twice as many tetrahedral holes as packed spheres. Closest packed structures contain the same number of octahedral holes as packed spheres.

Sample Exercise 10.3

Determining the Number of Ions in a Unit Cell

Determine the net number of Na^+ and Cl^- ions in the sodium chloride unit cell.

Solution

Note from Fig. 10.37(b) that the Cl^- ions are cubic closest packed and thus form a face-centered cubic unit cell. There is a Cl^- ion on each corner and one at the center of each face of the cube. Thus the net number of Cl^- ions present in a unit cell is

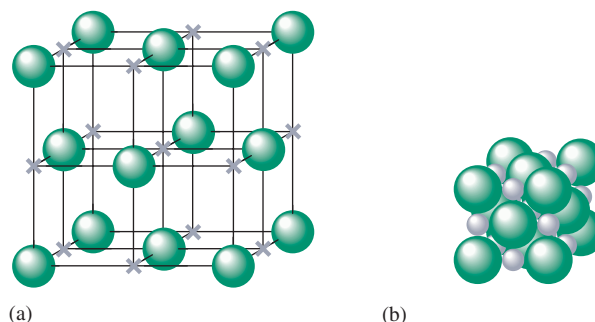
$$8\left(\frac{1}{8}\right) + 6\left(\frac{1}{2}\right) = 4$$



Visualization: Structure of an Ionic Solid (NaCl).

FIGURE 10.37

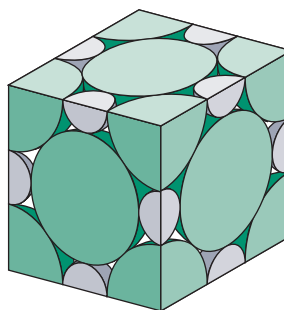
(a) The locations (gray X) of the octahedral holes in the face-centered cubic unit cell. (b) Representation of the unit cell for solid NaCl. The Cl^- ions (green spheres) have a ccp arrangement with Na^+ ions (gray spheres) in all the octahedral holes. Note that this representation shows the idealized closest packed structure of NaCl. In the actual structure, the Cl^- ions do not quite touch.



The Na^+ ions occupy the octahedral holes located in the center of the cube and midway along each edge. The Na^+ ion in the center of the cube is contained entirely in the unit cell, whereas those on the edges are shared by four unit cells (four cubes share a common edge). Since the number of edges in a cube is 12, the net number of Na^+ ions present is

$$1(1) + 12\left(\frac{1}{4}\right) = 4$$

We have shown that the net number of ions in a unit cell is 4 Na^+ ions and 4 Cl^- ions, which agrees with the 1:1 stoichiometry of sodium chloride.



See Exercises 10.61 through 10.68.

In this chapter we have considered various types of solids. Table 10.7 summarizes these types of solids and some of their properties.

TABLE 10.7 Types and Properties of Solids

Type of Solid:	Atomic			Molecular	Ionic
	Network	Metallic	Group 8A		
Structural Unit:	Atom	Atom	Atom	Molecule	Ion
Type of Bonding:	Directional covalent bonds	Nondirectional covalent bonds involving electrons that are delocalized throughout the crystal	London dispersion forces	Polar molecules: dipole–dipole interactions Nonpolar molecules: London dispersion forces	Ionic
Typical Properties:	Hard	Wide range of hardness	Very low melting point	Soft	Hard
	High melting point	Wide range of melting points		Low melting point	High melting point
	Insulator	Conductor		Insulator	Insulator
Examples:	Diamond	Silver Iron Brass	Argon(s)	Ice (solid H_2O) Dry ice (solid CO_2)	Sodium chloride Calcium fluoride

Sample Exercise 10.4

Types of Solids

Using Table 10.7, classify each of the following substances according to the type of solid it forms.

- Gold
- Carbon dioxide
- Lithium fluoride
- Krypton

Solution

- Solid gold is an atomic solid with metallic properties.
- Solid carbon dioxide contains nonpolar carbon dioxide molecules and is a molecular solid.
- Solid lithium fluoride contains Li^+ and F^- ions and is a binary ionic solid.
- Solid krypton contains krypton atoms that can interact only through London dispersion forces. It is an atomic solid but has properties characteristic of a molecular solid with nonpolar molecules.

See Exercises 10.71 and 10.72.

10.8 Vapor Pressure and Changes of State

Now that we have considered the general properties of the three states of matter, we can explore the processes by which matter changes state. One very familiar example of a change in state occurs when a liquid evaporates from an open container. This is clear evidence that the molecules of a liquid can escape the liquid's surface and form a gas, a process called **vaporization**, or **evaporation**. Vaporization is endothermic because energy is required to overcome the relatively strong intermolecular forces in the liquid. The energy required to vaporize 1 mole of a liquid at a pressure of 1 atm is called the **heat of vaporization**, or the **enthalpy of vaporization**, and is usually symbolized as ΔH_{vap} .

The endothermic nature of vaporization has great practical significance; in fact, one of the most important roles that water plays in our world is to act as a coolant. Because of the strong hydrogen bonding among its molecules in the liquid state, water has an unusually large heat of vaporization (40.7 kJ/mol). A significant portion of the sun's energy that reaches earth is spent evaporating water from the oceans, lakes, and rivers rather than warming the earth. The vaporization of water is also crucial to the body's temperature-control system through evaporation of perspiration.

Vapor Pressure

When a liquid is placed in a closed container, the amount of liquid at first decreases but eventually becomes constant. The decrease occurs because there is an initial net transfer of molecules from the liquid to the vapor phase (Fig. 10.38). This evaporation process occurs at a constant rate at a given temperature (see Fig. 10.39). However, the reverse process is different. Initially, as the number of vapor molecules increases, so does the rate of return of these molecules to the liquid. The process by which vapor molecules re-form a liquid is called **condensation**. Eventually, enough vapor molecules are present above the liquid so that the rate of condensation equals the rate of evaporation (see Fig. 10.39). *At this point no further net change occurs in the amount of liquid or vapor because the two opposite processes exactly balance each other; the system is at equilibrium.* Note that this system is highly *dynamic* on the molecular level—molecules are constantly escaping from and entering the liquid at a high rate. However, there is no *net* change because the two opposite processes just *balance* each other.

Vapor is the usual term for the gas phase of a substance that exists as a solid or liquid at 25°C and 1 atm.

ΔH_{vap} for water at 100°C is 40.7 kJ/mol.

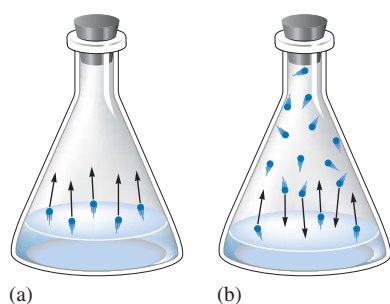
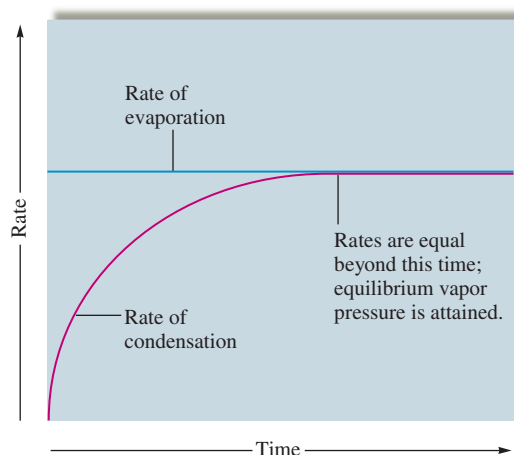


FIGURE 10.38

Behavior of a liquid in a closed container. (a) Initially, net evaporation occurs as molecules are transferred from the liquid to the vapor phase, so the amount of liquid decreases. (b) As the number of vapor molecules increases, the rate of return to the liquid (condensation) increases, until finally the rate of condensation equals the rate of evaporation. The system is at equilibrium, and no further changes occur in the amounts of vapor or liquid.

FIGURE 10.39

The rates of condensation and evaporation over time for a liquid sealed in a closed container. The rate of evaporation remains constant and the rate of condensation increases as the number of molecules in the vapor phase increases, until the two rates become equal. At this point, the equilibrium vapor pressure is attained.



The pressure of the vapor present at equilibrium is called the **equilibrium vapor pressure**, or more commonly, the **vapor pressure** of the liquid. A simple barometer can measure the vapor pressure of a liquid, as shown in Fig. 10.40(a). The liquid is injected at the bottom of the tube of mercury and floats to the surface because the mercury is so dense. A portion of the liquid evaporates at the top of the column, producing a vapor whose pressure pushes some mercury out of the tube. When the system reaches equilibrium, the vapor pressure can be determined from the change in the height of the mercury column since

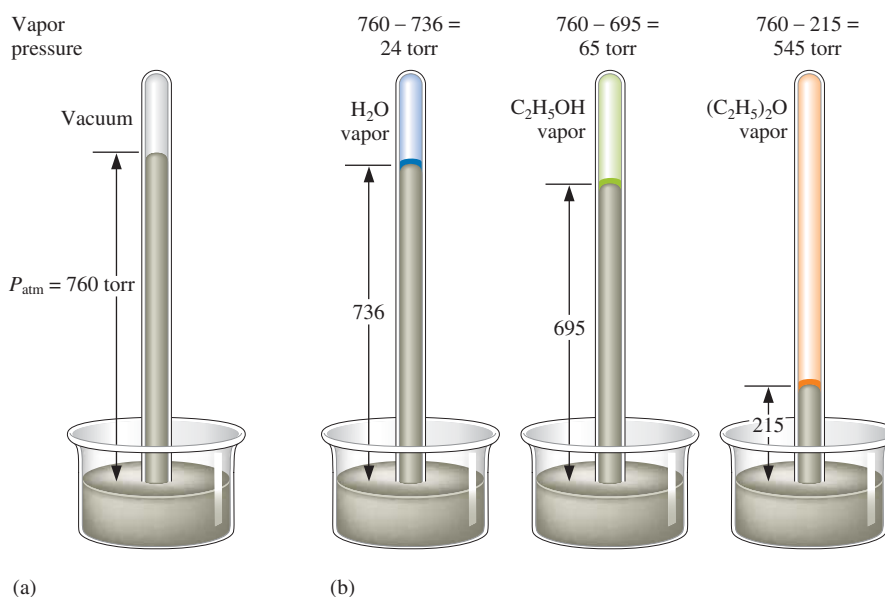
$$P_{\text{atmosphere}} = P_{\text{vapor}} + P_{\text{Hg column}}$$

Thus

$$P_{\text{vapor}} = P_{\text{atmosphere}} - P_{\text{Hg column}}$$

The vapor pressures of liquids vary widely [see Fig. 10.40(b)]. Liquids with high vapor pressures are said to be *volatile*—they evaporate rapidly from an open dish. The vapor pressure of a liquid is principally determined by the size of the *intermolecular forces* in the liquid. Liquids in which the intermolecular forces are large have relatively low vapor

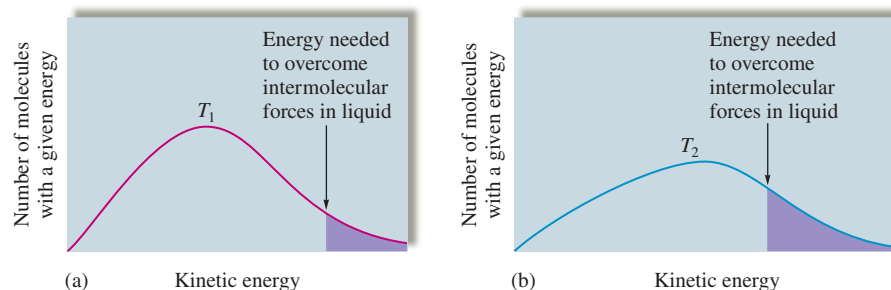
A system at equilibrium is dynamic on the molecular level but shows no macroscopic changes.

**FIGURE 10.40**

(a) The vapor pressure of a liquid can be measured easily using a simple barometer of the type shown here. (b) The three liquids, water, ethanol ($\text{C}_2\text{H}_5\text{OH}$), and diethyl ether [$(\text{C}_2\text{H}_5)_2\text{O}$], have quite different vapor pressures. Ether is by far the most volatile of the three. Note that in each case a little liquid remains (floating on the mercury).

FIGURE 10.41

The number of molecules in a liquid with a given energy versus kinetic energy at two temperatures. Part (a) shows a lower temperature than that in part (b). Note that the proportion of molecules with enough energy to escape the liquid to the vapor phase (indicated by shaded areas) increases dramatically with temperature. This causes vapor pressure to increase markedly with temperature.



pressures because the molecules need high energies to escape to the vapor phase. For example, although water has a much lower molar mass than diethyl ether, the strong hydrogen-bonding forces that exist among water molecules in the liquid cause water's vapor pressure to be much lower than that of diethyl ether [see Fig. 10.40(b)]. In general, substances with large molar masses have relatively low vapor pressures, mainly because of the large dispersion forces. The more electrons a substance has, the more polarizable it is, and the greater the dispersion forces are.

Measurements of the vapor pressure for a given liquid at several temperatures show that *vapor pressure increases significantly with temperature*. Figure 10.41 illustrates the distribution of molecular kinetic energy present in a liquid at two different temperatures. To overcome the intermolecular forces in a liquid, a molecule must have sufficient kinetic energy. As the temperature of the liquid is increased, the fraction of molecules having the minimum energy needed to overcome these forces and escape to the vapor phase increases markedly. Thus the vapor pressure of a liquid increases dramatically with temperature. Values for water at several temperatures are given in Table 10.8.

The quantitative nature of the temperature dependence of vapor pressure can be represented graphically. Plots of vapor pressure versus temperature for water, ethanol, and diethyl ether are shown in Fig. 10.42(a). Note the nonlinear increase in vapor pressure for all the liquids as the temperature is increased. We find that a straight line can be obtained by plotting $\ln(P_{\text{vap}})$ versus $1/T$, where T is the Kelvin temperature, as shown in Fig. 10.42(b). We can represent this behavior by the equation

$$\ln(P_{\text{vap}}) = -\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T} \right) + C \quad (10.4)$$

where ΔH_{vap} is the enthalpy of vaporization, R is the universal gas constant, and C is a constant characteristic of a given liquid. The symbol \ln means that the natural logarithm of the vapor pressure is taken.

Equation (10.4) is the equation for a straight line of the form $y = mx + b$, where

$$y = \ln(P_{\text{vap}})$$

$$x = \frac{1}{T}$$

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

$$b = \text{intercept} = C$$

TABLE 10.8 The Vapor Pressure of Water as a Function of Temperature

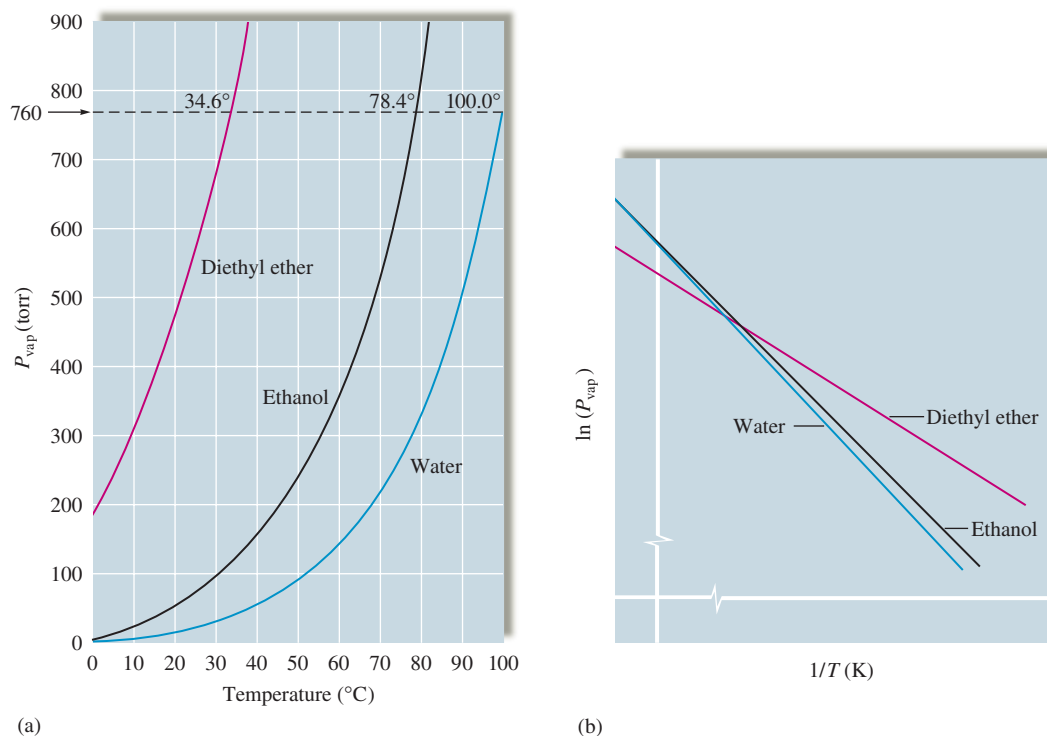
T ($^{\circ}\text{C}$)	P (torr)
0.0	4.579
10.0	9.209
20.0	17.535
25.0	23.756
30.0	31.824
40.0	55.324
60.0	149.4
70.0	233.7
90.0	525.8

Natural logarithms are reviewed in Appendix 1.2.

Sample Exercise 10.5

Determining Enthalpies of Vaporization

Using the plots in Fig. 10.42(b), determine whether water or diethyl ether has the larger enthalpy of vaporization.

**FIGURE 10.42**

(a) The vapor pressure of water, ethanol, and diethyl ether as a function of temperature. (b) Plots of $\ln(P_{\text{vap}})$ versus $1/T$ (Kelvin temperature) for water, ethanol, and diethyl ether.

Solution

When $\ln(P_{\text{vap}})$ is plotted versus $1/T$, the slope of the resulting straight line is

$$-\frac{\Delta H_{\text{vap}}}{R}$$

Note from Fig. 10.42(b) that the slopes of the lines for water and diethyl ether are both negative, as expected, and that the line for ether has the smaller slope. Thus ether has the smaller value of ΔH_{vap} . This makes sense because the hydrogen bonding in water causes it to have a relatively large enthalpy of vaporization.

See Exercise 10.79.

Equation (10.4) is important for several reasons. For example, we can determine the heat of vaporization for a liquid by measuring P_{vap} at several temperatures and then evaluating the slope of a plot of $\ln(P_{\text{vap}})$ versus $1/T$. On the other hand, if we know the values of ΔH_{vap} and P_{vap} at one temperature, we can use Equation (10.4) to calculate P_{vap} at another temperature. This can be done by recognizing that the constant C does not depend on temperature. Thus at two temperatures T_1 and T_2 we can solve Equation (10.4) for C and then write the equality

$$\ln(P_{\text{vap},T_1}) + \frac{\Delta H_{\text{vap}}}{RT_1} = C = \ln(P_{\text{vap},T_2}) + \frac{\Delta H_{\text{vap}}}{RT_2}$$

This can be rearranged to

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

or

$$\ln\left(\frac{P_{\text{vap},T_1}}{P_{\text{vap},T_2}}\right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (10.5)$$

Equation (10.5) is called the *Clausius–Clapeyron equation*.

Sample Exercise 10.6

Calculating Vapor Pressure

The vapor pressure of water at 25°C is 23.8 torr, and the heat of vaporization of water at 25°C is 43.9 kJ/mol. Calculate the vapor pressure of water at 50.°C.

Solution

We will use Equation (10.5):

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

For water we have

$$P_{\text{vap},T_1} = 23.8 \text{ torr}$$

$$T_1 = 25 + 273 = 298 \text{ K}$$

$$T_2 = 50. + 273 = 323 \text{ K}$$

$$\Delta H_{\text{vap}} = 43.9 \text{ KJ/mol} = 43,900 \text{ J/mol}$$

$$R = 8.3145 \text{ J/K mol}$$

Thus

$$\ln\left(\frac{23.8 \text{ torr}}{P_{\text{vap},T_2} \text{ (torr)}}\right) = \frac{43,900 \text{ J/mol}}{8.3145 \text{ J/K mol}} \left(\frac{1}{323 \text{ K}} - \frac{1}{298 \text{ K}} \right)$$

$$\ln\left(\frac{23.8}{P_{\text{vap},T_2}}\right) = -1.37$$

Taking the antilog (see Appendix 1.2) of both sides gives

$$\frac{23.8}{P_{\text{vap},T_2}} = 0.254$$

$$P_{\text{vap},T_2} = 93.7 \text{ torr}$$

See Exercises 10.81 through 10.84.

Like liquids, solids have vapor pressures. Figure 10.43 shows iodine vapor in equilibrium with solid iodine in a closed flask. Under normal conditions iodine **sublimes**; that is, it goes directly from the solid to the gaseous state without passing through the liquid state. **Sublimation** also occurs with dry ice (solid carbon dioxide).

Sublimation: A process in which a substance goes directly from the solid to the gaseous state.

Changes of State

What happens when a solid is heated? Typically, it will melt to form a liquid. If the heating continues, the liquid will at some point boil and form the vapor phase. This process can be represented by a **heating curve**: a plot of temperature versus time for a process where energy is added at a constant rate.

The heating curve for water is given in Fig. 10.44. As energy flows into the ice, the random vibrations of the water molecules increase as the temperature rises. Eventually, the molecules become so energetic that they break loose from their lattice positions, and the change from solid to liquid occurs. This is indicated by a plateau at 0°C on the



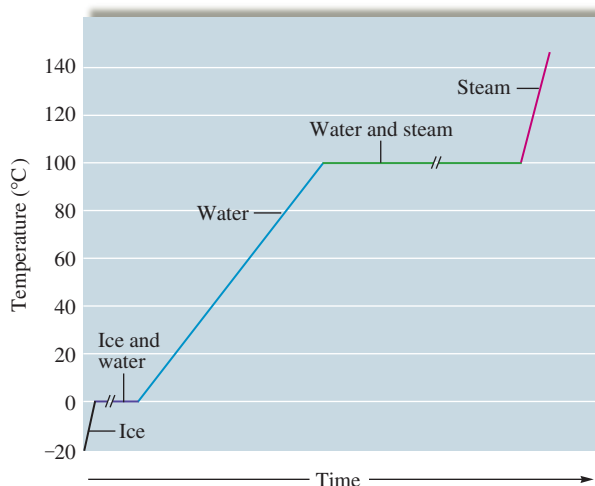
Visualization: Changes of State

**FIGURE 10.43**

Iodine being heated, causing it to sublime, forming crystals of $I_2(s)$ on the bottom of an evaporating dish cooled by ice.

Ionic solids such as NaCl and NaF have very high melting points and enthalpies of fusion because of the strong ionic forces in these solids. At the other extreme is $O_2(s)$, a molecular solid containing nonpolar molecules with weak intermolecular forces. (See Table 10.9.)

The melting and boiling points will be defined more precisely later in this section.

**FIGURE 10.44**

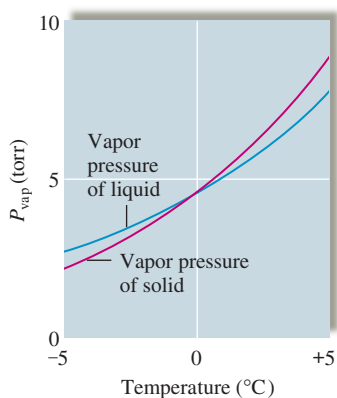
The heating curve (not drawn to scale) for a given quantity of water where energy is added at a constant rate. The plateau at the boiling point is longer than the plateau at the melting point because it takes almost seven times more energy (and thus seven times the heating time) to vaporize liquid water than to melt ice. The slopes of the other lines are different because the different states of water have different molar heat capacities (the energy required to raise the temperature of 1 mole of a substance by 1°C).

heating curve. At this temperature, called the *melting point*, all the added energy is used to disrupt the ice structure by breaking the hydrogen bonds, thus increasing the potential energy of the water molecules. The enthalpy change that occurs at the melting point when a solid melts is called the **heat of fusion**, or more accurately, the **enthalpy of fusion**, ΔH_{fus} . The melting points and enthalpies of fusion for several representative solids are listed in Table 10.9.

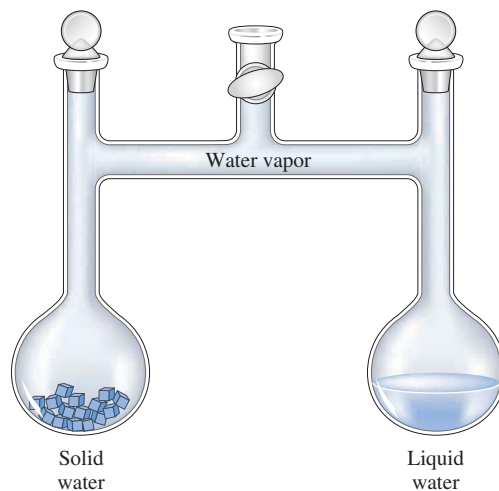
The temperature remains constant until the solid has completely changed to liquid; then it begins to increase again. At 100°C the liquid water reaches its *boiling point*, and the temperature then remains constant as the added energy is used to vaporize the liquid. When the liquid is completely changed to vapor, the temperature again begins to rise. Note that changes of state are physical changes; although intermolecular forces have been overcome, no chemical bonds have been broken. If the water vapor were heated to much higher temperatures, the water molecules would break down into the individual atoms. This would

TABLE 10.9 Melting Points and Enthalpies of Fusion for Several Representative Solids

Compound	Melting Point ($^\circ\text{C}$)	Enthalpy of Fusion (kJ/mol)
O_2	-218	0.45
HCl	-114	1.99
HI	-51	2.87
CCl_4	-23	2.51
$CHCl_3$	-64	9.20
H_2O	0	6.02
NaF	992	29.3
NaCl	801	30.2

**FIGURE 10.45**

The vapor pressures of solid and liquid water as a function of temperature. The data for liquid water below 0°C are obtained from supercooled water. The data for solid water above 0°C are estimated by extrapolation of vapor pressure from below 0°C.

**FIGURE 10.46**

An apparatus that allows solid and liquid water to interact only through the vapor state.

be a chemical change, since covalent bonds are broken. We no longer have water after this occurs.

The melting and boiling points for a substance are determined by the vapor pressures of the solid and liquid states. Figure 10.45 shows the vapor pressures of solid and liquid water as functions of temperature near 0°C. Note that below 0°C the vapor pressure of ice is less than the vapor pressure of liquid water. Also note that the vapor pressure of ice has a larger temperature dependence than that of the liquid. That is, the vapor pressure of ice increases more rapidly for a given rise in temperature than does the vapor pressure of water. Thus, as the temperature of the solid is increased, a point is eventually reached where the *liquid and solid have identical vapor pressures*. This is the melting point.

These concepts can be demonstrated experimentally using the apparatus illustrated in Fig. 10.46, where ice occupies one compartment and liquid water the other. Consider the following cases.

Case 1

A temperature at which the vapor pressure of the solid is greater than that of the liquid. At this temperature the solid requires a higher pressure than the liquid does to be in equilibrium with the vapor. Thus, as vapor is released from the solid to try to achieve equilibrium, the liquid will absorb vapor in an attempt to reduce the vapor pressure to its equilibrium value. The net effect is a conversion from solid to liquid through the vapor phase. In fact, no solid can exist under these conditions. The amount of solid will steadily decrease and the volume of liquid will increase. Finally, there will be only liquid in the right compartment, which will come to equilibrium with the water vapor, and no further changes will occur in the system. This temperature must be above the melting point of ice, since only the liquid state can exist.

Case 2

A temperature at which the vapor pressure of the solid is less than that of the liquid. This is the opposite of the situation in case 1. In this case, the liquid requires a higher pressure than the solid does to be in equilibrium with the vapor, so the liquid will gradually disappear, and the amount of ice will increase. Finally, only the solid will remain, which will achieve equilibrium with the vapor. This temperature must be *below the melting point* of ice, since only the solid state can exist.

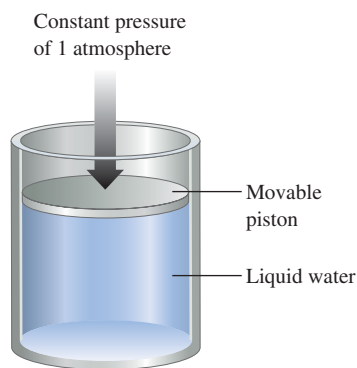


FIGURE 10.47 Water in a closed system with a pressure of 1 atm exerted on the piston. No bubbles can form within the liquid as long as the vapor pressure is less than 1 atm.

Case 3

A temperature at which the vapor pressures of the solid and liquid are identical. In this case, the solid and liquid states have the same vapor pressure, so they can coexist in the apparatus at equilibrium simultaneously with the vapor. This temperature represents the *freezing point* where both the solid and liquid states can exist.

We can now describe the melting point of a substance more precisely. The **normal melting point** is defined as *the temperature at which the solid and liquid states have the same vapor pressure under conditions where the total pressure is 1 atmosphere.*

Boiling occurs when the vapor pressure of a liquid becomes equal to the pressure of its environment. The **normal boiling point** of a liquid is *the temperature at which the vapor pressure of the liquid is exactly 1 atmosphere.* This concept is illustrated in Fig. 10.47. At temperatures where the vapor pressure of the liquid is less than 1 atmosphere, no bubbles of vapor can form because the pressure on the surface of the liquid is greater than the pressure in any spaces in the liquid where the bubbles are trying to form. Only when the liquid reaches a temperature at which the pressure of vapor in the spaces in the liquid is 1 atmosphere can bubbles form and boiling occur.

However, changes of state do not always occur exactly at the boiling point or melting point. For example, water can be readily **supercooled**; that is, it can be cooled below 0°C at 1 atm pressure and remain in the liquid state. Supercooling occurs because, as it is cooled, the water may not achieve the degree of organization necessary to form ice at 0°C , and thus it continues to exist as the liquid. At some point the correct ordering occurs and ice rapidly forms, releasing energy in the exothermic process and bringing the temperature back up to the melting point, where the remainder of the water freezes (see Fig. 10.48).

A liquid also can be **superheated**, or raised to temperatures above its boiling point, especially if it is heated rapidly. Superheating can occur because bubble formation in the interior of the liquid requires that many high-energy molecules gather in the same vicinity, and this may not happen at the boiling point, especially if the liquid is heated rapidly. If the liquid becomes superheated, the vapor pressure in the liquid is greater than the atmospheric pressure. Once a bubble does form, since its internal pressure is greater than that of the atmosphere, it can burst before rising to the surface, blowing the surrounding liquid out of the container. This is called *bumping* and has ruined many experiments. It can be avoided by adding boiling chips to the flask containing the liquid. Boiling chips are bits of porous ceramic material containing trapped air that escapes on heating, forming tiny bubbles that act as “starters” for vapor bubble formation. This allows a smooth onset of boiling as the boiling point is reached.



Boiling chip releasing air bubbles acts as a nucleating agent for the bubbles that form when water boils.

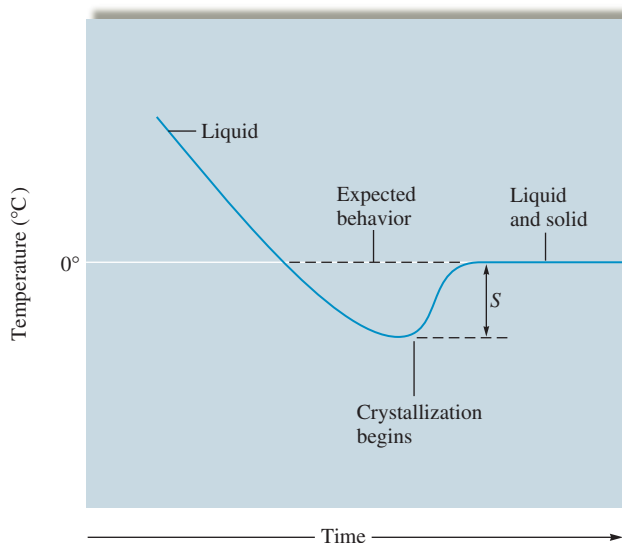


FIGURE 10.48 The supercooling of water. The extent of supercooling is given by S .

10.9 Phase Diagrams

A **phase diagram** is a convenient way of representing the phases of a substance as a function of temperature and pressure. For example, the phase diagram for water (Fig. 10.49) shows which state exists at a given temperature and pressure. It is important to recognize that a phase diagram describes conditions and events in a *closed* system of the type represented in Fig. 10.47, where no material can escape into the surroundings and no air is present. Notice that the diagram is not drawn to scale (neither axis is linear). This is done to emphasize certain features of the diagram that will be discussed below.

To show how to interpret the phase diagram for water, we will consider heating experiments at several pressures, shown by the dashed lines in Fig. 10.50.

Experiment 1

Pressure is 1 atm. This experiment begins with the cylinder shown in Fig. 10.47 completely filled with ice at a temperature of -20°C and the piston exerting a pressure of 1 atm directly on the ice (there is no air space). Since at temperatures below 0°C the vapor pressure of ice is less than 1 atm—which is the constant external pressure on the piston—no vapor is present in the cylinder. As the cylinder is heated, ice is the only component until the temperature reaches 0°C , where the ice changes to liquid water as energy is added. This is the normal melting point of water. Note that under these conditions no vapor exists in the system. The vapor pressures of the solid and liquid are equal, but this vapor pressure is less than 1 atm, so no water vapor can exist. This is true on the solid/liquid line everywhere except at the triple point (see Experiment 3 below). When the solid has completely changed to liquid, the temperature again rises. At this point, the cylinder contains only liquid water. *No vapor is present* because the vapor pressure of liquid water under these conditions is less than 1 atm, the constant external pressure on the piston. Heating continues until the temperature of the liquid water reaches 100°C . At this point, the vapor pressure of liquid water is 1 atm, and boiling occurs, with the liquid changing to vapor. This is the normal boiling point of water. After the liquid has been completely converted to steam, the temperature again rises as the heating continues. The cylinder now contains only water vapor.

Experiment 2

Pressure is 2.0 torr. Again, we start with ice as the only component in the cylinder at -20°C . The pressure exerted by the piston in this case is only 2.0 torr. As heating proceeds, the temperature rises to -10°C , where the ice changes directly to vapor, a process known as *sublimation*. Sublimation occurs when the vapor pressure of ice is equal to the

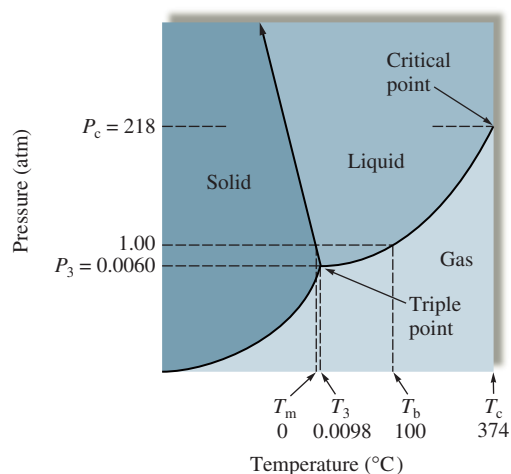


FIGURE 10.49

The phase diagram for water. T_m represents the normal melting point; T_3 and P_3 denote the triple point; T_b represents the normal boiling point; T_c represents the critical temperature; P_c represents the critical pressure. The negative slope of the solid/liquid line reflects the fact that the density of ice is less than that of liquid water. (Note that this line extends indefinitely, as indicated by the arrow.)

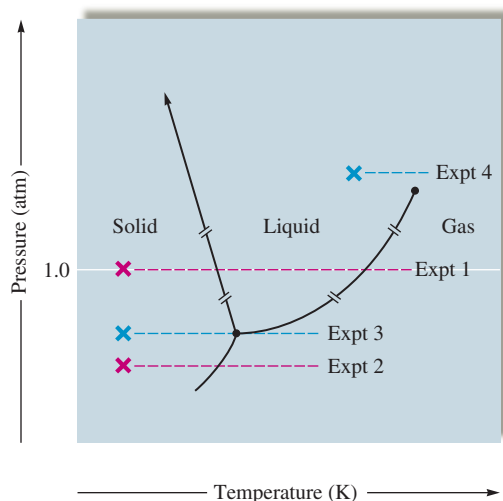


FIGURE 10.50
Diagrams of various heating experiments on samples of water in a closed system.

external pressure, which in this case is only 2.0 torr. No liquid water appears under these conditions because the vapor pressure of liquid water is always greater than 2.0 torr, and thus it cannot exist at this pressure. If liquid water were placed in a cylinder under such a low pressure, it would vaporize immediately at temperatures above -10°C or freeze at temperatures below -10°C .

Experiment 3

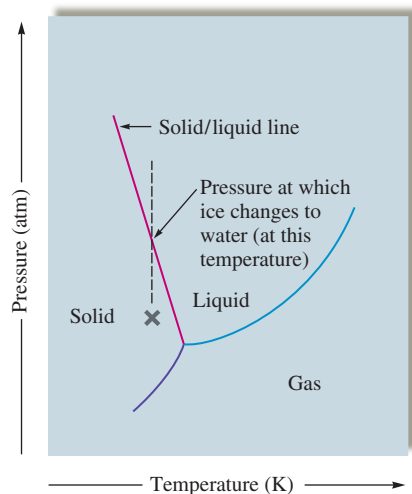
Pressure is 4.58 torr. Again, we start with ice as the only component in the cylinder at -20°C . In this case the pressure exerted on the ice by the piston is 4.58 torr. As the cylinder is heated, no new phase appears until the temperature reaches 0.01°C (273.16 K). At this point, called the **triple point**, solid and liquid water have identical vapor pressures of 4.58 torr. Thus at 0.01°C (273.16 K) and 4.58 torr all three states of water are present. In fact, only under these conditions can all three states of water coexist in a closed system.

Experiment 4

Pressure is 225 atm. In this experiment we start with liquid water in the cylinder at 300°C ; the pressure exerted by the piston on the water is 225 atm. Liquid water can be present at this temperature because of the high external pressure. As the temperature increases, something happens that we did not see in the first three experiments: The liquid gradually changes into a vapor but goes through an intermediate “fluid” region, which is neither true liquid nor vapor. This is quite unlike the behavior at lower temperatures and pressures, say at 100°C . and 1 atm, where the temperature remains constant while a definite phase change from liquid to vapor occurs. This unusual behavior occurs because the conditions are beyond the critical point for water. The **critical temperature** can be defined as the temperature above which the vapor cannot be liquefied no matter what pressure is applied. The **critical pressure** is the pressure required to produce liquefaction at the critical temperature. Together, the critical temperature and the critical pressure define the **critical point**. For water the critical point is 374°C and 218 atm. Note that the liquid/vapor line on the phase diagram for water ends at the critical point. Beyond this point the transition from one state to another involves the intermediate “fluid” region just described.

Applications of the Phase Diagram for Water

There are several additional interesting features of the phase diagram for water. Note that the solid/liquid boundary line has a negative slope. This means that the melting point of ice *decreases* as the external pressure *increases*. This behavior, which is opposite to that

**FIGURE 10.51**

The phase diagram for water. At point X on the phase diagram, water is a solid. However, as the external pressure is increased while the temperature remains constant (indicated by the vertical dotted line), the solid/liquid line is crossed and the ice melts.



Visualization: Boiling Water with Ice Water

Water boils at 89°C in Leadville, Colorado.



The effect of pressure on ice allows this skater to glide smoothly.

observed for most substances, occurs because the density of ice is *less* than that of liquid water at the melting point. The maximum density of water occurs at 4°C; when liquid water freezes, its volume increases.

We can account for the effect of pressure on the melting point of water using the following reasoning. At the melting point, liquid and solid water coexist—they are in dynamic equilibrium, since the rate at which ice is melting is just balanced by the rate at which the water is freezing. What happens if we apply pressure to this system? When subjected to increased pressure, matter reduces its volume. This behavior is most dramatic for gases but also occurs for condensed states. Since a given mass of ice at 0°C has a larger volume than the same mass of liquid water, the system can reduce its volume in response to the increased pressure by changing to liquid. Thus at 0°C and an external pressure greater than 1 atm, water is liquid. In other words, the freezing point of water is less than 0°C when the pressure is greater than 1 atm.

Figure 10.51 illustrates the effect of pressure on ice. At the point X on the phase diagram, ice is subjected to increased pressure at constant temperature. Note that as the pressure is increased, the solid/liquid line is crossed, indicating that the ice melts. This phenomenon may be important in ice skating. The narrow blade of the skate exerts a large pressure, since the skater's weight is supported by the small area of the blade. Also, the frictional heating due to the moving skate contributes to the melting of the ice.* After the blade passes, the liquid refreezes as normal pressure and temperature return. Without this lubrication effect due to the thawing ice, ice skating would not be the smooth, graceful activity that many people enjoy.

Ice's lower density has other implications. When water freezes in a pipe or an engine block, it will expand and break the container. This is why water pipes are insulated in cold climates and antifreeze is used in water-cooled engines. The lower density of ice also means that ice formed on rivers and lakes will float, providing a layer of insulation that helps prevent bodies of water from freezing solid in the winter. Aquatic life can therefore continue to live through periods of freezing temperatures.

A liquid boils at the temperature where the vapor pressure of the liquid equals the external pressure. Thus the boiling point of a substance, like the melting point, depends on the external pressure. This is why water boils at different temperatures at different elevations (see Table 10.10), and any cooking carried out in boiling water will be affected by this variation. For example, it takes longer to hard-boil an egg in Leadville, Colorado (elevation: 10,150 ft), than in San Diego, California (sea level), since water boils at a lower temperature in Leadville.

As we mentioned earlier, the phase diagram for water describes a closed system. Therefore, we must be very cautious in using the phase diagram to explain the behavior of water in a natural setting, such as on the earth's surface. For example, in dry climates (low humidity), snow and ice seem to sublime—a minimum amount of slush is produced. Wet clothes put on an outside line at temperatures below 0°C freeze and then dry while frozen. However, the phase diagram (Fig. 10.47) shows that ice should *not* be able to sublime at normal atmospheric pressures. What is happening in these cases? Ice in the natural environment is not in a closed system. The pressure is provided by the atmosphere rather than by a solid piston. This means that the vapor produced over the ice can escape from the immediate region as soon as it is formed. The vapor does not come to equilibrium with the solid, and the ice slowly disappears. Sublimation, which seems forbidden by the phase diagram, does in fact occur under these conditions, although it is not the sublimation under equilibrium conditions described by the phase diagram.

*The physics of ice skating is quite complex, and there is disagreement about whether the pressure or the frictional heating of the ice skate is most important. See "Letter to the Editor," by R. Silberman, *J. Chem. Ed.* **65** (1988): 186.

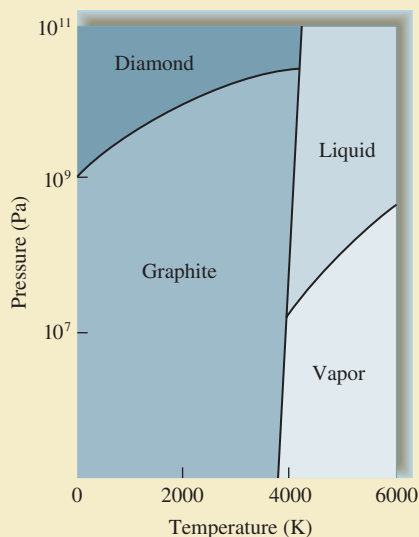


CHEMICAL IMPACT

Making Diamonds at Low Pressures: Fooling Mother Nature

In 1955 Robert H. Wentorf, Jr., accomplished something that borders on alchemy—he turned peanut butter into diamonds. He and his coworkers at the General Electric Research and Development Center also changed roofing pitch, wood, coal, and many other carbon-containing materials into diamonds, using a process involving temperatures of $\approx 2000^\circ\text{C}$ and pressures of $\approx 10^5$ atm. Although the first diamonds made by this process looked like black sand because of the impurities present, the process has now been developed to a point such that beautiful, clear, gem-quality diamonds can be produced. General Electric now has the capacity to produce 150 million carats (30,000 kg) of diamonds annually (virtually all of which is “diamond grit” used for industrial purposes such as abrasive coatings on cutting tools). The production of large, gem-quality diamonds by this process is still too expensive to compete with the natural sources of these stones. However, this may change as methods are developed for making diamonds at low pressures.

The high temperatures and pressures used in the GE process for making diamonds make sense if one looks at the accompanying phase diagram for carbon. Note that graphite—not diamond—is the most stable form of carbon



The phase diagram for carbon.

under ordinary conditions of temperature and pressure. However, diamond becomes more stable than graphite at very high pressures (as one would expect from the greater



A carbon dioxide fire extinguisher.

TABLE 10.10 Boiling Point of Water at Various Locations

Location	Feet Above Sea Level	P_{atm} (torr)	Boiling Point ($^\circ\text{C}$)
Top of Mt. Everest, Tibet	29,028	240	70
Top of Mt. McKinley, Alaska	20,320	340	79
Top of Mt. Whitney, Calif.	14,494	430	85
Leadville, Colo.	10,150	510	89
Top of Mt. Washington, N.H.	6,293	590	93
Boulder, Colo.	5,430	610	94
Madison, Wis.	900	730	99
New York City, N.Y.	10	760	100
Death Valley, Calif.	-282	770	100.3

The Phase Diagram for Carbon Dioxide

The phase diagram for carbon dioxide (Fig. 10.52) differs from that for water. The solid/liquid line has a positive slope, since solid carbon dioxide is more dense than liquid carbon dioxide. The triple point for carbon dioxide occurs at 5.1 atm and -56.6°C , and the critical point occurs at 72.8 atm and 31°C . At a pressure of 1 atm, solid carbon dioxide sublimates

density of diamond). The high temperature used in the GE process is necessary to disrupt the bonds in graphite so that diamond (the most stable form of carbon at the high pressures used in the process) can form. Once the diamond is produced, the elemental carbon is “trapped” in this form at normal conditions (25°C, 1 atm) because the reaction back to the graphite form is so slow. That is, even though graphite is more stable than diamond at 25°C and 1 atm, diamond can exist almost indefinitely because the conversion to graphite is a very *slow* reaction. As a result, diamonds formed at the high pressures found deep in the earth’s crust can be brought to the earth’s surface by natural geologic processes and continue to exist for millions of years.*

We have seen that diamond formed in the laboratory at high pressures is “trapped” in this form, but this process is very expensive. Can diamond be formed at low pressures? The phase diagram for carbon says no. However, researchers have found that under the right conditions diamonds can be

*In Morocco, a 50-km-long slab called Beni Bousera contains chunks of graphite that were probably once diamonds formed in the deposit when it was buried 150 km underground. As this slab slowly rose to the surface over millions of years, the very slow reaction changing diamond to graphite had time to occur. On the other hand, in the diamond-rich kimberlite deposits in South Africa, which rise to the surface much faster, the diamonds have not had sufficient time to revert to graphite.

“grown” at low pressures. The process used is called *chemical vapor deposition (CVD)*. CVD uses an energy source to release carbon atoms from a compound such as methane into a steady flow of hydrogen gas (some of which is dissociated to produce hydrogen atoms). The carbon atoms then deposit as a diamond film on a surface maintained at a temperature between 600 and 900°C. Why does diamond form on this surface rather than the favored graphite? Nobody is sure, but it has been suggested that at these relatively high temperatures the diamond structure grows faster than the graphite structure and so diamond is favored under these conditions. It also has been suggested that the hydrogen atoms present react much faster with graphite fragments than with diamond fragments, effectively removing any graphite from the growing film. Once it forms, of course, diamond is trapped. The major advantage of CVD is that there is no need for the extraordinarily high pressures used in the traditional process for synthesizing diamonds.

The first products with diamond films are already on the market. Audiophiles can buy tweeters that have diaphragms coated with a thin diamond film that limits sound distortion. Watches with diamond-coated crystals are planned, as are diamond-coated windows in infrared scanning devices used in analytical instruments and missile guidance systems. These applications represent only the beginning for diamond-coated products.

at -78°C , a property that leads to its common name, *dry ice*. No liquid phase occurs under normal atmospheric conditions, making dry ice a convenient refrigerant.

Carbon dioxide is often used in fire extinguishers, where it exists as a liquid at 25°C under high pressures. Liquid carbon dioxide released from the extinguisher into the environment at 1 atm immediately changes to a vapor. Being heavier than air, this vapor smothers the fire by keeping oxygen away from the flame. The liquid/vapor transition is highly endothermic, so cooling also results, which helps to put out the fire.

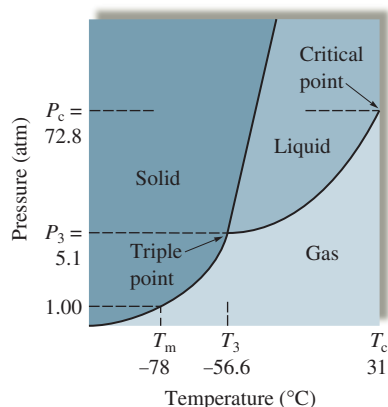


FIGURE 10.52

The phase diagram for carbon dioxide. The liquid state does not exist at a pressure of 1 atm. The solid/liquid line has a positive slope, since the density of solid carbon dioxide is greater than that of liquid carbon dioxide.

Key Terms

Section 10.1

condensed states
intermolecular forces
dipole–dipole attraction
hydrogen bonding
London dispersion forces

Section 10.2

surface tension
capillary action
viscosity

Section 10.3

crystalline solid
amorphous solid
lattice
unit cell
X-ray diffraction
ionic solid
molecular solid
atomic solid

Section 10.4

closest packing
hexagonal closest packed (hcp) structure
cubic closest packed (ccp) structure
band model
molecular orbital (MO) model
alloy
substitutional alloy
interstitial alloy

Section 10.5

network solid
silica
silicate
glass
ceramic
semiconductor
n-type semiconductor
p-type semiconductor
p–n junction

Section 10.8

vaporization (evaporation)
heat of vaporization
enthalpy of vaporization (ΔH_{vap})
condensation
equilibrium
equilibrium vapor pressure
sublimation
heating curve
enthalpy (heat) of fusion (ΔH_{fus})
normal melting point
normal boiling point
supercooled
superheated

For Review

Condensed states of matter: liquids and solids

- Held together by forces among the component molecules, atoms, or ions
- Liquids exhibit properties such as surface tension, capillary action, and viscosity that depend on the forces among the components

Dipole–dipole forces

- Attractions among molecules with dipole moments
- Hydrogen bonding is a particularly strong form of dipole–dipole attraction
 - Occurs in molecules containing hydrogen bonded to a highly electronegative element such as nitrogen, oxygen, or fluorine
 - Produces unusually high boiling points

London dispersion forces

- Caused by instantaneous dipoles that form in atoms or nonpolar molecules

Crystalline solids

- Have a regular arrangement of components often represented as a lattice; the smallest repeating unit of the lattice is called the unit cell
- Classified by the types of components:
 - Atomic solids (atoms)
 - Ionic solids (ions)
 - Molecular solids (molecules)
- Arrangement of the components can be determined by X-ray analysis

Metals

- Structure is modeled by assuming atoms to be uniform spheres
 - Closest packing
 - Hexagonal
 - Cubic
- Metallic bonding can be described in terms of two models
 - Electron sea model: valence electrons circulate freely among the metal cations
 - Band model: electrons are assumed to occupy molecular orbitals
 - Conduction bands: closely spaced molecular orbitals with empty electron spaces
- Alloys: mixtures with metallic properties
 - Substitutional
 - Interstitial

Network solids

- Contain giant networks of atoms covalently bound together
- Examples are diamond and graphite
- Silicates are network solids containing Si—O—Si bridges that form the basis for many rocks, clays, and ceramics

Semiconductors

- Very pure silicon is “doped” with other elements
 - n-type: doping atoms typically contain five valence electrons (one more than silicon)
 - p-type: doping elements typically contain three valence electrons
- Modern electronics are based on devices with p–n junctions

Molecular solids

- Components are discrete molecules
- Intermolecular forces are typically weak, leading to relatively low boiling and melting points

Section 10.9

phase diagram
triple point
critical temperature
critical pressure
critical point

Ionic solids

- Components are ions
- Interionic forces are relatively strong, leading to solids with high melting and boiling points
- Many structures consist of closest packing of the larger ions with the smaller ions in tetrahedral or octahedral holes

Phase changes

- The change from liquid to gas (vapor) is called vaporization or evaporation
- Condensation is the reverse of vaporization
- Equilibrium vapor pressure: the pressure that occurs over a liquid or solid in a closed system when the rate of evaporation equals the rate of condensation
 - Liquids whose components have high intermolecular forces have relatively low vapor pressures
 - Normal boiling point: the temperature at which the vapor pressure of a liquid equals one atmosphere
 - Normal melting point: the temperature at which a solid and its liquid have the same vapor pressure (at 1 atm external pressure)
- Phase diagram
 - Shows what state exists at a given temperature and pressure in a closed system
 - Triple point: temperature at which all three phases exist simultaneously
 - Critical point: defined by the critical temperature and pressure
 - Critical temperature: the temperature above which the vapor cannot be liquefied no matter the applied pressure
 - Critical pressure: the pressure required to produce liquefaction at the critical temperature

REVIEW QUESTIONS

1. What are intermolecular forces? How do they differ from intramolecular forces? What are dipole–dipole forces? How do typical dipole–dipole forces differ from hydrogen-bonding interactions? In what ways are they similar? What are London dispersion forces? How do typical London dispersion forces differ from dipole–dipole forces? In what ways are they similar? Describe the relationship between molecular size and strength of London dispersion forces. Place the major types of intermolecular forces in order of increasing strength. Is there some overlap? That is, can the strongest London dispersion forces be greater than some dipole–dipole forces? Give an example of such an instance.
2. Define the following terms and describe how each depends on the strength of the intermolecular forces.
 - a. surface tension
 - b. viscosity
 - c. melting point
 - d. boiling point
 - e. vapor pressure
3. Compare and contrast solids versus liquids versus gases.
4. Distinguish between the items in the following pairs.
 - a. crystalline solid; amorphous solid
 - b. ionic solid; molecular solid
 - c. molecular solid; network solid
 - d. metallic solid; network solid
5. What is a lattice? What is a unit cell? Describe a simple cubic unit cell. How many net atoms are contained in a simple cubic unit cell? How is the radius of the atom

related to the cube edge length for a simple cubic unit cell? Answer the same questions for the body-centered cubic unit cell and for the face-centered unit cell.

6. What is closest packing? What is the difference between hexagonal closest packing and cubic closest packing? What is the unit cell for each closest packing?
7. Use the band model to describe differences among insulators, conductors, and semiconductors. Also use the band model to explain why each of the following increases the conductivity of a semiconductor.
 - a. increasing the temperature
 - b. irradiating with light
 - c. adding an impurity

How do conductors and semiconductors differ as to the effect of temperature on electrical conductivity? How can an n-type semiconductor be produced from pure germanium? How can a p-type semiconductor be produced from pure germanium?

8. Describe, in general, the structures of ionic solids. Compare and contrast the structure of sodium chloride and zinc sulfide. How many tetrahedral holes and octahedral holes are there per closest packed anion? In zinc sulfide, why are only one-half of the tetrahedral holes filled with cations?
9. Define each of the following.
 - a. evaporation
 - b. condensation
 - c. sublimation
 - d. boiling
 - e. melting
 - f. enthalpy of vaporization
 - g. enthalpy of fusion
 - h. heating curve

Why is the enthalpy of vaporization for water much greater than its enthalpy of fusion? What does this say about the changes in intermolecular forces in going from solid to liquid to vapor? What do we mean when we say that a liquid is *volatile*? Do volatile liquids have large or small vapor pressures at room temperature? What strengths of intermolecular forces occur in highly volatile liquids?

10. Compare and contrast the phase diagrams of water versus carbon dioxide. Why doesn't CO_2 have a normal melting point and a normal boiling point, whereas water does? The slopes of the solid–liquid lines in the phase diagrams of H_2O and CO_2 are different. What do the slopes of the solid–liquid lines indicate in terms of the relative densities of the solid and liquid states for each substance? How do the melting points of H_2O and CO_2 depend on pressure? How do the boiling points of H_2O and CO_2 depend on pressure? Rationalize why the critical temperature for H_2O is greater than that for CO_2 .

Active Learning Questions

These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

1. It is possible to balance a paper clip on the surface of water in a beaker. If you add a bit of soap to the water, however, the paper clip sinks. Explain how the paper clip can float and why it sinks when soap is added.
2. Consider a sealed container half-filled with water. Which statement best describes what occurs in the container?
 - a. Water evaporates until the air is saturated with water vapor; at this point, no more water evaporates.
 - b. Water evaporates until the air is overly saturated (supersaturated) with water, and most of this water recondenses; this cycle continues until a certain amount of water vapor is present, and then the cycle ceases.
 - c. Water does not evaporate because the container is sealed.
 - d. Water evaporates, and then water evaporates and recondenses simultaneously and continuously.

- e. Water evaporates until it is eventually all in vapor form.
Explain each choice. Justify your choice, and for choices you did not pick, explain what is wrong with them.
- Explain the following: You add 100 mL of water to a 500-mL round-bottom flask and heat the water until it is boiling. You remove the heat and stopper the flask, and the boiling stops. You then run cool water over the neck of the flask, and the boiling begins again. It seems as though you are boiling water by cooling it.
 - Is it possible for the dispersion forces in a particular substance to be stronger than the hydrogen bonding forces in another substance? Explain your answer.
 - Does the nature of intermolecular forces change when a substance goes from a solid to a liquid, or from a liquid to a gas? What causes a substance to undergo a phase change?
 - Why do liquids have a vapor pressure? Do all liquids have vapor pressures? Explain. Do solids exhibit vapor pressure? Explain. How does vapor pressure change with changing temperature? Explain.
 - Water in an open beaker evaporates over time. As the water is evaporating, is the vapor pressure increasing, decreasing, or staying the same? Why?
 - What is the vapor pressure of water at 100°C? How do you know?
 - Refer to Fig. 10.44. Why doesn't temperature increase continuously over time? That is, why does the temperature stay constant for periods of time?
 - Which are stronger, intermolecular or intramolecular forces for a given molecule? What observation(s) have you made that support this? Explain.
 - Why does water evaporate?
- A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

- The nonpolar hydrocarbon $C_{25}H_{52}$ is a solid at room temperature. Its boiling point is greater than 400°C. Which has the stronger intermolecular forces, $C_{25}H_{52}$ or H_2O ? Explain your answer.
- Atoms are assumed to touch in closest packed structures, yet every closest packed unit cell contains a significant amount of empty space. Why?
- Define *critical temperature* and *critical pressure*. In terms of the kinetic molecular theory, why is it impossible for a substance to exist as a liquid above its critical temperature?
- Use the kinetic molecular theory to explain why a liquid gets cooler as it evaporates from an insulated container.
- Will a crystalline solid or an amorphous solid give a simpler X-ray diffraction pattern? Why?
- What is an alloy? Explain the differences in structure between substitutional and interstitial alloys. Give an example of each type.
- Describe what is meant by a dynamic equilibrium in terms of the vapor pressure of a liquid.
- How does each of the following affect the rate of evaporation of a liquid in an open dish?
 - intermolecular forces
 - temperature
 - surface area
- When a person has a severe fever, one therapy used to reduce the fever is an "alcohol rub." Explain how the evaporation of alcohol from a person's skin removes heat energy from the body.
- When wet laundry is hung on a clothesline on a cold winter day, it will freeze but eventually dry. Explain.
- Why is a burn from steam typically much more severe than a burn from boiling water?
- You have three covalent compounds with three very different boiling points. All of the compounds have similar molar mass and relative shape. Explain how these three compounds could have very different boiling points.
- Compare and contrast the structures of the following solids.
 - diamond versus graphite
 - silica versus silicates versus glass
- Compare and contrast the structures of the following solids.
 - $CO_2(s)$ versus $H_2O(s)$
 - $NaCl(s)$ versus $CsCl(s)$; See Exercise 61 for the structures.
- Silicon carbide (SiC) is an extremely hard substance that acts as an electrical insulator. Propose a structure for SiC.
- A plot of $\ln P_{\text{vap}}$ versus $1/T$ (K) is linear with a negative slope. Why is this the case?
- Iodine, like most substances, exhibits only three phases; solid, liquid, and vapor. The triple point of iodine is at 90 torr and 115°C. Which of the following statements concerning liquid I_2 must be true? Explain your answer.
 - $I_2(l)$ is more dense than $I_2(g)$.
 - $I_2(l)$ cannot exist above 115°C.
 - $I_2(l)$ cannot exist at 1 atmosphere pressure.
 - $I_2(l)$ cannot have a vapor pressure greater than 90 torr.
 - $I_2(l)$ cannot exist at a pressure of 10 torr.

Exercises

In this section similar exercises are paired.

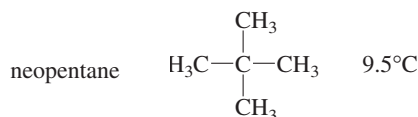
Intermolecular Forces and Physical Properties

- Identify the most important types of interparticle forces present in the solids of each of the following substances.

a. Ar	e. CH_4
b. HCl	f. CO
c. HF	g. $NaNO_3$
d. $CaCl_2$	
- Identify the most important types of interparticle forces present in the solids of each of the following substances.
 - NH_4Cl
 - Teflon, $CF_3(CF_2CF_2)_nCF_3$
 - Polyethylene, $CH_3(CH_2CH_2)_nCH_3$
 - $CHCl_3$
 - NH_3
 - NO
 - BF_3

31. Predict which substance in each of the following pairs would have the greater intermolecular forces.
- CO₂ or OCS
 - SeO₂ or SO₂
 - CH₃CH₂CH₂NH₂ or H₂NCH₂CH₂NH₂
 - CH₃CH₃ or H₂CO
 - CH₃OH or H₂CO
32. Consider the compounds Cl₂, HCl, F₂, NaF, and HF. Which compound has a boiling point closest to that of argon? Explain.
33. Rationalize the difference in boiling points for each of the following pairs of substances:

a. *n*-pentane CH₃CH₂CH₂CH₂CH₃ 36.2°C



- HF 20°C
HCl -85°C
 - HCl -85°C
LiCl 1360°C
 - n*-pentane CH₃CH₂CH₂CH₂CH₃ 36.2°C
n-hexane CH₃CH₂CH₂CH₂CH₂CH₃ 69°C
34. Consider the following compounds and formulas. (*Note:* The formulas are written in such a way as to give you an idea of the structure.)

ethanol: CH₃CH₂OH
dimethyl ether: CH₃OCH₃
propane: CH₃CH₂CH₃

The boiling points of these compounds are (in no particular order) -42.1°C, -23°C, and 78.5°C. Match the boiling points to the correct compounds.

35. In each of the following groups of substances, pick the one that has the given property. Justify your answer.
- highest boiling point: HBr, Kr, or Cl₂
 - highest freezing point: H₂O, NaCl, or HF
 - lowest vapor pressure at 25°C: Cl₂, Br₂, or I₂
 - lowest freezing point: N₂, CO, or CO₂
 - lowest boiling point: CH₄, CH₃CH₃, or CH₃CH₂CH₃
 - highest boiling point: HF, HCl, or HBr
- g. lowest vapor pressure at 25°C: CH₃CH₂CH₃, CH₃C(=O)CH₃, or CH₃CH₂CH₂OH
36. In each of the following groups of substances, pick the one that has the given property. Justify each answer.
- highest boiling point: CCl₄, CF₄, CBr₄
 - lowest freezing point: LiF, F₂, HCl
 - smallest vapor pressure at 25°C: CH₃OCH₃, CH₃CH₂OH, CH₃CH₂CH₃
 - greatest viscosity: H₂S, HF, H₂O₂

- greatest heat of vaporization: H₂CO, CH₃CH₃, CH₄
- smallest enthalpy of fusion: I₂, CsBr, CaO

Properties of Liquids

37. The shape of the meniscus of water in a glass tube is different from that of mercury in a glass tube. Why?



H₂O in glass



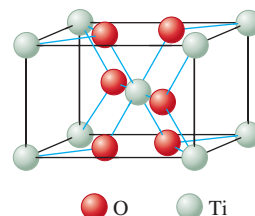
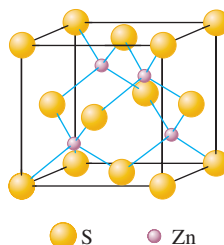
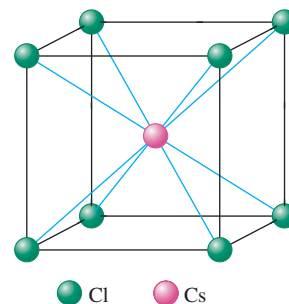
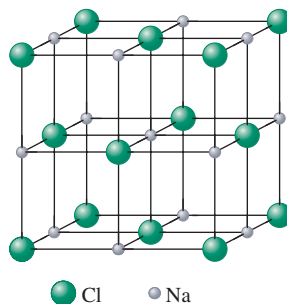
Hg in glass

38. Explain why water forms into beads on a waxed car finish.
39. Hydrogen peroxide (H₂O₂) is a syrupy liquid with a relatively low vapor pressure and a normal boiling point of 152.2°C. Rationalize the differences of these physical properties from those of water.
40. Carbon diselenide (CSe₂) is a liquid at room temperature. The normal boiling point is 125°C, and the melting point is -45.5°C. Carbon disulfide (CS₂) is also a liquid at room temperature with normal boiling and melting points of 46.5°C and -111.6°C, respectively. How do the strengths of the intermolecular forces vary from CO₂ to CS₂ to CSe₂? Explain.

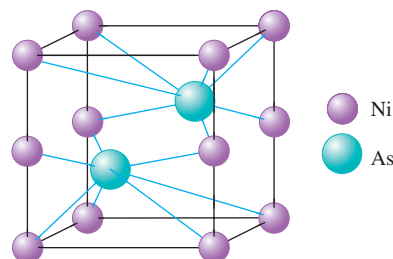
Structures and Properties of Solids

41. X rays from a copper X-ray tube ($\lambda = 154$ pm) were diffracted at an angle of 14.22 degrees by a crystal of silicon. Assuming first-order diffraction ($n = 1$ in the Bragg equation), what is the interplanar spacing in silicon?
42. The second-order diffraction ($n = 2$) for a gold crystal is at an angle of 22.20° for X rays of 154 pm. What is the spacing between these crystal planes?
43. A topaz crystal has an interplanar spacing (d) of 1.36 Å ($1 \text{ Å} = 1 \times 10^{-10} \text{ m}$). Calculate the wavelength of the X ray that should be used if $\theta = 15.0^\circ$ (assume $n = 1$).
44. X rays of wavelength 2.63 Å were used to analyze a crystal. The angle of first-order diffraction ($n = 1$ in the Bragg equation) was 15.55 degrees. What is the spacing between crystal planes, and what would be the angle for second-order diffraction ($n = 2$)?
45. Calcium has a cubic closest packed structure as a solid. Assuming that calcium has an atomic radius of 197 pm, calculate the density of solid calcium.
46. Nickel has a face-centered cubic unit cell. The density of nickel is 6.84 g/cm³. Calculate a value for the atomic radius of nickel.

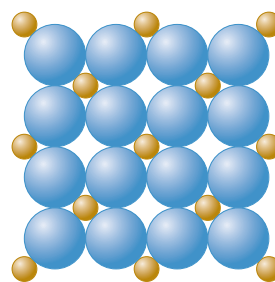
47. A certain form of lead has a cubic closest packed structure with an edge length of 492 pm. Calculate the value of the atomic radius and the density of lead.
48. You are given a small bar of an unknown metal X. You find the density of the metal to be 10.5 g/cm^3 . An X-ray diffraction experiment measures the edge of the face-centered cubic unit cell as 4.09 \AA ($1 \text{ \AA} = 10^{-10} \text{ m}$). Identify X.
49. Titanium metal has a body-centered cubic unit cell. The density of titanium is 4.50 g/cm^3 . Calculate the edge length of the unit cell and a value for the atomic radius of titanium. (*Hint:* In a body-centered arrangement of spheres, the spheres touch across the body diagonal.)
50. Barium has a body-centered cubic structure. If the atomic radius of barium is 222 pm, calculate the density of solid barium.
51. The radius of gold is 144 pm, and the density is 19.32 g/cm^3 . Does elemental gold have a face-centered cubic structure or a body-centered cubic structure?
52. The radius of tungsten is 137 pm and the density is 19.3 g/cm^3 . Does elemental tungsten have a face-centered cubic structure or a body-centered cubic structure?
53. What fraction of the total volume of a cubic closest packed structure is occupied by atoms? (*Hint:* $V_{\text{sphere}} = \frac{4}{3}\pi r^3$.) What fraction of the total volume of a simple cubic structure is occupied by atoms? Compare the answers.
54. Iron has a density of 7.86 g/cm^3 and crystallizes in a body-centered cubic lattice. Show that only 68% of a body-centered lattice is actually occupied by atoms, and determine the atomic radius of iron.
55. Explain how doping silicon with either phosphorus or gallium increases the electrical conductivity over that of pure silicon.
56. Explain how a p-n junction makes an excellent rectifier.
57. Selenium is a semiconductor used in photocopying machines. What type of semiconductor would be formed if a small amount of indium impurity is added to pure selenium?
58. The Group 3A/Group 5A semiconductors are composed of equal amounts of atoms from Group 3A and Group 5A—for example, InP and GaAs. These types of semiconductors are used in light-emitting diodes and solid-state lasers. What would you add to make a p-type semiconductor from pure GaAs? How would you dope pure GaAs to make an n-type semiconductor?
59. The band gap in aluminum phosphide (AlP) is 2.5 electron-volts ($1\text{eV} = 1.6 \times 10^{-19} \text{ J}$). What wavelength of light is emitted by an AlP diode?
60. An aluminum antimonide solid-state laser emits light with a wavelength of 730. nm. Calculate the band gap in joules.
61. The structures of some common crystalline substances are shown below. Show that the net composition of each unit cell corresponds to the correct formula of each substance.



62. The unit cell for nickel arsenide is shown below. What is the formula of this compound?

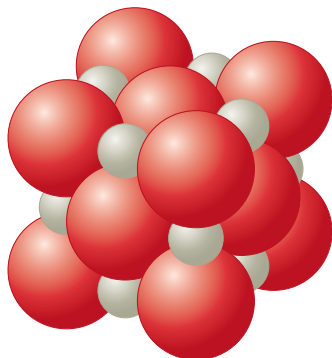


63. Cobalt fluoride crystallizes in a closest packed array of fluoride ions with the cobalt ions filling one-half of the octahedral holes. What is the formula of this compound?
64. The compounds Na_2O , CdS , and ZrI_4 all can be described as cubic closest packed anions with the cations in tetrahedral holes. What fraction of the tetrahedral holes is occupied for each case?
65. What is the formula for the compound that crystallizes with a cubic closest packed array of sulfur ions, and that contains zinc ions in $\frac{1}{8}$ of the tetrahedral holes and aluminum ions in $\frac{1}{2}$ of the octahedral holes?
66. Assume the two-dimensional structure of an ionic compound, M_xA_y , is



What is the empirical formula of this ionic compound?

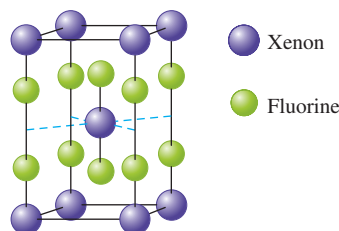
67. A certain metal fluoride crystallizes in such a way that the fluoride ions occupy simple cubic lattice sites, while the metal ions occupy the body centers of *half* the cubes. What is the formula of the metal fluoride?
68. The structure of manganese fluoride can be described as a simple cubic array of manganese ions with fluoride ions at the center of each edge of the cubic unit cell. What is the charge of the manganese ions in this compound?
69. The unit cell of MgO is shown below.



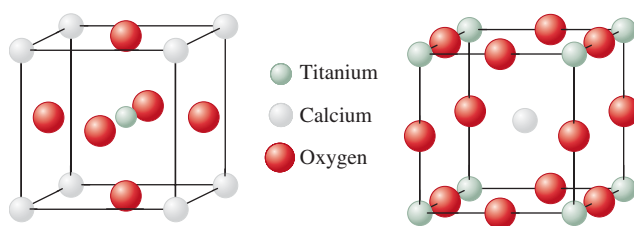
Does MgO have a structure like that of NaCl or ZnS? If the density of MgO is 3.58 g/cm^3 , estimate the radius (in centimeters) of the O^{2-} anions and the Mg^{2+} cations.

70. The CsCl structure is a simple cubic array of chloride ions with a cesium ion at the center of each cubic array (see Exercise 61). Given that the density of cesium chloride is 3.97 g/cm^3 , and assuming that the chloride and cesium ions touch along the body diagonal of the cubic unit cell, calculate the distance between the centers of adjacent Cs^+ and Cl^- ions in the solid. Compare this value with the expected distance based on the sizes of the ions. The ionic radius of Cs^+ is 169 pm, and the ionic radius of Cl^- is 181 pm.
71. What type of solid will each of the following substances form?
- | | | |
|-------------------|-------------------------|--------------------|
| a. CO_2 | e. Ru | i. NaOH |
| b. SiO_2 | f. I_2 | j. U |
| c. Si | g. KBr | k. CaCO_3 |
| d. CH_4 | h. H_2O | l. PH_3 |
72. What type of solid will each of the following substances form?
- | | | |
|------------------|-----------------------------|--|
| a. diamond | e. KCl | i. Ar |
| b. PH_3 | f. quartz | j. Cu |
| c. H_2 | g. NH_4NO_3 | k. $\text{C}_6\text{H}_{12}\text{O}_6$ |
| d. Mg | h. SF_2 | |
73. The memory metal, nitinol, is an alloy of nickel and titanium. It is called a *memory metal* because after being deformed, a piece of nitinol wire will return to its original shape. The structure of nitinol consists of a simple cubic array of Ni atoms and an inner penetrating simple cubic array of Ti atoms. In the extended lattice, a Ti atom is found at the center of a cube of Ni atoms; the reverse is also true.
- Describe the unit cell for nitinol.
 - What is the empirical formula of nitinol?
 - What are the coordination numbers (number of nearest neighbors) of Ni and Ti in nitinol?

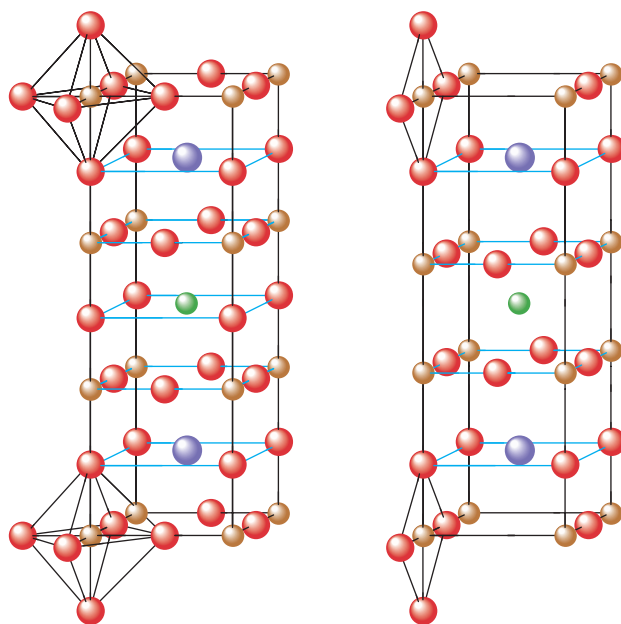
74. The unit cell for a pure xenon fluoride compound is shown below. What is the formula of the compound?



75. Perovskite is a mineral containing calcium, titanium, and oxygen. Two different representations of the unit cell are shown below. Show that both these representations give the same formula and the same number of oxygen atoms around each titanium atom.



76. A mineral crystallizes in a cubic closest packed array of oxygen ions with aluminum ions in some of the octahedral holes and magnesium ions in some of the tetrahedral holes. Deduce the formula of this mineral and predict the fraction of octahedral holes and tetrahedral holes that are filled by the various cations.
77. Materials containing the elements Y, Ba, Cu, and O that are superconductors (electrical resistance equals zero) at temperatures



Blue sphere: Barium Red sphere: Oxygen Orange sphere: Copper Green sphere: Yttrium

(a) Ideal perovskite structure

(b) Actual structure of superconductor

above that of liquid nitrogen were recently discovered. The structures of these materials are based on the perovskite structure. Were they to have the ideal perovskite structure, the superconductor would have the structure shown in part (a) of the figure above.

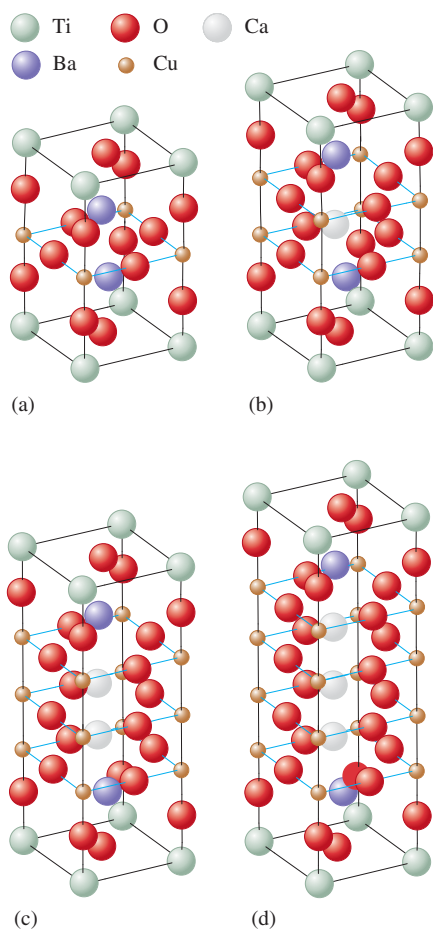
- What is the formula of this ideal perovskite material?
- How is this structure related to the perovskite structure shown in Exercise 75?

These materials, however, do not act as superconductors unless they are deficient in oxygen. The structure of the actual superconducting phase appears to be that shown in part (b) of the figure.

- What is the formula of this material?

78. The structures of another class of ceramic, high-temperature superconductors are shown in the figure below.

- Determine the formula of each of these four superconductors.
- One of the structural features that appears to be essential for high-temperature superconductivity is the presence of planar sheets of copper and oxygen atoms. As the number of sheets in each unit cell increases, the temperature for the onset of superconductivity increases. Order the four structures from lowest to the highest superconducting temperature.
- Assign oxidation states to Cu in each structure assuming Tl exists as Tl^{3+} . The oxidation states of Ca, Ba, and O are assumed to be +2, +2, and -2, respectively.
- It also appears that copper must display a mixture of oxidation states for a material to exhibit superconductivity. Explain how this occurs in these materials as well as in the superconductor in Exercise 77.



Phase Changes and Phase Diagrams

79. Plot the following data and determine ΔH_{vap} for magnesium and lithium. In which metal is the bonding stronger?

Vapor Pressure (mm Hg)	Temperature ($^{\circ}\text{C}$)	
	Li	Mg
1.	750.	620.
10.	890.	740.
100.	1080.	900.
400.	1240.	1040.
760.	1310.	1110.

80. From the following data for liquid nitric acid, determine its heat of vaporization and normal boiling point.

Temperature ($^{\circ}\text{C}$)	Vapor Pressure (mm Hg)
0.	14.4
10.	26.6
20.	47.9
30.	81.3
40.	133
50.	208
80.	670.

81. In Breckenridge, Colorado, the typical atmospheric pressure is 520. torr. What is the boiling point of water ($\Delta H_{\text{vap}} = 40.7$ kJ/mol) in Breckenridge?
82. What pressure would have to be applied to steam at $350.^{\circ}\text{C}$ to condense the steam to liquid water ($\Delta H_{\text{vap}} = 40.7$ kJ/mol)?
83. Carbon tetrachloride, CCl_4 , has a vapor pressure of 213 torr at $40.^{\circ}\text{C}$ and 836 torr at $80.^{\circ}\text{C}$. What is the normal boiling point of CCl_4 ?
84. The normal boiling point for acetone is 56.5°C . At an elevation of 5300 ft the atmospheric pressure is 630. torr. What would be the boiling point of acetone ($\Delta H_{\text{vap}} = 32.0$ kJ/mol) at this elevation? What would be the vapor pressure of acetone at 25.0°C at this elevation?

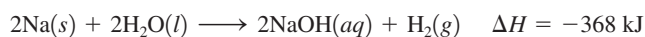
85. A substance, X, has the following properties:

Specific Heat Capacities			
ΔH_{vap}	20. kJ/mol	C(s)	3.0 J/g \cdot $^{\circ}\text{C}$
ΔH_{fus}	5.0 kJ/mol	C(l)	2.5 J/g \cdot $^{\circ}\text{C}$
bp	75°C	C(g)	1.0 J/g \cdot $^{\circ}\text{C}$
mp	-15°C		

Sketch a heating curve for substance X starting at $-50.^{\circ}\text{C}$.

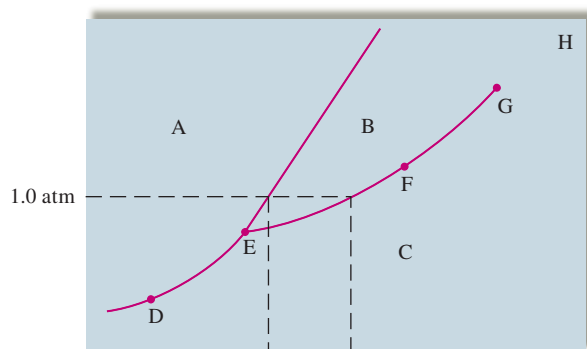
86. Given the data in Exercise 85 on substance X, calculate the energy that must be removed to convert 250. g of substance X from a gas at $100.^{\circ}\text{C}$ to a solid at $-50.^{\circ}\text{C}$. Assume X has a molar mass of 75.0 g/mol.

87. How much energy does it take to convert 0.500 kg ice at $-20.^\circ\text{C}$ to steam at $250.^\circ\text{C}$? Specific heat capacities: ice, $2.03 \text{ J/g} \cdot ^\circ\text{C}$; liquid, $4.2 \text{ J/g} \cdot ^\circ\text{C}$; steam, $2.0 \text{ J/g} \cdot ^\circ\text{C}$, $\Delta H_{\text{vap}} = 40.7 \text{ kJ/mol}$, $\Delta H_{\text{fus}} = 6.02 \text{ kJ/mol}$.
88. Consider a 75.0-g sample of $\text{H}_2\text{O}(g)$ at $125.^\circ\text{C}$. What phase or phases are present when 215 kJ of energy is removed from this sample? (See Exercise 87.)
89. An ice cube tray contains enough water at 22.0°C to make 18 ice cubes that each have a mass of 30.0 g. The tray is placed in a freezer that uses CF_2Cl_2 as a refrigerant. The heat of vaporization of CF_2Cl_2 is 158 J/g. What mass of CF_2Cl_2 must be vaporized in the refrigeration cycle to convert all the water at 22.0°C to ice at -5.0°C ? The heat capacities for $\text{H}_2\text{O}(s)$ and $\text{H}_2\text{O}(l)$ are $2.03 \text{ J/g} \cdot ^\circ\text{C}$ and $4.18 \text{ J/g} \cdot ^\circ\text{C}$, respectively, and the enthalpy of fusion for ice is 6.02 kJ/mol .
90. A 0.250-g chunk of sodium metal is cautiously dropped into a mixture of 50.0 g of water and 50.0 g of ice, both at 0°C . The reaction is

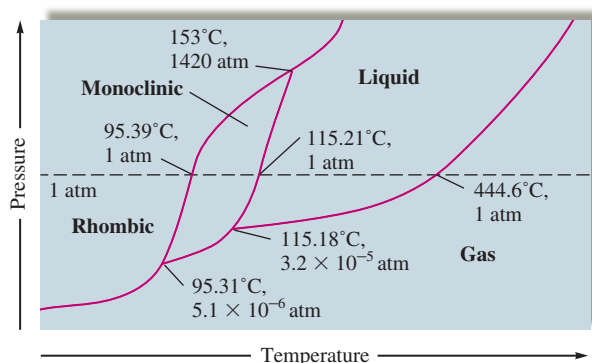


Will the ice melt? Assuming the final mixture has a specific heat capacity of $4.18 \text{ J/g} \cdot ^\circ\text{C}$, calculate the final temperature. The enthalpy of fusion for ice is 6.02 kJ/mol .

91. Consider the phase diagram given below. What phases are present at points A through H? Identify the triple point, normal boiling point, normal freezing point, and critical point. Which phase is denser, solid or liquid?



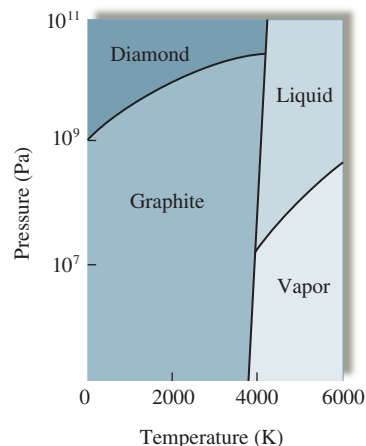
92. Sulfur exhibits two solid phases, rhombic and monoclinic. Use the accompanying phase diagram for sulfur to answer the following questions. (The phase diagram is not to scale.)



- a. How many triple points are in the phase diagram?
 b. What phases are in equilibrium at each of the triple points?
 c. What is the stable phase at 1 atm and $100.^\circ\text{C}$?
 d. What are the normal melting point and the normal boiling point of sulfur?
 e. Which is the densest phase?
 f. At a pressure of $1.0 \times 10^{-5} \text{ atm}$, can rhombic sulfur sublime?
 g. What phase changes occur when the pressure on a sample of sulfur at $100.^\circ\text{C}$ is increased from $1.0 \times 10^{-8} \text{ atm}$ to 1500 atm?

93. Use the accompanying phase diagram for carbon to answer the following questions.

- a. How many triple points are in the phase diagram?
 b. What phases can coexist at each triple point?
 c. What happens if graphite is subjected to very high pressures at room temperature?
 d. If we assume that the density increases with an increase in pressure, which is more dense, graphite or diamond?



94. Like most substances, bromine exists in one of the three typical phases. Br_2 has a normal melting point of -7.2°C and a normal boiling point of 59°C . The triple point for Br_2 is -7.3°C and 40 torr, and the critical point is 320°C and 100 atm. Using this information, sketch a phase diagram for bromine indicating the points described above. Based on your phase diagram, order the three phases from least dense to most dense. What is the stable phase of Br_2 at room temperature and 1 atm? Under what temperature conditions can liquid bromine never exist? What phase changes occur as the temperature of a sample of bromine at 0.10 atm is increased from -50°C to 200°C ?

95. The melting point of a fictional substance X is 225°C at 10.0 atm. If the density of the solid phase of X is 2.67 g/cm^3 and the density of the liquid phase is 2.78 g/cm^3 at 10.0 atm, predict whether the normal melting point of X will be less than, equal to, or greater than 225°C . Explain.

96. Consider the following data for xenon:

Triple point: -121°C , 280 torr
 Normal melting point: -112°C
 Normal boiling point: -107°C

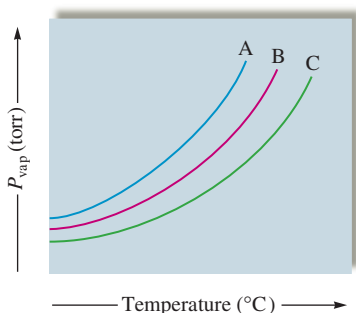
Which is more dense, $\text{Xe}(s)$, or $\text{Xe}(l)$? How do the melting point and boiling point of xenon depend on pressure?

Additional Exercises

97. Rationalize why chalk (calcium carbonate) has a higher melting point than motor oil (large compounds made from carbon and hydrogen), which has a higher melting point than water, which engages in relatively strong hydrogen-bonding interactions.
98. Rationalize the differences in physical properties in terms of intermolecular forces for the following organic compounds. Compare the first three substances with each other, compare the last three with each other, and then compare all six. Can you account for any anomalies?

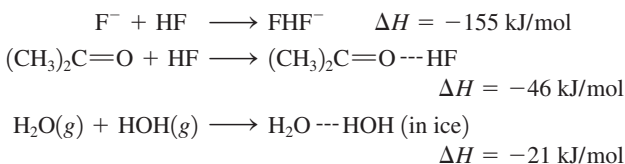
	bp (°C)	mp (°C)	ΔH_{vap} (kJ/mol)
Benzene, C ₆ H ₆	80	6	33.9
Naphthalene, C ₁₀ H ₈	218	80	51.5
Carbon tetra- chloride	76	-23	31.8
Acetone, CH ₃ COCH ₃	56	-95	31.8
Acetic acid, CH ₃ CO ₂ H	118	17	39.7
Benzoic acid, C ₆ H ₅ CO ₂ H	249	122	68.2

99. Consider the following vapor pressure versus temperature plot for three different substances A, B, and C.

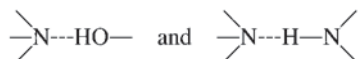


If the three substances are CH₄, SiH₄, and NH₃, match each curve to the correct substance.

100. Consider the following enthalpy changes:



How do the strengths of hydrogen bonds vary with the electronegativity of the element to which hydrogen is bonded? Where in the preceding series would you expect hydrogen bonds of the following type to fall?



101. How could you tell experimentally if TiO₂ is an ionic solid or a network solid?
102. Boron nitride (BN) exists in two forms. The first is a slippery solid formed from the reaction of BCl₃ with NH₃, followed by heating in an ammonia atmosphere at 750°C. Subjecting the first form of BN to a pressure of 85,000 atm at 1800°C produces a second form that is the second hardest substance known. Both forms of BN remain solids to 3000°C. Suggest structures for the two forms of BN.
103. Consider the following data concerning four different substances.

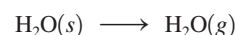
Compound	Conducts Electricity as a Solid	Other Properties
B ₂ H ₆	no	gas at 25°C
SiO ₂	no	high mp
CsI	no	aqueous solution conducts electricity
W	yes	high mp

Label the four substances as either ionic, network, metallic, or molecular solids.

104. A 20.0-g sample of ice at -10.0°C is mixed with 100.0 g of water at 80.0°C. Calculate the final temperature of the mixture assuming no heat loss to the surroundings. The heat capacities of H₂O(s) and H₂O(l) are 2.03 and 4.18 J/g · °C, respectively, and the enthalpy of fusion for ice is 6.02 kJ/mol.
105. In regions with dry climates, evaporative coolers are used to cool air. A typical electric air conditioner is rated at 1.00 × 10⁴ Btu/h (1 Btu, or British thermal unit = amount of energy to raise the temperature of 1 lb of water by 1°F). How much water must be evaporated each hour to dissipate as much heat as a typical electric air conditioner?
106. The critical point of NH₃ is 132°C and 111 atm, and the critical point of N₂ is -147°C and 34 atm. Which of these substances cannot be liquefied at room temperature no matter how much pressure is applied? Explain.

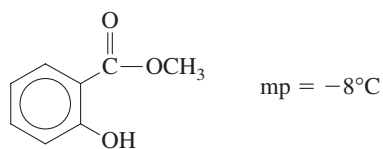
Challenge Problems

107. When 1 mol of benzene is vaporized at a constant pressure of 1.00 atm and its boiling point of 353.0 K, 30.79 kJ of energy (heat) is absorbed and the volume change is +28.90 L. What are ΔE and ΔH for this process?
108. You and a friend each synthesize a compound with the formula XeCl₂F₂. Your compound is a liquid and your friend's compound is a gas (at the same conditions of temperature and pressure). Explain how the two compounds with the same formulas can exist in different phases at the same conditions of pressure and temperature.
109. Using the heats of fusion and vaporization for water given in Exercise 87, calculate the change in enthalpy for the sublimation of water:

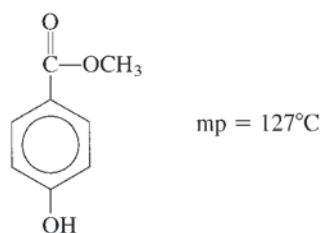


Using the ΔH value given in Exercise 100 and the number of hydrogen bonds formed with each water molecule, estimate what portion of the intermolecular forces in ice can be accounted for by hydrogen bonding.

110. Oil of wintergreen, or methyl salicylate, has the following structure:



Methyl-4-hydroxybenzoate is another molecule with exactly the same molecular formula; it has the following structure:



Account for the large difference in the melting points of the two substances.

111. Consider the following melting point data:

Compound:	NaCl	MgCl ₂	AlCl ₃	SiCl ₄	PCl ₃	SCl ₂	Cl ₂
mp (°C):	801	708	190	-70	-91	-78	-101
Compound:	NaF	MgF ₂	AlF ₃	SiF ₄	PF ₅	SF ₆	F ₂
mp (°C):	997	1396	1040	-90	-94	-56	-220

Account for the trends in melting points in terms of interparticle forces.

112. MnO has either the NaCl type structure or the CsCl type structure (see Exercise 70). The edge length of the MnO unit cell is 4.47×10^{-8} cm and the density of MnO is 5.28 g/cm^3 .
- Does MnO crystallize in the NaCl or the CsCl type structure?
 - Assuming that the ionic radius of oxygen is 140. pm, estimate the ionic radius of manganese.
113. Some ionic compounds contain a mixture of different charged cations. For example, some titanium oxides contain a mixture of Ti^{2+} and Ti^{3+} ions. Consider a certain oxide of titanium that is 28.31% oxygen by mass and contains a mixture of Ti^{2+} and Ti^{3+} ions. Determine the formula of the compound and the relative numbers of Ti^{2+} and Ti^{3+} ions.
114. Spinel is a mineral that contains 37.9% aluminum, 17.1% magnesium, and 45.0% oxygen, by mass, and has a density of 3.57 g/cm^3 . The edge of the cubic unit cell measures 809 pm. How many of each type of ion are present in the unit cell?

115. Mn crystallizes in the same type of cubic unit cell as Cu. Assuming that the radius of Mn is 5.6% larger than the radius of Cu and the density of copper is 8.96 g/cm^3 , calculate the density of Mn.
116. You are asked to help set up a historical display in the park by stacking some cannonballs next to a Revolutionary War cannon. You are told to stack them by starting with a triangle in which each side is composed of four touching cannonballs. You are to continue stacking them until you have a single ball on the top centered over the middle of the triangular base.
- How many cannonballs do you need?
 - What type of closest packing is displayed by the cannonballs?
 - The four corners of the pyramid of cannonballs form the corners of what type of regular geometric solid?
117. Some water is placed in a sealed glass container connected to a vacuum pump (a device used to pump gases from a container), and the pump is turned on. The water appears to boil and then freezes. Explain these changes using the phase diagram for water. What would happen to the ice if the vacuum pump was left on indefinitely?
118. The molar enthalpy of vaporization of water at 373 K and 1.00 atm is 40.7 kJ/mol. What fraction of this energy is used to change the internal energy of the water, and what fraction is used to do work against the atmosphere? (*Hint:* Assume that water vapor is an ideal gas.)
119. For a simple cubic array, solve for the volume of an interior sphere (cubic hole) in terms of the radius of a sphere in the array.
120. Consider two different compounds, each with the formula $\text{C}_2\text{H}_6\text{O}$. One of these compounds is a liquid at room conditions and the other is a gas. Write Lewis structures consistent with this observation and explain your answer. *Hint:* the oxygen atom in both structures satisfies the octet rule with two bonds and two lone pairs.

Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

121. A 0.132-mol sample of an unknown semiconducting material with the formula XY has a mass of 19.0 g. The element X has an electron configuration of $[\text{Kr}]5s^24d^{10}$. What is this semiconducting material? A small amount of the Y atoms in the semiconductor is replaced with an equivalent amount of atoms with an electron configuration of $[\text{Ar}]4s^23d^{10}4p^5$. Does this correspond to n-type or p-type doping?
122. A metal burns in air at 600°C under high pressure to form an oxide with formula MO_2 . This compound is 23.72% oxygen by mass. The distance between touching atoms in a cubic closest packed crystal of this metal is 269.0 pm. What is this metal? What is its density?
123. One method of preparing elemental mercury involves roasting cinnabar (HgS) in quicklime (CaO) at 600°C followed by condensation of the mercury vapor. Given the heat of vaporization of mercury (296 J/g) and the vapor pressure of mercury at 25.0°C (2.56×10^{-3} torr), what is the vapor pressure of the condensed mercury at 300°C ? How many atoms of mercury are present in the mercury vapor at 300°C if the reaction is conducted in a closed 15.0-L container?

Marathon Problem

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

124. General Zod has sold Lex Luthor what Zod claims to be a new copper-colored form of kryptonite, the only substance that can harm Superman. Lex, not believing in honor among thieves, decided to carry out some tests on the supposed kryptonite. From previous tests, Lex knew that kryptonite is a metal having a specific heat capacity of $0.082 \text{ J/g} \cdot ^\circ\text{C}$, and a density of 9.2 g/cm^3 .

Lex Luthor's first experiment was an attempt to find the specific heat capacity of kryptonite. He dropped a $10 \text{ g} \pm 3 \text{ g}$ sample of the metal into a boiling water bath at a temperature of $100.0^\circ\text{C} \pm 0.2^\circ\text{C}$. He waited until the metal had reached the bath temperature and then quickly transferred it to $100 \text{ g} \pm 3 \text{ g}$ of water that was contained in a calorimeter at an initial temperature of $25.0^\circ\text{C} \pm 0.2^\circ\text{C}$. The final temperature of the metal and water was 25.2°C . Based on these results, is it possible to distinguish between copper and kryptonite? Explain.

When Lex found that his results from the first experiment were inconclusive, he decided to determine the density of the sample. He managed to steal a better balance and determined the mass of another portion of the purported kryptonite to be $4 \text{ g} \pm 1 \text{ g}$. He dropped this sample into water contained in a 25-mL graduated cylinder and found that it displaced a volume of $0.42 \text{ mL} \pm 0.02 \text{ mL}$. Is the metal copper or kryptonite? Explain.

Lex was finally forced to determine the crystal structure of the metal General Zod had given him. He found that the cubic unit cell contained 4 atoms and had an edge length of 600. pm. Explain how this information enabled Lex to identify the metal as copper or kryptonite.

Will Lex be going after Superman with the kryptonite or seeking revenge on General Zod? What improvements could he have made in his experimental techniques to avoid performing the crystal structure determination?



Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at college.hmco.com/PIC/zumdahl7e.