An iceberg floats with about 10% of its mass above the surface of the surrounding water. The hydrogen bonding of water molecules in ice makes the solid less dense than liquid water, which is unusual. This property of water, however, is crucial for life on earth.
The properties of liquids and solids, like those of gases, can be understood on the molecular, nanoscale level. In common liquids and solids—water, salt crystals, metals—the atoms, molecules, or ions are close enough to have strong interactions with each other. The strength of these interactions accounts for the properties of liquids and solids. For example, the strong repulsions when the atoms, molecules, or ions in a liquid or solid are forced very close together account for the fact that solids and liquids can be compressed very little—in contrast to gases. Liquids are like gases in that their atoms, molecules, or ions (in the case of molten ionic compounds) can move freely. Liquids are therefore able to flow and fill a container to a certain level. Solids, on the other hand, are composed of atoms, molecules, or ions in relatively fixed positions, which explains the fact that solids have definite shapes. When the atoms, molecules, or ions making up a solid have enough energy to overcome the attractive forces holding them in place, the solid melts or sublimes.

In molecular liquids and solids, molecules having sufficient energy can leave the surface of the liquid or solid and enter the gaseous state. In the reverse process, as energy is removed, gases condense into liquids, and liquids solidify. All of these properties of solids and liquids have great practical importance.

11.1 The Liquid State

At low enough temperatures, gases condense to liquids. Condensation occurs when most molecules no longer have enough kinetic energy to overcome their intermolecular attractions (p. 407). Most liquids, such as water, alcohol, and gasoline, are substances whose condensation temperatures are above room temperature. Some liquids, such as molten salts and liquid polymers, have no corresponding vapor state, however, so condensation of their vapors has no meaning.

In a liquid, the molecules are much closer together than are those in a gas. Nevertheless, the molecules remain mobile enough that the liquid flows. At the nanoscale, liquids have a regular structure only in very small regions, and most of

The hydraulic lifts are raised and lowered by changes in the pressure on the hydraulic fluid in the cylinders. The lack of compressibility of the fluid makes this application possible.
the molecules continue to move about randomly. Because confined liquids are difficult to compress and their molecules move in all directions, they can transmit applied pressure equally in all directions. This property has a practical application in the hydraulic fluids that operate mechanical devices such as the hydraulic lifts that raise and lower autos in repair shops.

The resistance of a liquid to flow is called \textit{viscosity}. Water flows smoothly and quickly (low viscosity), while motor oil and honey flow more slowly (higher viscosity; Figure 11.1). The viscosity of a liquid is related to its intermolecular forces, which determine how easily the molecules can move past each other, and also the degree to which the molecules can become entangled. Viscosity decreases as temperature increases because the molecules have more kinetic energy at higher temperature and the attractive intermolecular forces are more easily overcome. Examples of common materials whose viscosity decreases as their temperature rises include motor oil, cooking oil, and honey.

Unlike gases, liquids have \textit{surface properties}. Molecules beneath the surface of the liquid are completely surrounded by other liquid molecules and experience intermolecular attractions in all directions. By contrast, molecules at the liquid surface have intermolecular interactions only with molecules below or beside them, but not above them (Figure 11.2). This unevenness of attractive forces at the liquid surface causes the surface to contract. The energy required to expand a liquid surface is called its \textit{surface tension}, and it is higher for liquids that have stronger intermolecular attractions. For example, water’s surface tension is high compared with those of most other liquids (Table 11.1) because extensive hydrogen bonding causes the water molecules to attract each other strongly (\textit{p. 411}). The surface tension of water, \(7.29 \times 10^{-2} \text{ J/m}^2\), is the quantity of energy required to increase the surface area of water by \(1 \text{ m}^2\) at \(20 ^\circ \text{C}\). The very high surface tension of mercury (six times that of water) is due to the much stronger metallic bonding (Section 11.9) that holds Hg atoms together in the liquid.

Even though their densities are greater than that of water, water bugs can walk on the surface of water and small metal objects can float. Surface tension prevents the objects from breaking through the surface and sinking. Surface tension also accounts for the nearly spherical shape of rain droplets, as well as the rounded shape of water droplets that bead up on waxed surfaces. A sphere has less surface area per unit volume than any other shape, so a spherical rain droplet has fewer surface H$_2$O molecules, minimizing the surface energy.

Surface tension answers the question posed in Chapter 1 (\textit{p. 2}), “Why does rain fall as drops instead of cubes or cylinders?”

The chemicals known as surfactants (soaps and detergents are examples) can dissolve in water and dramatically lower its surface tension. When this happens, water becomes “wetter” and does a better job of cleaning. You can see the effect of a surfactant by comparing how water alone beads on a surface such as the waxed hood of a car and how a soap solution fails to bead on the same surface. Surfactants are discussed in Section 15.10.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure11-1.png}
\caption{Viscosity. Honey is viscous, so it builds up rather than spreading out, as less viscous water would.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure11-2.png}
\caption{Surface tension. Surface tension, the energy required to increase the surface area of a liquid, arises from the difference between the forces acting on a molecule within the liquid and those acting on a molecule at the surface of the liquid.}
\end{figure}
11.1 Explaining Differences in Surface Tension

At 20 °C, chloroform (CHCl₃) has a surface tension of 2.68 \( \times 10^{-2} \) J/m², while bromoform (CHBr₃) has a higher surface tension of 4.11 \( \times 10^{-2} \) J/m². Explain this observation in terms of intermolecular forces.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>Surface Tension (J/m² at 20 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octane</td>
<td>C₈H₁₈</td>
<td>2.16 ( \times 10^{-2} )</td>
</tr>
<tr>
<td>Ethanol</td>
<td>CH₃CH₂OH</td>
<td>2.23 ( \times 10^{-2} )</td>
</tr>
<tr>
<td>Chloroform</td>
<td>CHCl₃</td>
<td>2.68 ( \times 10^{-2} )</td>
</tr>
<tr>
<td>Benzene</td>
<td>C₆H₆</td>
<td>2.85 ( \times 10^{-2} )</td>
</tr>
<tr>
<td>Water</td>
<td>H₂O</td>
<td>7.29 ( \times 10^{-2} )</td>
</tr>
<tr>
<td>Mercury</td>
<td>Hg</td>
<td>46 ( \times 10^{-2} )</td>
</tr>
</tbody>
</table>

11.2 Predicting Surface Tension

Predict which substance listed in Table 11.1 has a surface tension most similar to that of

(a) Glycerol, which has three —OH groups in each molecule
(b) Decane, C₁₀H₂₂

When a glass tube with a small diameter is put into water, the water rises in the tube due to capillary action. The glass walls of the tube are largely silicon dioxide (SiO₂), so the water molecules form hydrogen bonds to the oxygen atoms of the glass. This attractive force is stronger than the attractive forces among water molecules (also hydrogen bonding), so water creeps up the wall of the tube. Simultaneously, the surface tension of the water tries to keep the water’s surface area small. The combination of the forces raises the water level in the tube. The liquid surface—concave for water—is called a meniscus (Figure 11.3a). The water rises in the tube...
until the force of the water-to-wall hydrogen bonds is balanced by the pull of gravity. Capillary action is crucial to plant life because it helps water, with its dissolved nutrients, to move upward through plant tissues against the force of gravity.

Mercury behaves oppositely from water. Mercury in a small-diameter tube has a dome-shaped (convex) meniscus because the attractive forces between mercury atoms are stronger than the attraction between the mercury and the glass wall (Figure 11.3b).

11.2 Vapor Pressure

The tendency of a liquid to vaporize, its volatilety, increases as temperature increases. Everyday experiences such as heating water or soup in a pan on a stove, or evaporation of rain from hot pavement, demonstrate this phenomenon. Conversely, the volatility of a liquid is lower at lower temperatures.

The change of volatility with temperature can be explained by considering what is happening at the nanoscale. The molecules in a liquid have varying kinetic energies and speeds (Figure 11.4). At any time, some fraction of the molecules have sufficient energy to escape from the liquid into the gas phase. When the temperature of the liquid is raised, a larger number of molecules exceed the energy threshold, and evaporation proceeds more rapidly. Thus, hot water evaporates more quickly than cold water.

A liquid in an open container will eventually evaporate completely because air currents and diffusion take away most of the gas phase molecules before they can reenter the liquid phase. In a closed container, however, no molecules can escape. If a liquid is injected into an evacuated, closed container, the rate of vaporization (number of molecules vaporizing per unit time) will at first far exceed the rate of condensation. Over time the pressure of the gas above the liquid will increase as the number of gas phase molecules increases. Eventually the system will attain a state of dynamic equilibrium, in which molecules are entering and leaving the liquid state at equal rates. At this point the pressure of the gas will no longer increase; this pressure is known as the equilibrium vapor pressure (or just the vapor pressure) of the liquid.

As shown in Figure 11.5 for three liquids, the vapor pressure of a liquid increases with increasing temperature. The differences in vapor pressures among the three liquids are due to differences in the strengths of the intermolecular interactions that bind their molecules together in the liquid phase. Consider the vapor

An evacuated container is specified so that only the pure liquid is present.

Figure 11.4 Kinetic energy and evaporation. At any given temperature, a fraction of the molecules at the surface of a liquid have sufficient energy to escape to the vapor phase. When the temperature of the liquid is raised, a larger fraction of the molecules have energies greater than the kinetic energy threshold, so the vapor pressure increases.
pressures of ethyl alcohol and water at 60 °C (see Figure 11.5). At that temperature, ethyl alcohol has a higher vapor pressure, which means that it has weaker intermolecular interactions than those in water. Water’s stronger intermolecular interactions (due to more hydrogen bonds) require a higher temperature to disrupt them and volatilize liquid water (p. 411).

If a liquid is placed in an open container and heated, a temperature eventually is reached at which the vapor pressure of the liquid is equal to the atmospheric pressure. Below this temperature, only molecules at the surface of the liquid can go into the gas phase. But when the vapor pressure equals the atmospheric pressure, the liquid begins vaporizing throughout. Bubbles of vapor form and immediately rise to the surface due to their lower density. The liquid is said to be boiling (Figure 11.6). The temperature at which the equilibrium vapor pressure equals the atmospheric pressure is the normal boiling point of a substance.

Figure 11.5  Vapor pressure curves for diethyl ether (C₂H₅OC₂H₅), ethyl alcohol (C₂H₅OH), and water. Each curve represents the conditions of $T$ and $P$ where the two phases (pure liquid and its vapor) are in equilibrium. Each compound is a liquid in the temperature and pressure region to the left of its curve, and each compound is a vapor for all temperatures and pressures to the right of its curve.

The normal boiling point of diethyl ether is 34.6 °C… of ethyl alcohol (ethanol) is 78.5 °C… and of water is 100 °C.

Figure 11.6  Boiling liquid. From Figure 11.5, we see that the lower the atmospheric pressure, the lower the vapor pressure at which boiling can occur. It takes longer to hard-boil an egg high in the mountains, where the atmospheric pressure is lower, than it does at sea level, because water at a higher elevation boils at a lower temperature. In Salt Lake City, Utah (elevation 4390 ft), where the average barometric pressure is about 650 mm Hg, water boils at about 95 °C.

To shorten cooking times, one can use a pressure cooker, a sealed pot (with a relief valve for safety) that allows water vapor to build up pressures slightly greater than the external atmospheric pressure. At the higher pressure, the boiling point of water is higher, and foods cook faster.
atmospheric pressure is the **boiling point** of the liquid. When the atmospheric pressure is 1 atm (760 mm Hg), the temperature is designated the **normal boiling point**. The temperatures in Figure 11.5 where the vapor pressure curves cross the 760 mm Hg (1 atm) line are the normal boiling points of the three liquids.

**11.3 Estimating Boiling Points**

Use Figure 11.5 to estimate the boiling points of these liquids: (a) ethyl alcohol at 400 mm Hg; (b) diethyl ether at 200 mm Hg; (c) water at 400 mm Hg.

**11.4 Explaining Bubbles**

One of your classmates believes that the bubbles in a boiling liquid are air bubbles. Explain to him what is wrong with that idea and what the bubbles actually are. Suggest an experiment to show that the bubbles are not air.

**Clausius-Clapeyron Equation**

As seen in Figure 11.5, plotting the vapor pressure of a substance versus its temperature results in a curved line. The relationship between vapor pressure and temperature is given by the **Clausius-Clapeyron equation**:

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

which relates the natural logarithm of the vapor pressure \( P \) of the liquid to the absolute temperature \( T \), the universal gas constant \( R \) (8.31 J mol\(^{-1}\) K\(^{-1}\)), the molar enthalpy of vaporization \( \Delta H_{\text{vap}} \) (J/mol), and a constant \( C \) that is characteristic of the liquid. The form of the Clausius-Clapeyron equation shows that a graph of \( \ln P \) versus \( 1/T \) is a straight line with its slope equal to \( -\Delta H_{\text{vap}}/R \) and a \( y \)-axis intercept of \( C \). That is, \( \ln P \) equals \( C \) in the limit when \( T \) is very large and 1/\( T \) tends toward zero. Figure 11.7 shows a plot of \( \ln P \) versus 1/\( T \) for ethanol. A comparison of the plots for ethanol in Figures 11.5 and 11.7 illustrates the two different ways of expressing the relationship between \( T \) and \( P \).

The Clausius-Clapeyron equation can be recast for two sets of pressure and temperature of a liquid to give

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

which can be used to calculate \( \Delta H_{\text{vap}} \) from the two sets of data: \( T_1, T_2, P_1, P_2 \). If \( \Delta H_{\text{vap}} \) is known, then this form of the equation can be used to find the vapor pressure of a liquid at a new temperature given its vapor pressure at some other temperature.

**Problem-Solving Example 11.1 **

**Clausius-Clapeyron Equation**

Ethanol has a vapor pressure of 44.22 mm Hg at 20.0 °C and 350.8 mm Hg at 60.0 °C. What is \( \Delta H_{\text{vap}} \) for ethanol?

**Answer** 42.0 kJ/mol

**Strategy and Explanation** Use the Clausius-Clapeyron equation in the form that contains the four known quantities: \( T_1, T_2, P_1, \) and \( P_2 \). The temperatures must be converted to kelvins. Substitute the given values into the equation and solve for \( \Delta H_{\text{vap}} \).
At 30.0 °C the vapor pressure of carbon tetrachloride is 143.0 mm Hg. What is its vapor pressure at 60.0 °C? The $\Delta H_{\text{vap}}$ of carbon tetrachloride is 32.1 kJ/mol.

**Problem-Solving Practice 11.1**

At 30.0 °C the vapor pressure of carbon tetrachloride is 143.0 mm Hg. What is its vapor pressure at 60.0 °C? The $\Delta H_{\text{vap}}$ of carbon tetrachloride is 32.1 kJ/mol.

**Vapor Pressure of Water and Relative Humidity**

Water has an appreciable vapor pressure in the temperature range 10 °C to 25 °C, normal outdoor temperatures. Therefore, water vapor is present in the atmosphere at all times. The equilibrium vapor pressure depends on the temperature as shown in Table 10.5 (p. 459). The vapor pressure of water in the atmosphere is expressed as the relative humidity, which is the ratio of the actual partial pressure of the water vapor in the atmosphere, $P_{\text{H}_2\text{O}}$, to the equilibrium partial pressure of water vapor at the relevant temperature, $P^\circ_{\text{H}_2\text{O}}$. The factor of 100 changes a fraction into a percentage.

$$\text{Relative humidity} = \frac{P_{\text{H}_2\text{O}}}{P^\circ_{\text{H}_2\text{O}}} \times 100\%$$

As an example, consider a typical warm day with an outdoor temperature of 25 °C. The equilibrium water vapor pressure at this temperature is 23.8 mm Hg (see Table 10.5). If the actual partial pressure of water vapor were 17.8 mm Hg, then the relative humidity would be

$$\text{Relative humidity} = \frac{17.8 \text{ mm Hg}}{23.8 \text{ mm Hg}} \times 100\% = 75\%$$

If the temperature were lowered (which would lower the equilibrium water vapor pressure) and the partial pressure of water vapor remained constant, the relative humidity would rise. Eventually, it would reach 100%. The temperature at which the actual partial pressure of water vapor equals the equilibrium vapor pressure is the dew point. At this temperature, water vapor will condense as water droplets to form fog or dew. When the dew point rises above about 20 °C we consider it to be somewhat muggy; when it rises above about 25 °C we consider the day to be extremely uncomfortable. In desert conditions the relative humidity can fall to less than 10%; this, too, can be uncomfortable for some people.

**11.3 Phase Changes: Solids, Liquids, and Gases**

Substances in one of the three states of matter—solid, liquid, gas—can change from one state to another. Water evaporates from the street after a rain shower. Ice cubes melt in your cold drink, and water vapor in the air condenses to water droplets on the outside wall of the glass. Each of the three states of matter can be converted to the other two states through six important processes (Figure 11.8).
Vaporization and Condensation

Like molecules in a gas, molecules in a liquid are in constant motion and have a range of kinetic energies, as shown in Figure 11.4. A fraction of the molecules in the liquid have enough kinetic energy to overcome the intermolecular attractive forces among the liquid molecules. If such a molecule is at the surface of the liquid and moving in the right direction, it will leave the liquid phase and enter the gas phase (Figure 11.9). This process is called vaporization or evaporation.

As the high-energy molecules leave the liquid, they take some energy with them. Therefore, vaporization is endothermic; the enthalpy change is called the enthalpy of vaporization (p. 232). Vaporization increases with temperature because an increasingly larger fraction of the molecules have enough energy to vaporize.

11.5 Evaporative Cooling

In some countries where electric refrigeration is not readily available, drinking water is chilled by placing it in porous clay water pots. Water slowly passes through the clay, and when it reaches the outer surface, it evaporates. Explain how this process cools the water inside.

When a molecule in the gas phase hits the liquid’s surface, it can transfer some of its energy to the other liquid particles and remain in the liquid, a process called condensation. The overall effect of molecules reentering the liquid phase is a release of thermal energy, making condensation an exothermic process. The heat transferred out of the system upon condensation is equal to the heat transferred into the system upon vaporization.

\[
\text{Liquid} \xrightarrow{\text{heat of vaporization}} \text{Gas} \quad \Delta H_{\text{vaporization}} = -\Delta H_{\text{condensation}}
\]

For example, the quantity of heat required to completely vaporize 1 mol liquid water once it has reached the boiling point of 100 °C at 1 bar (the molar enthalpy of vaporization) and the quantity of heat released when 1 mol water vapor at 100 °C condenses to liquid water at 100 °C (the molar enthalpy of condensation) are
Table 11.2 illustrates the influence of noncovalent forces on enthalpies of vaporization and boiling points. In the series of nonpolar molecules and noble gases, the increasing noncovalent forces with increasing molecular size and numbers of electrons are shown by the increasing \( \Delta H^\circ \) values. Comparison of HF and H\(_2\)O with CH\(_4\) shows the effect of hydrogen bonding.

**PROBLEM-SOLVING EXAMPLE 11.2** Enthalpy of Vaporization

To vaporize 50.0 g carbon tetrachloride, CCl\(_4\), requires 9.69 kJ at its normal boiling point of 76.7 °C and 1 bar pressure. What is the molar enthalpy of vaporization of CCl\(_4\) under these conditions?
Answer  29.8 kJ/mol

Strategy and Explanation  The molar mass of CCl₄ is 153.8 g/mol, so

\[
50.0 \text{ g CCl}_4 \times \frac{1 \text{ mol CCl}_4}{153.8 \text{ g CCl}_4} = 0.325 \text{ mol CCl}_4
\]

The enthalpy change per mole of CCl₄ is given by

\[
\frac{9.69 \text{ kJ}}{0.325 \text{ mol}} = 29.8 \text{ kJ/mol}
\]

✓ Reasonable Answer Check  We have approximately one third mol CCl₄, so the energy required to vaporize this amount of CCl₄ should be approximately one third of the molar enthalpy of vaporization, and it is.

PROBLEM-SOLVING PRACTICE 11.2

Using data from Table 11.2, calculate the thermal energy transfer required to vaporize 0.500 mol Br₂ at its normal boiling point.

PROBLEM-SOLVING EXAMPLE 11.3  Enthalpy of Vaporization

You put 1.00 L water (about 4 cups) in a pan at 100 °C, and the water evaporates. How much thermal energy must have been transferred (at 1 bar) to the water for all of it to vaporize? (The density of liquid water at 100 °C is 0.958 g/mL.)

Answer  2.16 × 10³ kJ

Strategy and Explanation  You need three pieces of information to solve this problem:

(a) \( \Delta H_{\text{vap}} \) for water, which is 40.7 kJ/mol at 100 °C (Table 11.2).
(b) The density of water, which is needed because \( \Delta H_{\text{vap}} \) has units of kJ/mol, so you must first find the mass of water and then the molar amount.
(c) The molar mass of water, 18.02 g/mol, which is needed to convert grams to moles.

From the density of water, a volume of 1.00 L (or 1.00 × 10³ cm³) is equivalent to 958. g. Therefore,

\[
\text{Heat required for vaporization} = 958. \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} \times \frac{40.7 \text{ kJ}}{1 \text{ mol }} = 2164 \text{ kJ}
\]

This enthalpy change of 2164 kJ is equivalent to about one third to one half of the caloric energy in the daily food intake of an average person in the United States.

PROBLEM-SOLVING PRACTICE 11.3

A rainstorm deposits 2.5 × 10¹⁰ kg of rain. Using the heat of vaporization of water at 25 °C of 44.0 kJ/mol, calculate the quantity of thermal energy, in joules, transferred when this much rain forms. Is this process exothermic or endothermic?

CONCEPTUAL EXERCISE  11.6 Estimating \( \Delta H_{\text{vap}}^0 \)

Using the data from Table 11.2, estimate the \( \Delta H_{\text{vap}}^0 \) for Kr and NO₂. (Hint: Use the periodic table or choose a substance that has a similar number of electrons.)

CONCEPTUAL EXERCISE  11.7 Understanding Boiling Points

(a) Chlorine and bromine are both diatomic. Explain the difference in their boiling points.
(b) Methane and ammonia have the same number of electrons. Explain the difference in their boiling points.
Melting and Freezing

When a solid is heated, its temperature increases until the solid begins to melt. Unless the solid decomposes first, a temperature is reached at which the kinetic energies of the molecules or ions are sufficiently high that the intermolecular interactions in the solid are no longer strong enough to keep the particles in their fixed positions. The solid’s structure collapses, and the solid melts (Figure 11.10). This temperature is the melting point of the solid. Melting requires transfer of energy, the enthalpy of fusion, from the surroundings into the system, so it is always endothermic. The molar enthalpy of fusion (\( \text{p}. \ 231 \)) is the quantity of energy required to melt 1 mol of a pure solid. Solids with high enthalpies of fusion usually melt at high temperatures, and solids with low enthalpies of fusion usually melt at low temperatures. The reverse of melting—called solidification, freezing, or crystallization—is always an exothermic process. The molar enthalpy of crystallization has the same magnitude as the molar enthalpy of fusion, but the opposite sign.

\[
\Delta H_{\text{fusion}} = -\Delta H_{\text{crystallization}}
\]

Table 11.3 lists melting points and enthalpies of fusion for examples of three classes of compounds: (a) nonpolar molecular solids, (b) polar molecular solids, some capable of hydrogen bonding, and (c) ionic solids. Solids composed of low molecular weight nonpolar molecules have the lowest melting temperatures, because their intermolecular attractions are weakest. These molecules are held together by London forces only (\( \text{p}. \ 408 \)), and they form solids with melting points so low that we seldom encounter them in the solid state at normal temperatures. Melting points and enthalpies of fusion of nonpolar molecular solids increase with increasing number of electrons (which corresponds to increasing molar mass) as the London forces become stronger. The ionic compounds in Table 11.3 have the highest melting points and enthalpies of fusion because of the very strong ionic bonding that holds the ions together in the solid. The polar molecular solids have intermediate melting points.

**PROBLEM-SOLVING EXAMPLE 11.4 Enthalpy of Fusion**

The molar enthalpy of fusion of NaCl is 30.21 kJ/mol at its melting point. How much thermal energy will be absorbed when 10.00 g NaCl melts?

Some solids do not have measurable melting points, and some liquids do not have measurable boiling points, because increasing temperature causes them to decompose before they melt or boil. Making peanut brittle provides an example: Melted sucrose chars before it boils, but it produces great-tasting candy.

![Figure 11.10 The melting of naphthalene, \( \text{C}_{10}\text{H}_{8} \), at 80.22 °C.](image)
The molar mass of NaCl is 58.443 g/mol, so we can use the molar enthalpy of fusion to calculate the thermal energy needed to melt this sample of NaCl.

Now we can use the molar enthalpy of fusion to calculate the thermal energy needed to melt this sample of NaCl.

\[
0.1711 \text{ mol NaCl} \times \frac{30.21 \text{ kJ}}{\text{mol NaCl}} = 5.169 \text{ kJ}
\]

We have approximately one sixth mol NaCl, so the energy required to melt this amount of NaCl should be approximately one sixth of the molar enthalpy of fusion, and it is.

Calculate the thermal energy transfer required to melt 0.500 mol NaI at its normal melting point.

**EXERCISE 11.8 Heat Liberated upon Crystallization**

Which would liberate more thermal energy, the crystallization of 2 mol liquid bromine or the crystallization of 1 mol liquid water?

**Sublimation and Deposition**

Atoms or molecules can escape directly from the solid to the gas phase, a process known as **sublimation**. The enthalpy change is the **enthalpy of sublimation**. The reverse process, in which a gas is converted directly to a solid, is called **deposition**.
The enthalpy change for this exothermic process (the enthalpy of deposition) has the same magnitude as the enthalpy of sublimation, but the opposite sign.

$$\Delta H_{\text{sublimation}} = -\Delta H_{\text{deposition}}$$

One common substance that sublimes at normal atmospheric pressure is solid carbon dioxide (Dry Ice), which has a vapor pressure of 1 atm at $-78 \, ^\circ C$ (Figure 11.11). Having such a high vapor pressure below its melting point causes solid carbon dioxide to sublime rather than melt. Because of the high vapor pressure of the solid, liquid carbon dioxide can exist only at pressures much higher than 1 atm.

Have you noticed that snow outdoors and ice cubes in a frost-free refrigerator slowly disappear even if the temperature never gets above freezing? The enthalpy of sublimation of ice is 51 kJ/mol, and its vapor pressure at 0 °C is 4.60 mm Hg. Therefore, ice sublimes readily in dry air when the partial pressure of water vapor is below 4.60 mm Hg (Figure 11.12). Given enough air passing over it, a sample of ice will sublime completely, leaving no trace behind. In a frost-free refrigerator, a current of dry air periodically blows across any ice formed in the freezer compartment, taking away water vapor (and hence the ice) without warming the freezer enough to thaw the food.

In the reverse of sublimation, atoms or molecules in the gas phase can deposit (solidify directly) on the surface of a solid. Deposition is used to form thin coatings of metal atoms on surfaces. Audio CD discs and CD-ROM discs, for example, have shiny metallic surfaces of deposited aluminum or gold atoms. To make such discs, a metal filament is heated in a vacuum to a temperature at which metal atoms begin to sublime rapidly off the surface. The plastic compact disc is cooler than the filament, so the metal atoms in the gas phase quickly deposit on the cool surface. The purpose of the metal coating is to provide a reflective surface for the laser beam that reads the pits and lands (unpitted areas) containing the digital audio or data information (p. 286).

**CONCEPTUAL EXERCISE 11.9 Frost-Free Refrigeration**

Sometimes, because of humidity, a frost-free refrigerator doesn’t work as efficiently as it should. Explain why.
Sublimation is an excellent means of purification for compounds that will readily sublime. Explain how purification by sublimation works at the nanoscale.

Heating Curve

Heating a solid or liquid increases its temperature as long as its phase does not change. The size of this temperature increase is governed by the quantity of energy added (in joules), the mass of the substance (in grams), and its specific heat capacity \( (J \, g^{-1} \, ^\circ C^{-1}) \) (\( \equiv p. \, 223 \)). The temperature rises until a phase-transition temperature is reached—for example, 100 \( ^\circ C \) for water. At this point, the temperature no longer rises. Instead, the energy goes into changing the phase of the substance.

Once all of the substance has changed phase, then the addition of still more energy causes the temperature to rise. A plot of the temperature of a substance versus the energy added is called a heating curve (Figure 11.13).

For example, consider how much energy is required to heat 100. g water from \(-20 \, ^\circ C\) to \(20 \, ^\circ C\), as illustrated in Figure 11.13. The constants used to construct the heating curve are as follows: specific heat capacity of liquid water = 4.184 J g\(^{-1}\) \(^\circ C^{-1}\); specific heat capacity of solid water = 2.06 J g\(^{-1}\) \(^\circ C^{-1}\); specific heat capacity of water vapor = 1.84 J g\(^{-1}\) \(^\circ C^{-1}\); \(\Delta H\)\text{fusion} = 6.020 kJ/mol; \(\Delta H\)\text{vaporization} = 40.7 kJ/mol.

The heating curve has five distinct parts. Three parts relate to heating the water in its three states (red lines). Two parts relate to phase changes (horizontal blue lines).

1. **Heat the ice from \(-20 \, ^\circ C\) to \(0 \, ^\circ C\) (A \(\rightarrow\) B).**
   
   \[
   \text{H}_2\text{O}(s) \, \text{at} \, -20 \, ^\circ C \, \rightarrow \, \text{H}_2\text{O}(s) \, \text{at} \, 0 \, ^\circ C \\
   \Delta \text{H}^\circ = (100. \, \text{g})(2.06 \, \text{J} \, \text{g}^{-1} \, ^\circ C^{-1})(20 \, ^\circ C) = 4120 \, \text{J} = 4.12 \, \text{kJ}
   \]

2. **Melt the ice at \(0 \, ^\circ C\) (B \(\rightarrow\) C).**
   
   \[
   \text{H}_2\text{O}(s) \, \text{at} \, 0 \, ^\circ C \, \rightarrow \, \text{H}_2\text{O}(l) \, \text{at} \, 0 \, ^\circ C \\
   \Delta \text{H}^\circ = 100. \, \text{g} \times \frac{1 \, \text{mol}}{18.015 \, \text{g}} \times \frac{6.020 \, \text{kJ}}{1 \, \text{mol}} = 33.4 \, \text{kJ}
   \]

Notice that there is no temperature change during a phase change.

**Figure 11.13** Heating curve for water.
3. Heat the water from 0 °C to 100 °C (C → D).

\[ \Delta H^\circ = (100. \text{ g})(4.184 \text{ J g}^{-1} \text{ °C}^{-1})(100^\circ \text{C}) = 41800 \text{ J} = 41.8 \text{ kJ} \]

4. Boil the water at 100 °C (D → E).

\[ \Delta H^\circ = 100. \text{ g} \times \frac{1 \text{ mol}}{18.015 \text{ g}} \times \frac{40.7 \text{ kJ}}{1 \text{ mol}} = 226. \text{ kJ} \]

5. Heat the water vapor from 100 °C to 120 °C (E → F).

\[ \Delta H^\circ = (100. \text{ g})(1.84 \text{ J g}^{-1} \text{ °C}^{-1})(120^\circ \text{C}) = 3680 \text{ J} = 3.68 \text{ kJ} \]

The total energy required to complete the transformation is 309. kJ, the sum of the five steps. Notice that the largest portion of the energy, 226. kJ (73%), goes into vaporizing water at 100 °C to steam at 100 °C.

Phase Diagrams

All three phases and the six interconversions among them shown in Figure 11.8 (p. 495) can be represented in a phase diagram (Figure 11.14). The pressure-temperature values at which each phase exists are also shown on the phase diagram. Each of the three phases—solid, liquid, gas—is represented. Each solid line in the diagram represents the conditions of temperature and pressure at which equilibrium exists between the two phases on either side of the line. The point at which all three phases are in equilibrium is the triple point. Every pure substance that exists in all three phases has a characteristic phase diagram.

The phase diagram for water is shown in Figure 11.15 (p. 504). The three shaded regions represent the three phases—solid, liquid, and gas. The temperature scale has been exaggerated to better illustrate some of the features of water’s phase diagram. The temperatures and pressures along the line AD represent conditions at which liquid water and gaseous water are in equilibrium. This line, the vapor pressure curve, is the same one shown in Figure 11.5 (p. 493). The line AC, the melting point curve, represents the solid/liquid (ice/water) equilibrium, and the line BA

![Figure 11.14](image_url)  
**Figure 11.14**  
**Generic phase diagram.** The phase diagram shows the pressure-temperature regions in which the substance is solid, liquid, or gas. It also shows the melting point curve, the vapor pressure curve, and the six interconversions among the three phases.
represents the solid/gaseous (ice/water vapor) equilibrium. The triple point for water occurs at \( P = 4.58 \) mm Hg and \( T = 0.01 \) °C.

You are most likely familiar with the common situation in which ice and liquid water are in equilibrium because of keeping food cool in an ice chest. If you fill an ice chest with ice, some of the ice melts to produce liquid. (Thermal energy is slowly transferred into the ice chest, no matter how well it is insulated.) The ice-liquid water mixture remains at approximately 0 °C until all of the ice has melted. This equilibrium between solid water and liquid water is represented in the phase diagram (Figure 11.15) by point \( C \), at which \( P = 760 \) mm Hg and \( T = 0 \) °C.

On a very cold day, ice can have a temperature well below 0 °C. Look along the temperature axis of the phase diagram for water and notice that below 1 atm and 0 °C the only equilibrium possible is between ice and water vapor. As a result, if the partial pressure of water in the air is low enough, ice will sublime on a cold day. Sublimation, which is endothermic, takes place more readily when solar energy warms the ice. The sublimation of ice allows snow or ice to gradually disappear even though the temperature does not climb above freezing.

The phase diagram for water is unusual in that the melting point curve \( AC \) slopes in the opposite direction from that seen for almost every other substance. The right-to-left, or negative, slope of the solid/liquid water equilibrium line is a consequence of the lower density of ice compared to that of liquid water (which is discussed in the next section). Thus, when ice and water are in equilibrium, one way to melt the ice is to apply greater pressure. This is evident from Figure 11.15. If you start at the normal freezing point (0 °C, 1 atm) and increase the pressure, you will move into the area of the diagram that corresponds to liquid water.

Ice skating was long thought to provide a practical example of this property of water. The melting caused by one’s body weight applied to a very small area of a skate blade was thought to cause sufficient pressure to form liquid water to make the ice slippery. However, more recent investigations show that the water molecules on the surface of ice are actually in a mobile state, resembling their mobility in liquid water, due to “surface melting.” (See Chemistry in the News, Melting Below Zero, p. 509.) Ice is made much more slippery when a thin coating of liquid water is present. This thin coat of liquid water acts as a lubricant to help the skates move easily over the ice (Figure 11.16). Pressure plays very little role in making the ice slippery for skating. Although increasing the pressure on ice does cause it to melt, the effect is too small to contribute significantly in the context of ice skating.
The phase diagram for CO$_2$ (Figure 11.17) is similar to that of water, except for one very important difference—the solid/liquid equilibrium line has a positive slope, as it does for most substances. Solid CO$_2$ is more dense than liquid CO$_2$. Notice also that the values of the pressure and temperature axes in the phase diagram for CO$_2$ are much different from those in the diagram for water. For pressures below about 5 atm, the only equilibrium that can exist is between solid and gaseous CO$_2$. This means solid CO$_2$ sublimes when heated. Liquid CO$_2$ can be produced only at pressures above 5 atm. The temperature range for liquid CO$_2$ is narrower than that for water. Tanker trucks marked “liquid carbonic” carry liquid CO$_2$, a convenient source of CO$_2$ gas for making carbonated beverages.

**PROBLEM-SOLVING EXAMPLE 11.5**  
**Phase Diagrams**

Use the phase diagram for CO$_2$ (Figure 11.17) to answer these questions.

(a) What is the temperature and pressure at the triple point?

(b) Starting at the triple point, what phase exists when the pressure is held constant and the temperature is increased to 65 °C?

(c) Starting at $T = -70$ °C and $P = 4$ atm, what phase change occurs when the pressure is held constant and the temperature is increased to $-30$ °C?

(d) Starting at $T = -30$ °C and $P = 5$ atm, what phase change occurs when the temperature is held constant and the pressure is increased to 10 atm?

**Answer**

(a) $T = -57$ °C, $P = 5.2$ atm  
(b) Gas  
(c) Solid to gas (sublimation)  
(d) Gas to liquid (condensation)

**Strategy and Explanation**

In each case, consult the location on the phase diagram that corresponds to the given temperature and pressure conditions.

(a) The phase diagram shows that the triple point occurs at a temperature of $-57$ °C and a pressure of 5.2 atm.

(b) Increasing the temperature and holding the pressure constant means moving somewhat to the right from the triple point. This is the gas region of the phase diagram.

(c) At the starting temperature and pressure, the CO$_2$ is a solid. Increasing the temperature while holding the pressure constant causes the solid to sublime and change directly to the gas phase.

(d) At the starting temperature and pressure, the CO$_2$ is a liquid. Increasing the pressure while holding the temperature constant causes the gas to condense to the liquid phase.
PROBLEM-SOLVING PRACTICE 11.5

On the phase diagram for CO₂ (Figure 11.17), the point that corresponds to a temperature of \(-13^\circ\text{C}\) and a pressure of 7.5 atm is on the vapor pressure curve where liquid phase and gas phase are in equilibrium. What phase of CO₂ exists when the pressure remains the same and the temperature is increased by several degrees?

**EXERCISE 11.11 Using a Phase Diagram**

Consider the phase diagram for CO₂ (Figure 11.17). A curve connects the triple point and the critical point; what is the name of this curve? What phase transition occurs when you traverse this curve at its midpoint going upward, that is, increasing the pressure at constant temperature? Downward? What phase transition occurs when you traverse this curve at its midpoint going from left to right, that is, increasing the temperature at constant pressure? Right to left?

Critical Temperature and Pressure

On the phase diagram for CO₂, notice the upper point where the liquid/gas equilibrium line terminates (Figure 11.17). For CO₂, the conditions at this critical point are 73 atm and 31 °C. For water the termination of the solid/liquid curve occurs at a pressure of 217.7 atm and a temperature of 374.0 °C (Figure 11.15). These conditions at the critical point are called the critical pressure \(P_c\) and critical temperature \(T_c\). At any temperature above \(T_c\), the molecules of a substance have sufficient kinetic energy to overcome any attractive forces, and no amount of pressure can cause the substance to act like a liquid again. Above \(T_c\) and \(P_c\), the substance becomes a supercritical fluid, which has a density characteristic of a liquid but the flow properties of a gas, thereby enabling it to diffuse through many substances easily.
Supercritical CO$_2$ is present in a fire extinguisher under certain conditions. As the phase diagram shows, at any temperature below 31 °C, the pressurized CO$_2$ (usually at about 73 atm) is a liquid that can slosh around in the container. On a hot day, however, the CO$_2$ becomes a supercritical fluid and cannot be heard sloshing. In fact, under these conditions the only way to know whether CO$_2$ is in the extinguisher—without discharging it—is to weigh it and compare its mass with the mass of the empty container, which is usually indicated on a tag attached to the fire extinguisher.

Supercritical fluids are excellent solvents. Because supercritical CO$_2$ is nonpolar and is therefore a good solvent for nonpolar substances, it is used for dry cleaning. Supercritical CO$_2$ is also used to extract caffeine from coffee beans and for extracting toxic components from hazardous industrial wastes.

**CONCEPTUAL EXERCISE 11.12 The Behavior of CO$_2$**

If liquid CO$_2$ is slowly released to the atmosphere from a cylinder, what state will the CO$_2$ be in? If the liquid is suddenly released, as in the discharge of a CO$_2$ fire extinguisher, why is solid CO$_2$ seen? Can you explain this phenomenon on the basis of the phase diagram alone, or do you need to consider other factors?

### 11.4 Water: An Important Liquid with Unusual Properties

Earth is sometimes called the blue planet because the large quantities of water on its surface make it look blue from outer space. Three quarters of the globe is covered by oceans, and vast ice sheets cover the poles. Large quantities of water are present in soils and rocks on the surface. Water is essential to almost every form of life, has played a key role in human history, and is a significant factor in weather and climate. Water’s importance is linked to its unique properties (Table 11.4). Ice floats on water; in contrast, when most substances freeze, the solid sinks in its liquid. More thermal energy must be transferred to melt ice, heat water, and vaporize water than to accomplish these changes for the same mass of almost any other substance. Water has the largest thermal conductivity and the highest surface tension of any molecular substance in the liquid state. In other words, this most common of substances in our daily lives has properties that are highly unusual. These properties are crucial for the welfare of our planet and our species.

Most of water’s unusual properties can be attributed to its molecules’ unique capacity for hydrogen bonding. As seen from Figure 9.22 (p. 413), one water molecule can participate in four hydrogen bonds to other water molecules. When liquid water freezes, a three-dimensional network of water molecules forms to accommodate the maximum hydrogen bonding. In the crystal lattice of ice, the oxygen atoms lie at the corners of puckered, six-sided rings. Considerable open space is left within the rings, forming empty channels that run through the entire crystal lattice.

When ice melts to form liquid water, approximately 15% of the hydrogen bonds are broken and the rigid ice lattice collapses. This makes the density of liquid water greater than that of ice at the melting point. The density of ice at 0 °C is 0.917 g/mL, and that of liquid water at 0 °C is 0.998 g/mL. The density difference is not large, but it is enough so that ice floats on the surface of the liquid. This explains why about 90% of an iceberg is submerged and about 10% is above water.

As the liquid water is warmed further, more hydrogen bonds break, and more empty space is filled by water molecules. The density continues to increase until a temperature of 3.98 °C and a density of 1.000 g/mL are reached. As the temperature rises beyond 3.98 °C, increased molecular motion causes the molecules to push

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“If there is magic on this planet, it is contained in water . . . Its substance reaches everywhere.”
—Loren Eiseley

The six-sided symmetry of snowflakes corresponds to the symmetry of these hexagonal rings.
each other aside more vigorously, the empty space between molecules increases, and the density decreases by about 0.0001 g/mL for every 1 °C temperature rise above 3.98 °C (Figure 11.18).

Because of this unusual variation of density with temperature, when water in a lake is cooled to 3.98 °C, the higher density causes the cold water to sink to the bottom. Water cooled below 3.98 °C is less dense and stays on the surface, where it can be cooled even further. Consequently, the water at the bottom of the lake remains at 3.98 °C, while that on the surface freezes. Ice on the surface insulates the remaining liquid water from the cold air, and, unless the lake is quite shallow, not all of the water freezes. This allows fish and other organisms to survive without being frozen in the winter. When water at 3.98 °C sinks to the bottom of a lake in...
the fall, it carries with it dissolved oxygen. Nutrients from the bottom are brought to the surface by the water it displaces. This is called “turnover” of the lake. The same thing happens in the spring, when the ice melts and water on the surface warms to 3.98 °C. Spring and fall turnovers are essential to maintain nutrient and oxygen levels required by fish and other lake-dwelling organisms.

When water is heated, the increased molecular motion breaks additional hydrogen bonds. The strength of these intermolecular forces requires that considerable energy be transferred to raise the temperature of 1 g of water by 1 °C. That is, water’s specific heat capacity is quite large. Many hydrogen bonds are broken when liquid water vaporizes, because the molecules are completely separated. This gives rise to water’s very large enthalpy of vaporization, which is a factor in humans’ ability to regulate their body temperature by evaporation of sweat. As we have already described, hydrogen bonds are broken when ice melts, and this requires a large enthalpy of fusion. Its larger-than-normal enthalpy changes upon vaporization and freezing, together with its large specific heat capacity, allow water to moderate climate and influence weather by a much larger factor than other liquids could. In the vicinity of a large body of water, summer temperatures do not get as high and winter temperatures do not get as low (at least until the water freezes over) as they do

11.4 Water: An Important Liquid with Unusual Properties

CHEMISTRY IN THE NEWS

Melting Below Zero

Details on how the freezing of water and the thawing of ice proceed at the molecular level are being revealed by new research. The key lies in a very thin layer of water, only a few molecules thick, created by a process termed “surface melting.” This thin layer is very similar to the ice beneath it, but it has the mobility of the liquid state. Effects due to its presence include the sliding of ice skates over ice, the eruption of boulders from the ground during freeze-thaw cycles (frost heave), and the electrification of thunderclouds.

Surface melting is an intrinsic property of the ice surface, even at tens of degrees Celsius below the usual melting point. It arises due to the fact that the surface water molecules have interactions with fewer neighbors than do those molecules deeper in the solid. The ice lattice becomes less and less ordered closer to the surface because the surface molecules have the fewest hydrogen bonds holding them in place. That is, these molecules vibrate around their lattice positions more than the molecules deeper in the solid. At temperatures well below the melting point, the surface molecules begin to take on the characteristics of a liquid. Surface melting was first described by Michael Faraday in 1842, and scientists are even now refining their understanding of this phenomenon.

The presence of the surface liquid phase permits you to develop a snowball. The liquid on the surface of ice particles refreezes and joins them together into a snowball. Truly dry snow does not permit the formation of a snowball.

While the ice-water system is best known in the everyday world, this surface melting phenomenon occurs for virtually all solids.


At a sufficiently high temperature, well below their normal melting point, the water molecules become liquid-like.

Nearer the surface, the lattice is distorted, and the molecules are freer to move.

Deep in the ice crystal, water molecules are locked in a rigid lattice as each is H-bonded with its four nearest neighbors.

The surface of ice is slick due to a liquid-like film of water.

Water vapor in air

Liquid film

Solid ice

The surface of ice is slick due to a liquid-like film of water.
far away from water (p. 223). Seattle is farther north than Minneapolis, for example, but Seattle has a much more moderate climate because it borders the Pacific Ocean and Puget Sound.

11.5 Types of Solids

The relationship of nanoscale structure to macroscale properties is a central theme of this text. Nowhere is the influence of the nanoscale arrangement of atoms, molecules, or ions on properties more evident than in the study of solids. Practicing chemists, in collaboration with physicists, engineers, and other scientists, explore such relationships as they work to create new and useful materials. The nature of solid substances is determined by the type of forces holding them together. Ionic solids, such as common table salt (NaCl), are held together by electrostatic interactions between cations and anions. Molecular solids, such as water in the form of ice, are held together by intermolecular interactions such as London forces, dipole-dipole forces, and hydrogen bonding. Network solids, such as diamond, are bonded into infinite molecules by covalent bonds between atoms. Table 11.5 summarizes the characteristics and physical properties of the major types of solid substances. By classifying a substance as one of these types of solid, you will be able to form a reasonably good idea of what general physical properties to expect, even for a substance that you have never encountered before.

A solid is rigid, having its own shape rather than assuming the shape of its container as a liquid does. Solids have varying degrees of hardness that depend on the kinds of atoms in the solid and the types of forces that hold the atoms, molecules, or ions of the solid together. For example, talc (soapstone, Figure 11.19a), which is used as a lubricant and in talcum powder, is one of the softest solids known. At the atomic level, talc consists of layered sheets containing silicon, magnesium, and oxygen atoms. Attractive forces between these sheets are very weak, so one sheet of talc can slide along another and be removed easily from the rest. In contrast, diamond (Figure 11.19b) is one of the hardest solids known. In diamond, each carbon atom is strongly bonded to four neighbors. Each of those neighbor atoms is in turn

<table>
<thead>
<tr>
<th>Type</th>
<th>Examples</th>
<th>Structural Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic (p. 89)</td>
<td>NaCl, K₃SO₄, CaCl₂, (NH₄)₃PO₄</td>
<td>Positive and negative ions (some polyatomic); no discrete molecules</td>
</tr>
<tr>
<td>Metallic (Section 11.9)</td>
<td>Iron, silver, copper, other metals and alloys</td>
<td>Metal atoms (positive metal ions surrounded by an electron sea)</td>
</tr>
<tr>
<td>Molecular (p. 79)</td>
<td>H₂, O₂, I₂, H₂O, CO₂, CH₄, CH₃OH, CH₃COOH</td>
<td>Molecules with covalent bonds</td>
</tr>
<tr>
<td>Network (Section 11.7)</td>
<td>Graphite, diamond, quartz, feldspars, mica</td>
<td>Atoms held in an infinite one-, two-, or three-dimensional network</td>
</tr>
<tr>
<td>Amorphous (glassy)</td>
<td>Glass, polyethylene, nylon</td>
<td>Covalently bonded networks of atoms or collections of large molecules with short-range order only</td>
</tr>
</tbody>
</table>
strongly bonded to four other carbon atoms, and so on throughout the solid (a network solid, Section 11.7). Because of the number and strength of the bonds holding each carbon atom to its neighbors, diamond is so hard that it can scratch or cut almost any other solid. For this reason diamonds are used in cutting tools and abrasives, which are more important commercially than diamonds used as gemstones.

Although all solids consist of atoms, molecules, or ions in relatively immobile positions, some solids exhibit a greater degree of regularity than others. In crystalline solids, the ordered arrangement of the individual particles is reflected in the planar faces and sharp angles of the crystals. Salt crystals, minerals, gemstones, and ice are examples of crystalline solids. Amorphous solids are somewhat like liquids in that they exhibit very little long-range order, yet they are hard and have definite shapes. Ordinary glass is an amorphous solid, as are organic polymers such as polyethylene and polystyrene. The remainder of this chapter is devoted to explaining the nanoscale structures that give rise to the properties of solids summarized in Table 11.5.

### PROBLEM-SOLVING EXAMPLE 11.6 Types of Solids

What types of solids are these substances?

(a) Sucrose, C$_{12}$H$_{22}$O$_{11}$ (table sugar), has a melting point of about 185 °C. It has poor electrical conductance both as a solid and as a liquid.

(b) Solid Na$_2$SO$_4$ has a melting point of 884 °C and has low electrical conductivity that increases dramatically when the solid melts.

**Answer**

(a) Molecular solid  
(b) Ionic solid

**Strategy and Explanation**

(a) Sucrose molecules contain covalently bonded atoms. Sucrose’s properties correspond to those of a molecular solid since it has poor electrical conductance both as a solid and as a liquid.

(b) Sodium sulfate is composed of Na$^+$ and SO$_4^{2-}$ ions. The given properties are consistent with those of ionic solids. Ionic solids have high melting points and are poor conductors as solids but good conductors as liquids.

<table>
<thead>
<tr>
<th>Forces Holding Units Together</th>
<th>Typical Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic bonding; attractions among charges on positive and negative ions</td>
<td>Hard; brittle; high melting point; poor electrical conductor as solid, good as molten liquid; often water-soluble</td>
</tr>
<tr>
<td>Metallic bonding; electrostatic attraction among metal ions and electrons</td>
<td>Malleable; ductile; good electrical conductor in solid and liquid; good heat conductor; wide range of hardness and melting point</td>
</tr>
<tr>
<td>London forces, dipole-dipole forces, hydrogen bonds</td>
<td>Low to moderate melting point and boiling point; soft; poor electrical conductor in solid and liquid</td>
</tr>
<tr>
<td>Covalent bonds; directional electron-pair bonds</td>
<td>Wide range of hardness and melting point (three-dimensional bonding &gt; two-dimensional bonding &gt; one-dimensional bonding); poor electrical conductor with some exceptions</td>
</tr>
<tr>
<td>Covalent bonds; directional electron-pair bonds</td>
<td>Noncrystalline; wide temperature range for melting; poor electrical conductor, with some exceptions</td>
</tr>
</tbody>
</table>
PROBLEM-SOLVING PRACTICE 11.6
What types of solids are these substances?
(a) The hydrocarbon decane, $C_{10}H_{22}$, has a melting point of $-31 \, ^\circ C$ and is a poor electrical conductor.
(b) Solid $\text{MgCl}_2$ has a melting point of $780 \, ^\circ C$ and conducts electricity only when melted.

CONCEPTUAL EXERCISE 11.13 Lead into Gold?
Imagine a sample of gold and a sample of lead, each with a smoothly polished surface. The surfaces of these two samples are placed in contact with one another and held in place, under pressure, for about one year. After that time the two surfaces are analyzed. The gold surface is tested for the presence of lead, and the lead surface is tested for the presence of gold. Predict what the outcome of these two tests will be and explain what has happened, if anything.

11.6 Crystalline Solids
The beautiful regularity of ice crystals, crystalline salts, and gemstones suggests that they must have some internal regularity. Toward the end of the eighteenth century, scientists found that shapes of crystals can be used to identify minerals. The angles at which crystal faces meet are characteristic of a crystal’s composition. The shape of each crystalline solid reflects the shape of its crystal lattice—the orderly, repeating arrangement of ions, molecules, or atoms that shows the position of each individual particle. In such a lattice each ion, molecule, or atom is surrounded by neighbors in exactly the same arrangement. Each crystal is built up from a three-dimensional repetition of the same pattern, which gives the crystal long-range order throughout.

Unit Cells
A convenient way to describe and classify the repeating pattern of atoms, molecules, or ions in a crystal is to define a small segment of a crystal lattice as a unit cell—a small part of the lattice that, when repeated along the directions defined by its edges, reproduces the entire crystal structure. To help understand the idea of the unit cell, look at the simple two-dimensional array of circles shown in Figure 11.20. The same size circle is repeated over and over, but a circle is not a proper unit cell because it gives no indication of its relationship to all the other circles. A better choice is to recognize that the centers of four adjacent circles lie at the corners of a square and to draw four lines connecting those centers. A square unit cell results. Figure 11.20 shows this simple unit cell superimposed on the circles. As you look at the unit cell drawn in darker blue, notice that each of four circles contributes one quarter of its area to the unit cell, so a net of one circle is located within the unit cell. When this unit cell is repeated by moving the square parallel to its edges (that is, when unit cells are placed next to and above and below the first one), the two-dimensional lattice results. Notice that the corners of a unit cell are equivalent to each other and that collectively they define the crystal lattice.

The three-dimensional unit cells from which all known crystal lattices can be constructed fall into only seven categories. These seven types of unit cells have edges of different relative lengths that meet at different angles. We will limit our discus-
sion here to one of these types—cubic unit cells composed of atoms or monatomic ions. Such unit cells are quite common in nature and are simpler and easier to visualize than the other types of unit cells. The principles illustrated, however, apply to all unit cells and all crystal structures, including those composed of polyatomic ions and large molecules.

**Cubic unit cells** have edges of equal length that meet at 90° angles. There are three types: *primitive cubic* or *simple cubic* (sc), *body-centered cubic* (bcc), and *face-centered cubic* (fcc) (Figure 11.21). Many metals and ionic compounds crystallize in cubic unit cells.

In metals, all three types of cubic unit cells have identical atoms centered at each corner of the cube. When the cubes pack into three-dimensional space, an atom at a corner is shared among eight cubes (Figure 11.21); thus only one eighth of each corner atom is actually within the unit cell. Since a cube has eight corners and since one eighth of the atom at each corner belongs to the unit cell, the net result is \( \frac{1}{8} \times 8 = 1 \) atom per primitive (simple) cubic unit cell.

In the bcc unit cell an additional atom is at the center of the cube and lies entirely within the unit cell. This atom, combined with the net of one atom from the corners, gives a total of two atoms per body-centered cubic unit cell.

In the face-centered cubic unit cell six atoms or ions lie in the centers of the faces of the cube. One half of each of these atoms or ions belongs to the unit cell (Figure 11.21). In this case there is a net result of \( 6 \times \frac{1}{2} = 3 \) atoms per unit cell, plus the net of one atom contributed by the corners, for a total of four atoms per face-centered cubic unit cell. The number of atoms per unit cell helps to determine the density of a solid.

**Examples of metals with cubic unit cells:**
- Primitive (simple) cubic: Po
- Body-centered cubic: alkali metals, V, Cr, Mo, W, Fe
- Face-centered cubic: Ni, Cu, Ag, Au, Al, Pb

**Figure 11.21** The three different types of cubic unit cells. The top row shows the lattice points of the three cells superimposed on space-filling spheres centered on the lattice points. The bottom row shows the three cubic unit cells with only those atoms included that belong to the unit cell.
The third-layer atoms are placed directly above the atoms in the first layer, forming an \( ababab \) arrangement.

In \( abab \) packing, the repeat occurs every third layer; in \( abcabc \) packing, it is every fourth layer.

Each layer is formed by packing the spheres as closely as possible—each sphere touches six others.

The second layer is placed on top of the first.

The third-layer atoms are placed directly above the holes in the first layer, forming an \( abcabc \) arrangement.

Figure 11.22  Closest packing of spheres. Hexagonal close-packed structure (part 3) and cubic close-packed structure (part 4).

**Exercise 11.14 Counting Atoms in Unit Cells of Metals**

Crystalline polonium has a primitive (simple) cubic unit cell, lithium has a body-centered cubic unit cell, and calcium has a face-centered cubic unit cell. How many Po atoms belong to one unit cell? How many Li atoms belong to one unit cell? How many Ca atoms belong to one unit cell? Draw each unit cell. Indicate on your drawing what fraction of each atom lies within the unit cell.

Closest Packing of Spheres

In crystalline solids, the atoms, molecules, or ions are usually arranged as closely as possible so that their interactions are maximized, which results in a stable structure. This arrangement is most easily illustrated for metals, in which the individual particles are identical atoms that can be represented as spheres. The arrangement known as closest packing can be built up as a series of layers of atoms. In each layer of equal-sized spheres, as shown in Figure 11.22, part 1, each sphere is surrounded by six neighbors. A second layer can be put on top of the first layer so the spheres nestle into the depressions of the first layer (Figure 11.22, part 2). Then a third layer can be added. There are two ways to add the third layer, each of which yields a different structure, as shown in Figure 11.22, parts 3 and 4. If the third layer is directly above the first layer, an \( ababab \) arrangement results, called a hexagonal close-packed structure. In this \( ababab \) structure, the centers of the spheres of the...
third layer are directly above the centers of the spheres of the first layer. If the third layer is not directly above the first layer, an abcabc arrangement results, giving a cubic close-packed structure. In the abcabc structure, the centers of the spheres of the third layer are directly above the holes between the spheres of the first layer. In the abcabc structure, the centers of the spheres of the fourth layer are directly above the centers of the spheres of the first layer. The unit cell for a cubic close-packed structure is face-centered cubic (fcc).

In each of these two close-packed structures, each sphere has 12 nearest-neighbor spheres that are equidistant. In each of these arrangements, 74% of the total volume of the structure is occupied by spheres and 26% is empty. Compare these percentages with those for the body-centered cubic structure, which is 68% occupied, and for the simple cubic structure, which is only 52% occupied.

Unit Cells and Density

The information given so far about unit cells allows us to check whether a proposed unit cell is reasonable. Because a unit cell can be replicated to give the entire crystal lattice, the unit cell should have the same density as the crystal. As an example, we will consider platinum.

PROBLEM-SOLVING EXAMPLE 11.7 Unit Cell Dimension, Type, and Density

Platinum crystals are fcc, with a density of 21.45 g/cm$^3$. Platinum has a molar mass of 195.08 g/mol, and platinum atoms have a 139-pm radius. What is the length of a unit cell edge? Is this consistent with Pt being fcc?

**Answer** 392 pm. Yes, it is consistent with fcc.

**Strategy and Explanation** Starting with the radius of a Pt atom, we can calculate the diagonal length of the unit cell, the length of an edge of the unit cell, and the unit cell's volume. From the mass of Pt atoms per unit cell and the unit cell's volume we can calculate the density and compare this to the known density.

The mass of one Pt atom is

$$\frac{195.08 \text{ g Pt}}{1 \text{ mol Pt}} \times \frac{1 \text{ mol Pt}}{6.022 \times 10^{23} \text{ atoms Pt}} = 3.239 \times 10^{-22} \text{ g}$$

In an fcc unit cell there are four atoms per unit cell, so the mass of Pt atoms per unit cell is

$$4 \times 3.239 \times 10^{-22} \text{ g} = 1.296 \times 10^{-21} \text{ g Pt per unit cell}$$

Now we calculate the volume of the unit cell. To start we calculate the face diagonal length (see figure in margin).

Face diagonal length = 4 × Pt atom radius = 4 × 139 pm = 556 pm

For an fcc unit cell, the relationship between the edge length of the unit cell and its face diagonal length is (see figure in margin)

$$(\text{Diagonal length})^2 = \text{edge}^2 + \text{edge}^2 = 2(\text{edge})^2$$

so

$$\text{Edge} = \frac{\text{diagonal length}}{\sqrt{2}} = \frac{556 \text{ pm}}{1.414} = 393 \text{ pm}$$

The volume of the unit cell is

$$V = \text{edge}^3 = (393 \text{ pm})^3 = 6.07 \times 10^{-25} \text{ cm}^3$$

(1 pm = $10^{-12}$ m = $10^{-10}$ cm)

The density is the mass of Pt atoms per unit cell divided by the unit cell's volume.

Recently, a rigorous mathematical proof was developed that showed the impossibility of packing spheres to get a packing fraction greater than 74%.
This density value compares well with the given value, and the calculation shows that the data are consistent with an fcc unit cell for the Pt crystal.

✓ Reasonable Answer Check The density, atomic weight, unit cell edge length and diagonal length, and Pt atom radius are all in agreement.

PROBLEM-SOLVING PRACTICE 11.7

Gold crystals have a bcc structure. The radius of a gold atom is 144 pm, and the atomic weight of gold is 196.97 amu. Calculate the density of gold.

For each of the three cubic unit cells, there is a close relationship between the radius of the atom forming the unit cell and the unit cell size. For the simple cubic unit cell, halves of two atoms form the edge of the unit cell. For the face-centered cubic unit cell, one complete atom and halves of two other atoms form the face diagonal of the unit cell. For the body-centered cubic unit cell, one complete atom and halves of two other atoms form the body diagonal of the unit cell. To summarize:

Simple cubic: \(2 \times (\text{atomic radius}) = \text{edge}\)

Face-centered cubic: \(4 \times (\text{atomic radius}) = \text{edge} \times \sqrt{2}\)

Body-centered cubic: \(4 \times (\text{atomic radius}) = \text{edge} \times \sqrt{3}\)

Ionic Crystal Structures

The crystal structures of many ionic compounds can be described as simple cubic or face-centered cubic lattices of spherical negative ions, with positive ions occupying spaces (called holes) among the negative ions. The number and locations of the occupied holes are the keys to understanding the relation between the lattice structure and the formula of an ionic compound. The simplest example is an ionic compound in which the hole in a primitive (simple) cubic unit cell (Figure 11.21) is occupied. The ionic compound cesium chloride, CsCl, has such a structure. In it, each simple cube of Cl\(^-\) ions has a Cs\(^+\) ion at its center (Figure 11.23). The spaces occupied by the Cs\(^+\) ions are called cubic holes, and each Cs\(^+\) has eight nearest-neighbor Cl\(^-\) ions.

The structure of sodium chloride, NaCl, is one of the most common ionic crystal lattices (Figures 11.24 and 11.25). If you look carefully at Figure 11.24, it is possible to determine the number of Na\(^+\) and Cl\(^-\) ions in the NaCl unit cell. There is
one eighth of a Cl\(^-\) ion at each corner of the unit cell and one half of a Cl\(^-\) ion in the middle of each face. The total number of Cl\(^-\) ions within the unit cell is

\[
\frac{1}{8} \text{ Cl}^- \times 8 \text{ corners} = 1 \text{ Cl}^-
\]
\[
\frac{1}{2} \text{ Cl}^- \times 6 \text{ faces} = 3 \text{ Cl}^-
\]
Total of 4 Cl\(^-\) in a unit cell

There is one fourth of a Na\(^+\) at the midpoint of each edge and a whole Na\(^+\) in the center of the unit cell. For Na\(^+\) ions, the total is

\[
\frac{1}{4} \text{ Na}^+ \times 12 \text{ edges} = 3 \text{ Na}^+
\]
1 Na\(^+\) per center \times 1 center = 1 Na\(^+\)
Total of 4 Na\(^+\) in a unit cell

Thus, the unit cell contains four Na\(^+\) and four Cl\(^-\) ions. This result agrees with the formula of NaCl for sodium chloride.

As shown in Figure 11.25, the NaCl crystal lattice consists of an fcc lattice of the larger Cl\(^-\) ions, in which Na\(^+\) ions occupy so-called octahedral holes—octahedral because each Na\(^+\) ion is surrounded by six Cl\(^-\) ions at the corners of an octahedron. Likewise, each Cl\(^-\) ion is surrounded by six Na\(^+\) ions. Figure 11.25 also shows a space-filling model of the NaCl lattice, in which each ion is drawn to scale based on its ionic radius.

**EXERCISE 11.15 Formulas and Unit Cells**

Cesium chloride has a cubic unit cell, as seen in Figure 11.23. Show that the formula for the salt must be CsCl.
PROBLEM-SOLVING EXAMPLE 11.8  Calculating the Volume and Density of a Unit Cell

The unit cell of NaCl is shown in Figure 11.24. The ionic radii for Na\(^+\) and Cl\(^-\) are 116 pm and 167 pm, respectively. Calculate the density of NaCl.

**Answer**  2.14 g/cm\(^3\)

**Strategy and Explanation**  To calculate the density, we need to determine the mass and the volume of the unit cell. The mass can be found from the number of formula units in a unit cell and the molar mass of NaCl. The volume can be found from the length of an array; in fact, they are as small as possible. For this reason the layer you have made is called a close-packed layer. Now add a second layer, and let the spheres nestle into the holes in the first layer. Now add a third layer. If you look carefully, you will see that there are two ways to put down the third layer. One of these places spheres directly above holes in the first layer. This is called cubic close packing, and the unit cell is face-centered cubic (fcc) (Figure 11.22). The other arrangement, also found for many metals, places third-layer spheres directly above spheres in the first layer. This is hexagonal close packing, and its unit cell is not cubic. Cubic and hexagonal close packing are the most efficient ways possible for filling space with spheres; 74% of the available space is occupied. The atoms in most metals are arranged in cubic close packing, in hexagonal close packing, or in lattices composed of body-centered cubic unit cells. Efficient packing of the atoms or ions in the crystal lattice allows stronger bonding, which gives greater stability to the crystal.

1. In either the cubic close-packed or the hexagonal close-packed arrangement, each atom has six neighbors in the same plane. How many closest neighbors does each atom have, considering all three dimensions?

2. How many closest neighbors does each atom have in the primitive (simple) cubic structure?
edge of the cubic unit cell. As seen in Figure 11.24, the Na⁺ and Cl⁻ ions touch along the edge of the unit cell. Thus, the edge length is equal to two Cl⁻ radii plus two Na⁺ radii.

\[
\text{Edge} = 167 \text{ pm} + (2 \times 116 \text{ pm}) + 167 \text{ pm} = 566 \text{ pm}
\]

The volume of the cubic unit cell is the cube of the edge length.

\[
\text{Volume of unit cell} = (\text{edge})^3 = (566 \text{ pm})^3 = 1.81 \times 10^8 \text{ pm}^3
\]

Converting this to cm³ gives

\[
1.81 \times 10^8 \text{ pm}^3 \times \left( \frac{10^{-10} \text{ cm}}{1 \text{ pm}} \right)^3 = 1.81 \times 10^{-22} \text{ cm}^3
\]

Next we can calculate the mass of a unit cell and divide it by the volume to get the density. With four NaCl formula units per unit cell,

\[
4 \text{ NaCl formula units} \times \frac{58.44 \text{ g}}{\text{mol NaCl}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ formula units}} = 3.88 \times 10^{-22} \text{ g}
\]

This means the density of a NaCl unit cell is

\[
\frac{3.88 \times 10^{-22} \text{ g}}{1.81 \times 10^{-22} \text{ cm}^3} = 2.14 \text{ g/cm}^3
\]

✓ Reasonable Answer Check  The experimental density is 2.164 g/cm³, which is in reasonable agreement with the calculated value. Remember, however, that all experiments have uncertainties associated with them. The density of NaCl calculated from unit cell dimensions could easily have given a value closer to the experimental density if the tabulated radii for the Na⁺ and Cl⁻ ions were slightly smaller. There is, of course, a slight uncertainty in the published radii of all ions.

PROBLEM-SOLVING PRACTICE 11.8

KCl has the same crystal structure as NaCl. Calculate the volume of the unit cell for KCl, given that the ionic radii are K⁺ = 152 pm and Cl⁻ = 167 pm. Compute the density of KCl. Which has the larger unit cell, NaCl or KCl?

11.7 Network Solids

A number of solids are composed of nonmetal atoms connected by a network of covalent bonds. Such network solids really consist of one huge molecule in which all the atoms are connected to all the others via such a network. Separate small molecules do not exist in a network solid.

The most important network solids are the silicates. Many bonding patterns exist among the silicates, but extended arrays of covalently bonded silicon and oxygen atoms are common, such as quartz, SiO₂. Silicates will be discussed in depth in Chapter 21.

Graphite, Diamond, and Fullerenes

Graphite, diamond, and fullerenes are allotropes of carbon ( p. 27). Graphite’s name comes from the Greek graphein, meaning “to write,” because one of its earliest uses was for writing on parchment. Artists today still draw with charcoal, an impure form of graphite, and we write with graphite pencil leads. Graphite is an example of a planar network solid (Figure 11.26). Each carbon atom is covalently bonded to three other carbon atoms. The planes consist of six-membered rings of carbon atoms (like those in benzene) ( p. 364). Each hexagon shares all six of its sides with other hexagons around it, forming a two-dimensional network resembling chicken wire. Some of the bonding electrons are able to move freely around this network, so graphite readily conducts electricity. Within a plane, there are strong...
The distance between graphite planes is more than twice the distance between the nearest carbon atoms within a plane.

Figure 11.26 The structure of graphite. Three of the many layers of six-membered carbon rings are shown. These layers can slide past one another relatively easily, making graphite a good lubricant. In addition, some of the carbon valence electrons in the layers are delocalized, allowing graphite to be a good conductor of electricity parallel to the layers.

Covalent bonds between carbon atoms, but attractions between the planes are caused by London forces and hence are weaker. Because of this, the planes can easily slip across one another, which makes graphite an excellent solid lubricant for uses such as in locks, where greases and oils are undesirable.

Diamonds are also built of six-membered carbon rings, with each carbon atom bonded to four others by single covalent bonds. This structure forms a three-dimensional network (Figure 11.27). Because of the tetrahedral arrangement of bonds around each carbon atom, the six-membered rings in the diamond structure are puckered. As a result, diamond (3.51 g/cm³) is much denser than graphite (2.22 g/cm³). Also, because its valence electrons are localized in covalent bonds between carbon atoms, diamond does not conduct electricity. Diamond is one of the hardest materials and also one of the best conductors of heat known. It is also transparent to visible, infrared, and ultraviolet radiation.

Figure 11.27 The structure of diamond. Each carbon atom is covalently bonded to four other carbon atoms in an extended tetrahedral arrangement.
In the 1950s, scientists at General Electric in Schenectady, New York, first produced man-made diamonds. Their technique, still in use today, was to heat graphite to a temperature of 1500 °C in the presence of a metal catalyst, such as nickel or iron, and under a pressure of 50,000 to 65,000 atm. Under these conditions, the carbon dissolves in the metal and recrystallizes in its higher-density form, slowly becoming diamond. Today a $500 million worldwide market exists for diamonds made this way, many of which are used for abrasives and diamond-coated cutting tools for drilling.

Buckyballs, the prototype of the third allotrope of carbon, were discovered in the 1980s. Since then, a variety of carbon structures have been developed, all classified as fullerenes. The prototype structure, \( C_{60} \), is a sphere composed of pentagons and hexagons of carbon atoms similar to a soccer ball (Figure 1.22c, p. 27). Larger cage-like structures have also been synthesized. In fullerenes, each carbon atom has three carbon atom neighbors. Each carbon atom has \( sp^2 \) hybridization, and has one unhybridized \( p \) orbital. Electrons can be delocalized over these \( p \) orbitals, just as they can in graphite. Unlike graphite, each carbon atom and its three bonds are not quite planar, resulting in the curved fullerene structures. Another fullerene geometry is elongated tubes of carbon atoms, called nanotubes because of their small size. Nanotubes have been formed with a single wall of carbon atoms similar to graphite rolled into a tube, resembling rolled-up chicken wire. The nanotube is capped at each end with a truncated buckyball (Figure 11.28). Nanoscale materials such as nanotubes have physical and chemical properties different from bulk materials. Scientists are now exploring the possible useful properties of nanotubes and other similar materials.

11.8 Materials Science

Humans have long adapted or altered naturally occurring materials for use in clothing, structures, and devices. The tanning of leather and firing of clay pots predate recorded history. Operations such as these alter the nanoscale structure of the material to improve its resulting properties. The names of the periods of early civilization reflect the defining materials of the time—Stone Age, Bronze Age, Iron Age. This same close relationship between the nature of societies and their materials continues to hold in the modern world. The critical role played by materials is a cornerstone of life today. Only recently has the scientific understanding of the relationships among the processing, structure, and properties of materials been developed and exploited; the creation of new materials has accelerated as a consequence. Furthermore, new phenomena have been discovered that permit the invention of new materials.

Figure 11.28 A single-walled carbon nanotube composed of hexagons of carbon atoms.

Dorothy Crowfoot Hodgkin was born in Egypt, where her father was a supervisor of schools and ancient monuments. Schooled in England, she graduated from Oxford University in 1931. She was fascinated by the study of crystals and went to Cambridge University, where she eventually joined the faculty. Hodgkin’s first major achievement in crystallography was the determination of the structure of penicillin in 1945. In 1964 she received the Nobel Prize in chemistry for determining the molecular structure of vitamin B-12. Much of her work required pioneering and painstaking experimental techniques that, as one biographer put it, “transformed crystallography from a black art into an indispensable scientific tool.”
X-Ray Crystallography

**X-ray crystallography** is used to determine the absolute atomic arrangement of the atoms in solid samples. One of the most powerful tools of solid-state chemistry, it is routinely applied to solids as varied as crystalline minerals, proteins, and semiconductors. When X-rays strike crystals, the X-rays are scattered in different directions and with different intensities due to interference effects. X-rays have wavelengths on the order of 1 nm, the same scale as atomic dimensions. When an X-ray beam strikes a crystal, the X-rays are scattered. When the interference is **constructive**, the waves combine to produce X-rays that can be observed indirectly because they expose a spot on photographic film. When the interference is **destructive**, the waves partly or entirely cancel each other; so little or no X-ray intensity is recorded.

Interference effects among the scattered X-rays from the different atoms cause the intensity of the scattered radiation to show maxima and minima in various directions, creating a diffraction pattern. The particular diffraction pattern obtained depends on the X-ray wavelength and the distances between the planes of atoms in the crystal. The Bragg equation relates the X-ray wavelength (λ), the spacing between atomic layers in the crystal (d), the angle of scattering (θ), and an integer (n, usually considered as 1):

\[ n\lambda = 2d \sin \theta \]

Waves \( a \) and \( b \) reinforce each other when the Bragg equation is satisfied—that is, when the additional distance traveled by wave \( b \) to reach the detector is an integer multiple of the X-ray wavelength. Therefore, the X-ray diffraction pattern can be related back to the nanoscale arrangement of the atoms in the crystal. The intensity of the scattered X-ray beam depends on the electron density of the atoms in the crystal. Therefore, a hydrogen atom is least effective in causing X-rays to scatter, while heavy atoms such as lead or mercury are quite effective.

Photographic film was used to record the diffraction patterns in early instruments. Today, crystallographers use computer-controlled instruments, highly sensitive solid-state detectors, and other advanced instrumentation to measure the angles of reflection and the intensities of X-ray beams diffracted by crystals. Sophisticated software allows the atomic arrangements in crystalline materials to be determined quickly enough that X-ray crystallography is used routinely.

In one of the most famous uses of X-ray crystallography, James Watson and Francis Crick in 1953 interpreted X-ray data obtained by Maurice Wilkins and Rosalind Franklin to discover the double helix structure of DNA, the biological macromolecule that carries genetic information (p. 416). Watson, Crick, and Wilkins were awarded the Nobel Prize in medicine and physiology in 1962 for this discovery (Franklin was deceased and therefore could not share the prize).

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**Constructive interference** occurs when two in-phase waves combine to produce a wave of greater amplitude.

**Destructive interference** results from the combination of two waves of equal magnitude that are exactly out of phase. The result is zero amplitude.

---

**Materials**. For example, superconducting ceramic oxides that conduct electricity without resistance at critical temperatures greater than the boiling point of liquid nitrogen may pave the way to astounding advances in information technology and computing in the coming decades. The study of materials on the nanoscale has led to an entire field of science and technology and the creation of nanostructures.

Just what are **materials** anyway? By materials we mean matter used to construct the devices and macroscopic structures of our highly developed technology. Application areas include transportation, communication and information technology, infrastructure, consumer goods, health care, and biomaterials. Properties that can be important in materials cover the entire range of characteristics of matter: electronic, optical, magnetic, superconducting, strength, and flexibility.

The four major classes of materials are metals, polymers, ceramics, and composites. Materials in each of the four major categories tend to have specific properties that are similar:
• **Metals** Opaque with shiny surface (unless covered by an oxidized coating, as in rusted iron). Usually crystalline. Generally ductile—can be drawn into wires (copper). Strong and stiff (steel). Most are not magnetic, except Fe, Ni, and Co or alloys. Usually conduct heat and electricity well (Cu). Form alloys such as stainless steel, bronze, and brass.

• **Polymers** Both natural (wool, cotton, rubber) and synthetic (polyethylene, polystyrene). Most are flexible and can be bent, but some are brittle. Thermoplastics become more flexible when heated; thermoset polymers become hard and brittle when heated. Usually thermal and electrical insulators. Not magnetic.

• **Ceramics** Nonmetallic materials, often based on clays. Porcelain, bricks, glass, and cement are examples. Usually brittle and cannot be bent. Poor thermal conductors and good thermal insulators; can withstand high temperatures. Usually poor electrical conductors and good electrical insulators. Some ceramics are

---

**X-ray diffraction from a solid.** The relationships among the variables in the Bragg equation are shown. For wave \( b \) to reach the detector in phase with wave \( a \), \( b \) must travel farther by \( 2d \sin \theta \), and this distance must be an integral multiple of the X-ray wavelength.
magnetic. Usually crystalline. Many are transparent (glass). Semiconductors are ceramics with special electrical properties. Glasses, a special class of ceramics, are brittle yet often strong and are amorphous.

- **Composites** Materials combining components from the other three categories with properties that blend the best of both components depending on the application.

**Materials science** is the science of the relationships between the structure and the chemical and physical properties of materials. How strong is the material? How dense? How easily formed? How does it react to acid, stress, magnetic fields, high pressure, heat? Does it conduct electricity? **Structure** refers to the organization of the material on scales ranging from the nanoscale (electron structure, arrangement of atoms, crystal arrangement) through the microscale and to the macroscale.

The major breakthrough of the second half of the twentieth century with respect to materials was that scientists and engineers can now often **design** a material for a specific application. That is, scientific understanding at the nanoscale permits synthesis and fabrication of new materials with precise properties desired for a particular application. Coupling this capability with inventiveness and technological know-how results in cost-effective manufacture of materials and devices.

Communications and information systems provide examples of advances that moved hand in hand with advances in materials. The development of vacuum tubes, transistors, and integrated circuits has enabled our technology to advance. Lasers, which provide intense, coherent, monochromatic light, and optical fibers (Section 11.11), which provide a means of carrying optical signals over long distances, have revolutionized communications and many other fields.

The twentieth-century transportation revolution was also enabled by advances in materials. Aircraft require light yet strong materials, and the advances from aluminum and its alloys to titanium to composite materials (graphite- and boron fiber-reinforced polymers, aluminum or titanium reinforced with fibers, and graphite-reinforced epoxy) have advanced the modern aircraft industry. Similar materials are used in high-performance mountain bike frames, tennis racquets, skis, and other sporting equipment. At the same time, the development of materials that can withstand the extreme temperatures and stresses in rocket and jet engine turbine blades has made modern aircraft and rockets possible. Automobiles have an ever-growing number of parts made from aluminum alloys, engineered plastics, and ceramics.

### 11.9 Metals, Semiconductors, and Insulators

All metals are solids except mercury (m.p. $-38.8 \, ^\circ C$) at room temperature, and exhibit common properties that we call metallic.

- **High electrical conductivity** Metal wires are used to carry electricity from power plants to homes and offices because electrons in metals are highly mobile.
- **High thermal conductivity** We learn early in life not to touch any part of a hot metal pot because it will transfer heat rapidly and painfully.
- **Ductility and malleability** Most metals are easily drawn into wire (ductility) or hammered into thin sheets (malleability); some metals (gold, for example) are more easily formed into shapes than others.
- **Luster** Polished metal surfaces reflect light. Most metals have a silvery-white color because they reflect all wavelengths equally well.
• **Insolubility in water and other common solvents** No metal dissolves in water, but a few (mainly from Groups 1A and 2A) react with water to form hydrogen gas and solutions of metal hydroxides.

As you will see, these properties are explained by the kinds of bonding that hold atoms together in metals.

The enthalpies of fusion and melting points of metals vary greatly. Low melting points correlate with low enthalpies of fusion, which implies weaker attractive forces holding the metal atoms together. Mercury, which is a liquid at room temperature, has an enthalpy of fusion of only 2.3 kJ/mol. The alkali metals and gallium also have very low enthalpies of fusion and notably low melting points (Table 11.6). Compare these values with those in Table 11.3 for nonmetals (p. 500).

Figure 11.29 shows the relative enthalpies of fusion of the metals related to their positions in the periodic table. The transition metals, especially those in the third transition series, have very high melting points and extraordinarily high enthalpies of fusion. Tungsten (W) has the highest melting point (3410 °C) of all the metals, and among all the elements it is second only to carbon as graphite, which has a melting point of 3550 °C. Pure tungsten is used in incandescent light bulbs as the filament, the wire that glows white-hot. No other material has been found to be better since the invention of commercially successful, long-lived light bulbs in 1908 by Thomas Edison and his co-workers.

### PROBLEM-SOLVING EXAMPLE 11.9 Calculating Enthalpies of Fusion

Use data from Table 11.6 to calculate the thermal energy transfer required to melt 10.0 g chromium at its melting point.

**Answer** 3.25 kJ

**Strategy and Explanation** First, we determine how many moles of chromium are present. Then we calculate the energy required from the \( \Delta H_{\text{fusion}} \) value in Table 11.6.

\[
10.0 \text{ g Cr} \times \frac{1 \text{ mol Cr}}{52.00 \text{ g Cr}} = 0.192 \text{ mol Cr} \\
0.192 \text{ mol Cr} \times \frac{16.9 \text{ kJ}}{1 \text{ mol Cr}} = 3.25 \text{ kJ}
\]

---

**Table 11.6 Enthalpies of Fusion and Melting Points of Some Metals**

<table>
<thead>
<tr>
<th>Metal</th>
<th>( \Delta H_{\text{fusion}} ) (kJ/mol)</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>2.3</td>
<td>-38.8</td>
</tr>
<tr>
<td>Ga</td>
<td>7.5</td>
<td>29.78*</td>
</tr>
<tr>
<td>Na</td>
<td>2.59</td>
<td>97.9</td>
</tr>
<tr>
<td>Li</td>
<td>3.0</td>
<td>180.5</td>
</tr>
<tr>
<td>Al</td>
<td>10.7</td>
<td>660.4</td>
</tr>
<tr>
<td>U</td>
<td>12.6</td>
<td>1132.1</td>
</tr>
<tr>
<td>Fe</td>
<td>13.8</td>
<td>1535.0</td>
</tr>
<tr>
<td>Ti</td>
<td>20.9</td>
<td>1660.1</td>
</tr>
<tr>
<td>Cr</td>
<td>16.9</td>
<td>1857.0</td>
</tr>
<tr>
<td>W</td>
<td>35.2</td>
<td>3410.1</td>
</tr>
</tbody>
</table>

*This means that gallium metal will melt in the palm of your hand from the warmth of your body (37 °C). It happens that gallium is a liquid over the largest range of temperature of any metal. Its boiling point is approximately 2250 °C.

---

**Figure 11.29** Relative enthalpies of fusion for the metals in the periodic table. See Table 11.6 for some numerical values of enthalpies of fusion.
We have about two tenths of a mole of chromium, so the energy required should be about two tenths of the molar enthalpy of fusion, about 17 kJ/mol, or about 3.4 kJ, which compares well with our more accurate answer.

**PROBLEM-SOLVING PRACTICE 11.9**
Use data from Table 11.6 to calculate the heat transfer required to melt 1.45 g aluminum.

**CONCEPTUAL EXERCISE 11.16 Cooling a Liquid Metal Until It Solidifies**
When a liquid metal is cooled at a constant rate to the temperature at which it solidifies, and the solid is then cooled to an even lower temperature, the “cooling curve”—a plot of temperature against time—looks like the chart to the left. Account for the shape of this curve. Would all substances exhibit similar curves?

**CONCEPTUAL EXERCISE 11.17 Heats of Fusion and Electronic Configuration**
Look in Appendix D and compare the electron configurations shown there with the heats of fusion for the metals shown in Table 11.6. Is there any correlation between these configurations and this property? Does strength of attraction among metal atoms correlate with number of valence electrons? Explain.

### Electrons in Metals, Semiconductors, and Insulators
Metals behave as though metal cations exist in a “sea” of mobile electrons—the valence electrons of all the metal atoms. **Metallic bonding** is the nondirectional attraction between positive metal ions and the surrounding sea of negative charge (valence electrons). Each metal ion has a large number of near neighbors. The valence electrons are spread throughout the metal’s crystal lattice, holding the positive metal ions together. When an electric field is applied to a metal, these valence electrons move toward the positive end of the field, and the metal conducts electricity.

The mobile valence electrons provide a uniform charge distribution in a metal lattice, so the positions of the positive ions can be changed without destroying the attractions among positive ions and electrons. Thus, most metals can be bent and drawn into wire. Conversely, when we try to deform an ionic solid, which consists of a lattice of positive and negative ions, the crystal usually shatters because the balance of positive ions surrounded by negative ions, and vice versa, is disrupted.

To visualize how bonding electrons behave in a metal, first consider the arrangement of electrons in an individual atom far enough away from any neighbor so that no bonding occurs. In such an atom the electrons occupy orbitals that have definite energy levels. In a large number of separated, identical atoms, all of the energy levels are identical. If the atoms are brought closer together, however, they begin to influence one another. The identical energy levels shift up or down and become bands of energy levels characteristic of the large collections of metal atoms (Figure 11.30). An **energy band** is a large group of orbitals whose energies are closely spaced and whose average energy is the same as the energy of the corresponding orbital in an individual atom. In some cases, energy bands for different types of electrons ($s$, $p$, $d$, and so on) overlap; in other cases there is a gap between different energy bands.

Within each band, electrons fill the lowest energy orbitals much as electrons fill orbitals in atoms or molecules. The number of electrons in a given energy band...
depends on the number of metal atoms in the crystal. In considering conductivity and other metallic properties, it is usually necessary to consider only valence electrons, as other electrons all occupy completely filled bands in which two electrons occupy every orbital. In these bands, no electron can move from one orbital to another, because there is no empty spot for it.

A band containing the valence electrons is called the **valence band**. If the valence band is partially filled it requires little added energy to excite a valence electron to a slightly higher energy orbital. Such a small increment of energy can be provided by applying an electric field, for example. The presence of low-energy, empty orbitals into which electrons can move allows the electrons to be mobile and to conduct an electric current (Figure 11.31).

Another band containing higher energy orbitals (the **conduction band**) exists at an average energy above the valence band. In a metal, the valence band and the conduction band overlap, so electrons can move from the valence band to the conduction band freely; this ability explains metals’ electrical conductivity. Such a metal with overlapping valence and conduction bands is a **conductor**.

When the conduction band is close in energy to the valence band, the electrons can absorb a wide range of wavelengths in the visible region of the spectrum. As the excited electrons fall back to their lower energy states, they emit their extra energy as visible light, producing the luster characteristic of metals.

The energy band theory also explains why some solids are **insulators**, which do not conduct electricity. In an insulator the valence band and conduction band do not overlap. Rather, there is a large band gap between them (Figure 11.31). Very few electrons have enough energy to move across the large gap from a filled lower energy band to an empty higher energy band, so no current flows through an insulator when an external electric field is applied.

In a **semiconductor** a very narrow energy gap separates the valence band and the conduction band (Figure 11.31). At quite low temperatures, electrons remain in the filled lower energy valence band, and semiconductors are not good conductors. At higher temperatures, or when an electric field is applied, some electrons have enough energy to jump across the band gap into the conduction band. This allows an electric current to flow. This property of semiconductors—to switch from insulator to conductor with the application of an external electric field—is the basis for the operation of transistors, the cornerstone of modern electronics.

**Superconductors**

One interesting property of metals is that their electrical conductivity decreases with increasing temperature. In Figure 11.32b a metal in a burner flame shows higher resistance (lower conductivity) than the same metal at room temperature (Figure 11.32a). The lower conductivity of metals at higher temperatures can be explained by considering valence electrons in the lattice of metal ions as waves. As an electron wave moves through the metal crystal under the influence of an electrical voltage, the wave encounters lattice positions where the metal ions are close enough together to scatter it. This scattering is analogous to the scattering of X-rays caused by atoms in crystals. The scattered electron wave moves off in another direction, only to be scattered again when it encounters some other occupied lattice position. All of this scattering lowers the conductivity of the metal. At higher temperatures, the metal ions vibrate more, and the distances between lattice positions change more from their average values. This effect causes more scattering of electron waves as they move through the crystal, because there are now more possibilities of unfavorable lattice spacings. Hence electrical conductivity is lower.

From this picture of electrical conductivity, it might be expected that the conductivity of a metal crystal at absolute zero (0 K or −273.15 °C) might be very large.
In fact, the conductivity of a pure metal crystal approaches infinity as absolute zero is approached. In some metals, however, a more interesting phenomenon occurs. At a critical temperature \( T_c \) that is low but finite, the conductivity abruptly increases to infinity, which means that the resistance drops to zero (Figure 11.33). As a result, the metal becomes a superconductor of electricity. A superconductor offers no resistance whatsoever to electric current. Once a current has been started in a superconducting circuit, it continues to flow indefinitely. No clear theory explaining superconductivity has yet emerged, but it appears that the scattering of electron waves by vibrating atoms is replaced in a superconductor by some cooperative action that allows the electrons to move through the crystal unhindered.

If a material could be made superconducting at a high enough temperature, the material would find uses in the transmission of electrical energy, in high-efficiency motors, and in computers and other devices. Table 11.7 lists some metals that have superconducting critical temperatures. While some useful devices can be fabricated

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**Table 11.7 Superconducting Transition Temperatures of Some Metals***

<table>
<thead>
<tr>
<th>Metal</th>
<th>Superconducting Transition Temperature (K)</th>
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<tbody>
<tr>
<td>Gallium</td>
<td>1.10</td>
</tr>
<tr>
<td>Aluminum</td>
<td>1.15</td>
</tr>
<tr>
<td>Tin</td>
<td>3.72</td>
</tr>
<tr>
<td>Mercury</td>
<td>4.15</td>
</tr>
<tr>
<td>Lanthanum</td>
<td>4.9</td>
</tr>
<tr>
<td>Lead</td>
<td>7.2</td>
</tr>
</tbody>
</table>

*Not all metals have superconducting properties. Those that can become superconductors at atmospheric pressure are Al, Ti, Zn, Ga, Zr, Mo, Tc, Ru, Cd, In, Sn, La, Hf, Ta, W, Re, Os, Ir, Hg, Tl, Pb, Th, Pa, and U.

---

**Figure 11.32** Resistance, temperature, and electrical conductivity. (a) A piece of metal at room temperature exhibits a small resistance (high electrical conductivity). (b) While being heated, this same piece of metal exhibits a higher resistance value, indicating a lower conductivity.

Superconductivity was discovered in 1911 by the Dutch physicist Kamerlingh Onnes, who won a Nobel Prize for his work.

Information about superconductors is available at this Web site: [http://superconductors.org](http://superconductors.org).

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**Figure 11.33** The resistance of a superconducting metal and a non-superconducting metal as a function of temperature.
from these metals, the very low temperatures at which they become superconductors make them impractical for most applications. Shortly after superconductivity of metals was discovered, alloys were prepared that had higher transition temperatures. Niobium alloys were the best, but still required cooling to below 23 K (−250 °C) to exhibit superconductivity. Maintenance of such a low temperature requires liquid helium, which is expensive.

This picture abruptly changed in January 1986, when Alex Müller and Georg Bednorz, IBM scientists in Switzerland, discovered that a lanthanum-barium-copper oxide became superconducting at 35 K (−238 °C). This type of mixed metal oxide is a ceramic with the same structure as the mineral perovskite (CaTiO₃) and, therefore, would be expected to have insulating properties. The announcement of the superconducting properties of LaBa₂Cu₃Oₓ (x means that varying amounts of oxygen are incorporated) rocked the world of science and provoked a flurry of activity to prepare related compounds in the hope that even higher critical temperatures could be found. Within four months, a material (YBa₂Cu₃O₇) that became superconducting at 90 K (−183 °C) was announced. Its identification was a major breakthrough because 90 K exceeds the boiling point of liquid nitrogen (bp = 77 K or −196 °C), which is easily obtainable and cheap. The current record critical temperature of 138 K (−135 °C) at atmospheric pressure is for a thallium-doped mercuric-cuprate ceramic with the composition Hg₀.₈Tl₀.₂Ba₂Ca₂Cu₃O₈₋₂₅.

Why the great excitement over the potential of superconductivity? Superconducting materials would allow the building of more powerful electromagnets such as those used in nuclear particle accelerators and in magnetic resonance imaging (MRI) machines for medical diagnosis (p. 308). Such electromagnets would permit higher energies to be maintained for longer periods of time (and at lower cost) in the case of the particle accelerators, and support better imaging of problem areas in a patient’s body. Currently, the main barrier to their wider application is the cost of cooling the magnets used in these devices.

Many scientists say that the discovery of high-temperature superconducting materials is more important than the discovery of the transistor because of its potential effect on electrical and electronic technology. For example, the use of superconducting materials for transmission of electric power could save as much as 30% of the energy now lost because of the resistance of the wire. Superchips for computers could be as much as 1000 times faster than existing silicon chips. Since a superconductor repels magnetic materials (Figure 11.34), trains can be levitated above a track and move with no friction other than air resistance to slow them down. When a maglev (magnetic levitation) rail line in Japan was tested on April 4, 1999, the test train attained a speed of 343 mi/h (552 km/h). On December 2, 2003, a Japanese three-car test train attained a maximum speed of 581 km/h. On December 31, 2002, the world’s first commercial maglev train service ran at 430 km/h over a 30-km link from Pudong airport to Pudong (adjacent to Shanghai). The German government is now engaged in the Transrapid Project, which will connect Berlin to Hamburg, a distance of 292 km, with a maglev train traveling at about 300 km/h.

11.10 Silicon and the Chip

Silicon is known as an “intrinsic” semiconductor because the element itself is a semiconductor. Silicon of about 98% purity can be obtained by heating silica (purified sand) and coke (an impure form of carbon) at 3000 °C in an electric arc furnace.

\[
\text{SiO}_2(s) + 2 \text{C}(s) \xrightarrow{\text{heat}} \text{Si}(s) + 2 \text{CO(g)}
\]

Silicon of this purity can be alloyed with aluminum and magnesium to increase the hardness and durability of the metals and is used for making silicone polymers. For
use in electronic devices, however, a much higher degree of purification is needed. High-purity silicon can be prepared by reducing SiCl\textsubscript{4} with magnesium.

\[
\text{SiCl}_4(l) + 2 \text{Mg}(s) \rightarrow \text{Si}(s) + 2 \text{MgCl}_2(s)
\]

Magnesium chloride, which is water-soluble, is washed from the silicon. The final purification of the silicon takes place by a melting process called **zone refining** (Figure 11.35), which produces silicon containing less than one part per billion of impurities such as boron, aluminum, and arsenic. Zone refining takes advantage of the fact that impurities are often more soluble in the liquid phase than in the solid phase. As a hot molten zone is moved through a sample being purified, the impurities move along in the liquefied portion of the sample. As the heated zone cools, the sample that resolidifies is purer than it was. Multiple passes of the hot molten zone are usually necessary to achieve the degree of purity necessary to fabricate semiconducting devices.

Like all semiconductors, high-purity silicon fails to conduct an electric current until a certain electrical voltage is applied, but at higher voltages it conducts moderately well. Silicon’s semiconducting properties can be improved dramatically by a process known as doping. **Doping** is the addition of a tiny amount of some other element (a dopant) to the silicon.

For example, consider what happens when a few atoms of a Group 5A element such as arsenic are added to silicon. Arsenic has five valence electrons, whereas silicon has four. Thus, only four of the five valence electrons of As are used for bonding with four Si atoms, leaving one electron relatively free to move. This type of doped silicon is referred to as negative-type or **n-type silicon** because it has extra (negative) valence electrons. In **n-type semiconductors**, electrons are the charge carriers.

On the other hand, consider what happens when a small number of boron atoms (or atoms of some other Group 3A element) replace silicon atoms (Group 4A) in solid silicon. Boron has only three valence electrons. This leaves a deficiency of one electron around the B atom, creating what is called a **hole** for every B atom added. Hence silicon doped in this manner is referred to as positive-type or **p-type silicon** (Figure 11.36). In **p-type semiconductors**, holes are the charge carriers. It is important to remember that such holes in semiconductors are the absence of electrons. Thus, the flow of holes in one direction is in reality the flow of electrons in the opposite direction.

When **p-type** and **n-type** semiconductors are brought together, a **p-n junction** results. Such a junction can act as a rectifier; that is, it allows current to flow in one direction but not the other. When the two materials are joined, some of the excess...
electrons in the \( n \)-type material migrate across the junction and some of the holes in the \( p \)-type material migrate in the opposite direction. The result is the buildup of a negative charge on the \( p \)-type region and a positive charge on the \( n \)-type region. This charge buildup is called the *junction potential*, and it prevents the further migration of electrons or holes. However, if an external potential is applied to the \( p-n \) junction, one of two effects can result. If a negative charge is connected to the \( p \)-type side and a positive charge to the \( n \)-type side, then the electrons and holes migrate away from the junction, and no current flows through the junction (Figure 11.37, bottom). If a negative charge is connected to the \( n \)-type side and a positive charge to the \( p \)-type side, then both electrons and holes flow across the junction, and current flows through the device (Figure 11.37, top). Thus, the \( p-n \) junction acts to pass current one way but not the other.

**Figure 11.36** Schematic drawing of semiconductor crystals derived from silicon.

**Figure 11.37** A \( p-n \) junction. Placing a \( p \)-type semiconductor next to an \( n \)-type semiconductor creates a \( p-n \) junction. The charge carriers in the \( p \)-type region are holes, and the charge carriers in the \( n \)-type region are electrons. *Top:* The negative battery terminal is connected to the \( n \)-type region, and the positive battery terminal is connected to the \( p \)-type region. The holes and electrons move as indicated by the arrows. Electric current flows through the junction and the overall device. *Bottom:* If the battery terminals are reversed, the holes and electrons are attracted to the edges of the regions, charge depletion occurs near the junction, and no current flows through the junction or the overall device.
These $p$-$n$ junctions can be joined together into larger composite structures to create transistors and integrated circuits. A single integrated circuit often contains thousands or even millions of transistors, as well as the circuits to carry the electrical signals. These devices, in the form of computer memories and central processing units (CPUs), permeate our society.

Doped silicon is also the basis of the solar cell. When a layer of $n$-type doped silicon is next to a $p$-type layer, there is a strong tendency for the extra electrons in the $n$-type layer to pair with the unpaired electrons in the holes of the $p$-type layer. If the two layers are connected by an external electrical circuit, light that strikes the silicon provides enough energy to cause an electrical current to flow. When a photon is absorbed, it excites an electron to a higher-energy orbital, allowing the electron to leave the $n$-type silicon layer and flow through the external circuit to the $p$-type layer. As the $p$-type layer becomes more negative (because of added electrons), the extra electrons are repelled internally back into the $n$-type layer (which has become positive because of the loss of electrons via the circuit). This process can continue as long as the silicon layers are exposed to sunlight and the circuit remains closed. Figure 11.38 shows a schematic diagram of a typical solar cell.

Solar cells are on the threshold of a major technological breakthrough, perhaps comparable to the computer chip. Although experimental solar-powered automobiles are now available and many novel applications of solar cells exist, the real breakthrough will come from the general use of banks of solar cells at utility power plants to produce huge quantities of electricity. One plant operating in California uses banks of solar cells to produce 20 megawatts (MW) of power—enough to supply the daily electricity needs of a city the size of Tampa, Florida.

11.11 Cement, Ceramics, and Glass

Cement, ceramics, and glass are examples of amorphous solids; that is, they lack crystalline structures with easily defined unit cells. Thanks to their useful properties, all three are extremely important in practical applications.
Cement

Cement consists of microscopic particles containing compounds of calcium, iron, aluminum, silicon, and oxygen in varying proportions. In the presence of water, cement forms hydrated particles with large surface areas, which subsequently undergo recrystallization and reaction to bond to themselves as well as to the surfaces of bricks, stone, or other silicate materials.

Cement is made by roasting a powdered mixture of calcium carbonate (limestone or chalk), silica (sand), aluminosilicate mineral (kaolin, clay, or shale), and iron oxide at a temperature of up to 870 °C in a rotating kiln. As the materials pass through the kiln, they lose water and carbon dioxide and ultimately form a “clinker,” in which the materials are partially fused. A small amount of calcium sulfate is added, and the cooled clinker is then ground to a very fine powder. A typical composition of cement is 60% to 67% CaO, 17% to 25% SiO₂, 3% to 8% Al₂O₃, up to 6% Fe₂O₃, and small amounts of magnesium oxide, magnesium sulfate, and oxides of potassium and sodium.

Cement is usually mixed with other substances. Mortar is a mixture of cement, sand, water, and lime. Concrete is a mixture of cement, sand, and aggregate (crushed stone or pebbles) in proportions that vary according to the application and the strength required.

In cement, the oxides are not isolated into ionic crystals, but an entire nanoscale structure forms that is a complex network of ions, each satisfying its charge requirements with ions of opposite charge. Many different reactions occur during the setting of cement. Various constituents react with water and with carbon dioxide in the air. The initial reaction of cement with water involves the hydrolysis of the calcium silicates, which forms a gel that sticks to itself and to the other particles (sand, crushed stone, or gravel). This gel has a very large surface area and ultimately is responsible for the great strength of concrete once it has set. The setting process involves formation of small, densely interlocked crystals. Their formation continues after the initial setting and increases the compressive strength of the cement (Figure 11.39). For this reason, freshly poured concrete is kept moist for several days.

Concrete, like many other materials containing Si—O bonds, is highly noncompressible but lacks tensile strength. When concrete is to be used where it will be subject to tension, as in a bridge or building, it must be reinforced with steel.

Ceramics

Ceramics are generally fashioned from clay or other natural earths at room temperature and then permanently hardened by heat in a baking (“firing”) process that binds the particles together.

Silicate ceramics include objects made from clays (aluminosilicates), such as pottery, bricks, and table china. China clay, or kaolin, is primarily kaolinite that is practically free of iron, which otherwise imparts a red color to the clay. As a result, china clay is white and particularly valuable in making fine pottery. Clays mixed with water form a moldable paste consisting of tiny silicate sheets that can easily slide past one another. When heated, the water is driven off, and new Si—O—Si bonds form so that the mass becomes permanently rigid.

Oxide ceramics are produced from powdered metal oxides such as alumina (Al₂O₃) and magnesia (MgO) by heating the solids under pressure, causing the particles to bind to one another and thereby form a rigid solid. Because it has a high electrical resistivity, alumina is used in spark plug insulators. High-density alumina has very high mechanical strength, so it is also used in armor plating and in high-speed cutting tools for machining metals. Magnesia is an insulator with a high melting point (2800 °C), so it is often used as insulation in electric heaters and electric stoves.

A third class of ceramics includes the nonoxide ceramics such as silicon nitride (Si₃N₄), silicon carbide (SiC), and boron nitride (BN). Heating the solids under...
pressure forms ceramics that are hard and strong, but brittle. Boron nitride has the same average number of electrons per atom as does elemental carbon and exists in the graphite structure or the diamond structure, making it comparable in hardness with diamond and more resistant to oxidation. For this reason, boron nitride cups and tubes are used to contain molten metals that are being evaporated. Silicon carbide (trade name Carborundum) is a widely used abrasive that can be regarded as the diamond structure with half of the C atoms replaced by Si atoms.

The one severely limiting problem in using ceramics is their brittleness. Ceramics deform very little before they fail catastrophically, with the failure resulting from a weak point in the bonding within the ceramic matrix. Such weak points are not consistent from sample to sample, so the failure is not readily predicted. Stress failure of ceramic composites occurs due to nanoscale irregularities resulting from impurities or disorder in the atomic arrangements, so much attention is now being given to using purer starting materials and more strictly controlling the processing steps. Adding fibers to ceramic composites makes them less susceptible to brittleness and sudden fracture.

Glasses

One of the more common glasses is soda-lime glass, which is clear and colorless if the purity of the ingredients is carefully controlled. Various substances give color to the glass (Table 11.8).

The simplest glass is probably amorphous silica, SiO₂ (known as vitreous silica); it is prepared by melting and quickly cooling either quartz or cristobalite. Such glass is built up of corner-sharing SiO₄ tetrahedra linked into a three-dimensional network that lacks symmetry or long-range order. Another common glass is borosilicate glass or Pyrex, which contains SiO₂, B₂O₃, and Al₂O₃. It is made from melting boric acid (H₃BO₃), soda ash (Na₂CO₃), silica sand (SiO₂), alumina (Al₂O₃), and borax (Na₂B₄O₇·10H₂O) and is valuable because of its low expansion with temperature and high chemical durability.

If another oxide is added to SiO₂, the melting point of the SiO₂ mixture is lowered considerably (from 1800 °C for quartz to about 800 °C if about 25 mole percent of Na₂O is added). The resulting melt cools to form a glass that is somewhat water-soluble and definitely soluble in strongly basic solutions. It is also prone to convert back to a crystalline solid. If other metal oxides such as CaO, MgO, or Al₂O₃

<table>
<thead>
<tr>
<th>Table 11.8 Substances Used to Color Glass</th>
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<tbody>
<tr>
<td>Substance</td>
</tr>
<tr>
<td>Calcium fluoride</td>
</tr>
<tr>
<td>Cobalt(II) oxide</td>
</tr>
<tr>
<td>Copper(I) oxide</td>
</tr>
<tr>
<td>Finely divided gold</td>
</tr>
<tr>
<td>Iron(II) compounds</td>
</tr>
<tr>
<td>Iron(III) compounds</td>
</tr>
<tr>
<td>Manganese(IV) oxide</td>
</tr>
<tr>
<td>Tin(IV) oxide</td>
</tr>
<tr>
<td>Uranium compounds</td>
</tr>
</tbody>
</table>

"Lead glass," as the name implies, contains lead as PbO. It is highly prized for its massive feel, acoustic properties, and high index of refraction.

Mole percent is just another way of expressing concentration. If 0.75 mol SiO₂ and 0.25 mol Na₂O are mixed, 1.00 mol matter is present. The mole percent of SiO₂ is 75%, and the mole percent of Na₂O is 25%.

Colored glass. Adding small amounts of metal oxides to colorless glass creates various colors.
are added, the mixture still melts at a fairly low temperature, but it becomes resistant to chemical attack. Common glass like that used for windows, bottles, and lamps contains these metal oxides in addition to SiO$_2$.

It is important that glass be annealed properly during the manufacturing process. Annealing means cooling the glass slowly as it passes from a viscous liquid state to a solid at room temperature. If a glass is cooled too quickly, bonding forces become uneven because small regions of crystallinity develop. Poorly annealed glass may crack or shatter when subjected to mechanical shocks or sudden temperature changes. High-quality glass, such as that used in optics, must be annealed very carefully. For example, the 200-in mirror for the telescope at Mt. Palomar, California, was annealed from 500 °C to 300 °C over a period of nine months.

Optical Fibers

Our technological culture’s dependence on instantaneous communication relies on the properties of many materials, but none more so than optical fibers. These fibers have rapidly replaced copper wire for the transmission of data such as telephone conversations as well as Internet-based digital data.

An optical fiber has three parts: core glass, which carries the light; cladding glass, which surrounds the core; and a polymer on the outside for physical protection and strength (Figure 11.40). The cladding glass has a slightly lower refractive index than the core glass, so there is total internal reflection of light traveling through the fiber as long as the light hits the surface of the core at a sufficiently small angle.

A good optical fiber must have two properties: (1) It must contain the light—that is, it must produce total internal reflection and have no defects on the surface that would let light out of the fiber; and (2) it must pass light over long distances without significant loss of intensity. To pass light with no attenuation, the core glass must be pure—in fact, ultrapure. Before 1965, when light was put into the best
available optical fiber 1000 m long, no light came out, because it was all absorbed. In the decades that followed, sophisticated manufacturing methods were developed that allowed the generation of core glass appropriate for optical fiber. Pure silica, \( \text{SiO}_2 \), is evaporated into a rod that can be heated and pulled (like taffy) to make a tiny optical fiber. The attenuation of the light signals was decreased by as much as 100 orders of magnitude by the materials scientists working on this problem. At present, optical fibers carrying signals over long distances need to have optical amplifiers only every 50 km or so to keep the signals from becoming too weak. Using such methodology, very long fiber optic cables are now in routine use.

The two main advantages of optical fibers for transmission of voice and electronic information are the capability of the fibers to carry many more streams of data than copper wire can and the decreased interference when fibers rather than wires are used. In addition, optical fibers are made from cheap, abundant materials.

**SUMMARY PROBLEM**

**Part 1**

Use the vapor pressure curves shown in Figure 11.5 to answer these questions.

(a) What is the vapor pressure of diethyl ether at 0 °C?

(b) Does diethyl ether have stronger or weaker intermolecular attractions than ethanol?

(c) At what temperature does diethyl ether have a vapor pressure of 600 mm Hg?

(d) If the normal boiling point of diethyl ether is 34.6 °C and it has a vapor pressure of 410 mm Hg at 20 °C, calculate \( \Delta H_{vap} \) for diethyl ether.

**Part 2**

Consider the phase diagram for xenon shown below. Answer these questions.

(a) In what phase is xenon found at room temperature and a pressure of 1.0 atm?
(b) If the pressure exerted on a sample of xenon is 0.75 atm and the temperature is \(-114 ^\circ C\), in what phase does xenon exist?

(c) If the vapor pressure of a sample of liquid xenon is 375 mm Hg, what is the temperature of the liquid phase?

(d) What is the vapor pressure of solid xenon at \(-122 ^\circ C\)?

(e) Which is the denser phase, solid or liquid? Explain.

Part 3
Consider the CsCl unit cell shown in Figure 11.23.

(a) How many Cs\(^+\) ions are there per unit cell?

(b) How many Cl\(^-\) ions are there per unit cell?

(c) How many Cl\(^-\) ions share each face of the unit cell?

**IN CLOSING**

**Having studied this chapter, you should be able to . . .**

- Explain the properties of surface tension, capillary action, vapor pressure, and boiling point, and describe how these properties are influenced by intermolecular forces (Sections 11.1 and 11.2). ThomsonNOW homework: Study Questions 25, 28, 46, 109

- Calculate the energy transfers associated with vaporization and fusion (Section 11.3). ThomsonNOW homework: Study Questions 21, 32, 34, 94

- Describe the phase changes that occur among solids, liquids, and gases (Section 11.3). ThomsonNOW homework: Study Questions 40, 42, 44

- Use phase diagrams to predict what happens when temperature and pressure are changed for a sample of matter (Section 11.3). ThomsonNOW homework: Study Questions 49, 51, 101

- Understand critical temperature and critical pressure (Section 11.5).

- Describe and explain the unusual properties of water (Section 11.4).

- Differentiate among the major types of solids (Section 11.5). ThomsonNOW homework: Study Questions 56, 58

- Do calculations based on knowledge of simple unit cells and the dimensions of atoms and ions that occupy positions in those unit cells (Section 11.6). ThomsonNOW homework: Study Questions 62, 67

- Explain the bonding in network solids and how it results in their properties (Section 11.7). ThomsonNOW homework: Study Question 71

- Explain the basis of materials science (Section 11.8).

- Explain metallic bonding and how it results in the properties of metals and semiconductors (Section 11.9). ThomsonNOW homework: Study Question 79

- Describe the phenomenon of superconductivity (Section 11.9).

- Describe n-type and p-type semiconductors and the use of p-n junctions as rectifiers (Section 11.10).

- Explain how the lack of regular structure in amorphous solids affects their properties (Section 11.11). ThomsonNOW homework: Study Question 90
### KEY TERMS

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### QUESTIONS FOR REVIEW AND THOUGHT

- **Blue-numbered questions** have short answers at the back of this book and fully worked solutions in the Student Solutions Manual.
- **ThomsonNOW**
  Assess your understanding of this chapter's topics with sample tests and other resources found by signing in to ThomsonNOW at www.thomsonedu.com.

#### Review Questions

1. Name three properties of solids that are different from those of liquids. Explain the differences for each.
2. List the concepts of the kinetic-molecular theory that apply to liquids.
3. What causes surface tension in liquids? Name a substance that has a very high surface tension. What kinds of intermolecular forces account for the high value?
4. Explain how the equilibrium vapor pressure of a liquid might be measured.
5. Define boiling point and normal boiling point.

- **ThomsonNOW**
  denotes questions available in ThomsonNOW and assignable in OWL.

6. What is the heat of crystallization of a substance, and how is it related to the substance's heat of fusion?
7. What is sublimation?
8. Which of these processes are endothermic?
   - Condensation
   - Melting
   - Evaporation
   - Sublimation
   - Deposition
   - Freezing
9. What is the unit cell of a crystal?
10. Assuming the same substance could form crystals with its atoms or ions in either simple cubic packing or hexagonal closest packing, which form would have the higher density? Explain.
11. How does conductivity vary with temperature for (a) a conductor, (b) a nonconductor, (c) a semiconductor, and (d) a superconductor? In your answer, begin at high temperatures and come down to low temperatures.

#### Topical Questions

##### The Liquid State

12. Predict which substance in Table 11.1 has a surface tension most similar to that of each liquid:
   - Ethylene glycol, \( \text{HOCH}_2\text{CH}_2\text{OH} \)
   - Hexane, \( \text{C}_6\text{H}_{14} \)
   - Gallium metal at 40 °C
13. The surface tension of a liquid decreases with increasing temperature. Using the idea of intermolecular attractions, explain why this is so.

14. Explain on the molecular scale the processes of condensation and vaporization.

15. How would you convert a sample of liquid to vapor without changing the temperature?

16. What is the heat of vaporization of a liquid? How is it related to the heat of condensation of that liquid? Using the idea of intermolecular attractions, explain why the process of vaporization is endothermic.

17. After exercising on a hot summer day and working up a sweat, you often become cool when you stop. What is the molecular-level explanation of this phenomenon?

18. The substances Ne, HF, H₂O, NH₃, and CH₄ all have the same number of electrons. In a thought experiment, you can make HF from Ne by removing a single proton a short distance from the nucleus and having the electrons follow the new arrangement of nuclei so as to make a new chemical bond. You can do the same for each of the other compounds. (Of course, none of these thought experiments can actually be done because of the enormous energies required to remove protons from nuclei.) For all of these substances, make a plot of (a) the boiling point in kelvins versus the number of hydrogen atoms and (b) the molar heat of vaporization versus the number of hydrogen atoms. Explain any trend that you see in terms of intermolecular forces.

19. How much heat energy transfer is required to vaporize 1.0 metric ton of ammonia? (1 metric ton = 10⁶ kg.) The ΔH_vap for ammonia is 25.1 kJ/mol.

20. The chlorofluorocarbon CCl₃F has an enthalpy of vaporization of 24.8 kJ/mol. To vaporize 1.00 kg of the compound, how much heat energy transfer is required?

21. The molar enthalpy of vaporization of methanol is 38.0 kJ/mol at 25 °C. How much heat energy transfer is required to convert 250. mL of the alcohol from liquid to vapor? The density of CH₃OH is 0.787 g/mL at 25 °C.

22. Some camping stoves contain liquid butane (C₄H₁₀). They work only when the outside temperature is warm enough to allow the butane to have a reasonable vapor pressure (so they are not very good for camping in temperatures below about 0 °C). Assume the enthalpy of vaporization of butane is 24.5 kJ/mol. If the camp stove fuel tank contains 190. g liquid C₄H₁₀, how much heat energy transfer is required to vaporize all of the butane?

23. Mercury is a highly toxic metal. Although it is a liquid at room temperature, it has a high vapor pressure and a low enthalpy of vaporization (294 J/g). What quantity of heat energy transfer is required to vaporize 0.500 mL of mercury at 357 °C, its normal boiling point? The density of Hg (ℓ) is 13.6 g/mL. Compare this heat energy transfer with the amount needed to vaporize 0.500 mL water. See Table 11.2 for the molar enthalpy of vaporization of H₂O.

24. Rationalize the observation that 1-propanol (CH₃CH₂CH₂OH) has a boiling point of 97.2 °C, whereas a compound with the same empirical formula, ethyl methyl ether (CH₃CH₂OCH₃), boils at 7.4 °C.

25. Briefly explain the variations in the boiling points in the table following. In your discussion be sure to mention the types of intermolecular forces involved.

### Vapor Pressure

26. Give a molecular-level explanation of why the vapor pressure of a liquid increases with temperature.

27. Methanol, CH₃OH, has a normal boiling point of 64.7 °C and a vapor pressure of 100 mm Hg at 21.2 °C. Formaldehyde, H₂C=O, has a normal boiling point of −19.5 °C and a vapor pressure of 100 mm Hg at −57.3 °C. Explain why these two compounds have different boiling points and require different temperatures to achieve the same vapor pressure.

28. ■ The vapor pressure curves for four substances are shown in the plot. Which one of these four substances will have the greatest intermolecular attractive forces at 25 °C? Explain the reason for your answer.

29. The lowest sea-level barometric pressure ever recorded was 25.90 in mercury, recorded in a typhoon in the South Pacific. Suppose you were in this typhoon and, to calm yourself, boiled water to make yourself a cup of tea. At what temperature would the water boil? Remember that 1 atm is 760 mm (29.92 in) Hg, and use Figure 11.5. The temperature at which water would boil at the top of the mountain.

30. The highest mountain in the western hemisphere is Mt. Aconcagua, in the central Andes of Argentina (22,834 ft). If atmospheric pressure decreases at a rate of 3.5 millibar every 100 ft, estimate the atmospheric pressure at the top of Mt. Aconcagua, and then estimate from Figure 11.5 the temperature at which water would boil at the top of the mountain.

31. A liquid has a ΔH_vap of 38.7 kJ/mol and a boiling point of 110 °C at 1 atm pressure. What is the vapor pressure of the liquid at 97 °C?

32. A liquid has a ΔH_vap of 44.0 kJ/mol and a vapor pressure of 570 mm Hg at 90 °C. What is the vapor pressure of the liquid at 130 °C?

33. The vapor pressure of ethanol, C₂H₅OH, at 50.0 °C is 233 mm Hg, and its normal boiling point at 1 atm is 78.3 °C. What is the ΔH_vap of ethanol?

34. What would the ΔH_vap be for a substance whose vapor pressure doubled when its temperature was raised from 70.0 °C to 80.0 °C?
Phase Changes: Solids, Liquids, and Gases

35. What does a low enthalpy of fusion for a solid tell you about the solid (its bonding or type)?
36. What does a high melting point and a high enthalpy of fusion tell you about a solid (its bonding or type)?
37. Which would you expect to have the higher enthalpy of fusion, N2 or I2? Explain your choice.
38. The enthalpy of fusion for H2O is about 2.5 times larger than the enthalpy of fusion for HF. What does this say about the relative strengths of the forces between the molecules in these two solids? Explain.
39. Benzene is an organic liquid that freezes at 5.5 °C and forms beautiful, feather-like crystals. How much heat is evolved when 15.5 g benzene freezes at 5.5 °C? The enthalpy of fusion of benzene is 127 J/g. If the 15.5-g sample is remelted, again at 5.5 °C, what quantity of heat transfer is required to convert it to a liquid?
40. What is the total quantity of heat energy transfer required to change 0.50 mol ice at −5 °C to 0.50 mol steam at 100 °C?
41. How much thermal energy is needed to melt a 56.00 g ice cube that is initially at −10 °C and bring it to room temperature (20 °C)? The solid ice and liquid water have heat capacities of 2.06 J g−1 °C−1 and 4.184 J g−1 °C−1, respectively. The enthalpy of fusion for solid ice is 6.02 kJ/mol and the enthalpy of vaporization of liquid water is 40.7 kJ/mol.
42. The chlorofluorocarbon CCl2F2 was once used as a refrigerant. What mass of this substance must evaporate to freeze 2 mol water initially at 20 °C? The enthalpy of vaporization for CCl2F2 is 280 J/g. The enthalpy of fusion for solid ice is 6.02 kJ/mol and specific heat capacity for liquid water is 4.184 J g−1 °C−1.
43. The ions of NaF and MgO all have the same number of electrons, and the internuclear distances are about the same (235 pm and 212 pm). Why, then, are the melting points of NaF and MgO so different (992 °C and 2642 °C, respectively)?
44. For the pair of compounds LiF and CsI, tell which compound is expected to have the higher melting point, and briefly explain why.
45. Which of these substances has the highest melting point? Explain your choice briefly.
   (a) LiBr
   (b) CaO
   (c) CO
   (d) CH3OH
46. Which of these substances has the highest melting point? The lowest melting point? Explain your choice briefly.
   (a) SiC
   (b) I2
   (c) Rb
   (d) CH3CH2CH2CH3
47. Why is solid CO2 called Dry Ice?
48. During thunderstorms, very large hailstones can fall from the sky. To preserve some of these stones, you place them in the freezer compartment of your frost-free refrigerator. A friend, who is a chemistry student, tells you to put the hailstones in a tightly sealed plastic bag. Why?
49. In this phase diagram, make the following identifications:
   (a) What phase is present in region A? Region B? Region C?
   (b) What phases are in equilibrium at point 1? Point 2? Point 3? Point 5?
50. From memory, sketch the phase diagram of water. Label all the regions as to the physical state of water. Draw either horizontal (constant pressure) or vertical (constant temperature) paths (i.e., lines with arrows indicating a direction) for these changes of state:
   (a) Sublimation
   (b) Condensation to a liquid
   (c) Melting
   (d) Vaporization
   (e) Crystallization
51. Consult the phase diagram of CO2 in Figure 11.17. What phase or phases are present under these conditions:
   (a) T = −70 °C and P = 1.0 atm
   (b) T = −40 °C and P = 15.5 atm
   (c) T = −80 °C and P = 4.7 atm
52. At the critical point for carbon dioxide, the substance is very far from being an ideal gas. Prove this statement by calculating the density of an ideal gas in g/cm3 at the conditions of the critical point and comparing it with the experimental value. Compute the experimental value from the fact that a mole of CO2 at its critical point occupies 94 cm3.

Types of Solids

53. Classify each of these solids as ionic, metallic, molecular, network, or amorphous.
   (a) KF
   (b) I2
   (c) SiO2
   (d) BN
54. Classify each of these solids as ionic, metallic, molecular, network, or amorphous.
   (a) Tetraphosphorus decaoxide
   (b) Brass
   (c) Graphite
   (d) Ammonium phosphate
55. On the basis of the description given, classify each of these solids as molecular, metallic, ionic, network, or amorphous, and explain your reasoning.
   (a) A brittle, yellow solid that melts at 113 °C; neither its solid nor its liquid conducts electricity
   (b) A soft, silvery solid that melts at 40 °C; both its solid and its liquid conduct electricity
   (c) A hard, colorless, crystalline solid that melts at 1713 °C; neither its solid nor its liquid conducts electricity
   (d) A soft, slippery solid that melts at 65 °C; neither its solid nor its liquid conducts electricity
56. On the basis of the description given, classify each of these solids as molecular, metallic, ionic, network, or amorphous, and explain your reasoning.
(a) A soft, slippery solid that has no definite melting point but decomposes at temperatures above 250 °C; the solid does not conduct electricity
(b) Violet crystals that melt at 114 °C and whose vapor irritates the nose; neither the solid nor the liquid conducts electricity
(c) Hard, colorless crystals that melt at 2800 °C; the liquid conducts electricity, but the solid does not
(d) A hard solid that melts at 3410 °C; both the solid and the liquid conduct electricity

57. Describe how each of these materials would behave if it were deformed by a hammer strike. Explain why the materials behave as they do.
(a) A metal, such as gold
(b) A nonmetal, such as sulfur
(c) An ionic compound, such as NaCl

58. ■ What type of solid exhibits each of these sets of properties?
(a) Melts below 100 °C and is insoluble in water
(b) Conducts electricity only when melted
(c) Insoluble in water and conducts electricity
(d) Noncrystalline and melts over a wide temperature range

Crystalline Solids

59. Each diagram below represents an array of like atoms that would extend indefinitely in two dimensions. Draw a two-dimensional unit cell for each array. How many atoms are in each unit cell?

60. Name and draw the three cubic unit cells. Describe their similarities and differences.

61. Explain how the volume of a simple cubic unit cell is related to the radius of the atoms in the cell.

62. ■ Solid xenon forms crystals with a face-centered unit cell that has an edge of 620 pm. Calculate the atomic radius of xenon.

63. Gold (atomic radius = 144 pm) crystallizes in an fcc unit cell. What is the length of a side of the cell?

64. Using the NaCl structure shown in Figure 11.24, how many unit cells share each of the Na⁺ ions in the front face of the unit cell? How many unit cells share each of the Cl⁻ ions in this face?

65. The ionic radii of Cs⁺ and Cl⁻ are 181 and 167 pm, respectively. What is the length of the body diagonal in the CsCl unit cell? What is the length of the side of this unit cell? (See Figure 11.23.)

66. You know that thallium chloride, TlCl, crystallizes in either a simple cubic or a face-centered cubic lattice of Cl⁻ ions with Tl⁺ ions in the holes. If the density of the solid is 7.09 g/cm³ and the edge of the unit cell is 3.85 × 10⁻⁸ cm, what is the unit cell geometry?

67. ■ Could CaCl₂ possibly have the NaCl structure? Explain your answer briefly.

68. A simple cubic unit cell is formed so that the spherical atoms or ions just touch one another along the edge. Prove mathematically that the percentage of empty space within the unit cell is 47.6%. (The volume of a sphere is \( \frac{4}{3}\pi r^3 \), where \( r \) is the radius of the sphere.)

69. Metallic lithium has a body-centered cubic structure, and its unit cell is 351 pm along an edge. Lithium iodide has the same crystal lattice structure as sodium chloride. The cubic unit cell is 600 pm along an edge.
(a) Assume that the metal atoms in lithium touch along the body diagonal of the cubic unit cell, and estimate the radius of a lithium atom.
(b) Assume that in lithium iodide the I⁻ ions touch along the face diagonal of the cubic unit cell and that the Li⁺ and I⁻ ions touch along the edge of the cube; calculate the radius of an I⁻ ion and of an Li⁺ ion.
(c) Compare your results in parts (a) and (b) for the radius of a lithium atom and a lithium ion. Are your results reasonable? If not, how could you account for the unexpected result? Could any of the assumptions that were made be in error?

Network Solids

70. Explain why diamond is denser than graphite.

71. ■ Determine, by looking up data in a reference such as the Handbook of Chemistry and Physics, whether the examples of network solids given in the text are soluble in water or other common solvents. Explain your answer in terms of the chemical bonding in network solids.

72. Explain why diamond is an electrical insulator and graphite is an electrical conductor.

Tools of Chemistry: X-Ray Crystallography

73. The surface of a CD-ROM disc contains narrowly separated lines that diffract light into its component colors. The lines are spaced at distances approximately the same as the wavelength of the light. Taking the middle of the visible spectrum to be green light with a wavelength of 550 nm, calculate how many aluminum atoms (radius = 143 pm) touching its neighbors would make a straight line 550 nm long. Using this result, explain why an optical microscope using visible radiation will never be able to detect an individual aluminum atom (or any other atom, for that matter).

74. For a clear diffraction pattern to be seen from a regularly spaced lattice, the radiation falling on the lattice must have a wavelength less than the lattice spacing. From the unit cell size of the NaCl crystal, estimate the maximum wavelength of the radiation that would be diffracted by this crystal. Calculate the frequency of the radiation and the energy associated with (a) one photon and (b) one mole of photons of the radiation. In what region of the spectrum is this radiation?

75. The first-order Bragg reflection (\( n = 1 \)) from an aluminum crystal for X-rays with a wavelength of 154 pm is 19.3°. What is the spacing between the planes of aluminum atoms?

76. The second-order Bragg reflection (\( n = 2 \)) from a copper crystal for X-rays with a wavelength of 166 pm is 27.35°. What is the spacing between the planes of copper atoms?

77. If the first-order Bragg reflection (\( n = 1 \)) from a NaCl crystal with a spacing of 282 pm is seen at 23.0°, what is the wavelength of the X-ray radiation used?
Metals, Semiconductors, and Insulators

78. What is the principal difference between the orbitals that electrons occupy in individual, isolated atoms and the orbitals they occupy in solids?

79. In terms of band theory, what is the difference between a conductor and an insulator? Between a conductor and a semiconductor?

80. Name three properties of metals, and explain them by using a theory of metallic bonding.

81. Which substance has the greatest electrical conductivity? The smallest electrical conductivity? Explain your choice briefly.

(a) Si
(b) Ge
(c) Ag
(d) P₄

82. Which substance has the greatest electrical conductivity? The smallest electrical conductivity? Explain your choices briefly.

(a) RbCl
(b) NaBr(s)
(c) Rb
(d) Diamond

83. Define the term “superconductor.” Give the chemical formulas of two kinds of superconductors and their associated transition temperatures.

84. What is the main technological or economic barrier to the widespread use of superconductors?

Silicon and the Chip

85. What are the two main chemical reactions involved in the production of electronic-grade silicon? Identify the elements being reduced and being oxidized.

86. Extremely high-purity silicon is required to manufacture semiconductors such as the memory chips found in calculators and computers. If a silicon wafer is 99.9999999% pure, approximately how many silicon atoms per gram have been replaced by impurity atoms of some other element?

87. What is the process of doping, as applied to semiconductors? Why are Group 3A and Group 5A elements used to dope silicon?

88. Explain the difference between n-type semiconductors and p-type semiconductors.

Cement, Ceramics, and Glass

89. Define the term “amorphous.”

90. What makes a glass different from a solid such as NaCl? Under what conditions could NaCl become glass-like?

91. A typical cement contains, by weight, 65% CaO, 20% SiO₂, 5% Al₂O₃, 6% Fe₂O₃, and 4% MgO. Determine the mass percent of each element present. Then determine an empirical formula of the material from the percent composition, setting the coefficient of the least abundant element to 1.00.

92. Give two examples of (a) oxide ceramics and (b) nonoxide ceramics.

General Questions

93. The chlorofluorocarbon CCl₂F₂ was once used in air conditioners as the heat transfer fluid. Its normal boiling point is −30 °C, and its enthalpy of vaporization is 165 J g⁻¹. The gas and the liquid have specific heat capacities of 0.61 J g⁻¹ °C⁻¹ and 0.97 J g⁻¹ °C⁻¹, respectively. How much heat is evolved when 10.0 g CCl₂F₂ is cooled from 40 °C to −40 °C?

94. Liquid ammonia, NH₃(ℓ), was used as a refrigerant fluid before the discovery of the chlorofluorocarbons and is still widely used today. Its normal boiling point is −33.4 °C, and its enthalpy of vaporization is 23.5 kJ/mol. The gas and liquid have specific heat capacities of 2.2 J g⁻¹ °K⁻¹ and 4.7 J g⁻¹ °K⁻¹, respectively. How much heat transfer is required to 10.0 kg liquid ammonia to raise its temperature from −50.0 °C to −33.4 °C, and then to 0.0 °C?

95. Potassium chloride and rubidium chloride both have the sodium chloride structure. X-ray diffraction experiments indicate that their cubic unit cell dimensions are 629 pm and 658 pm, respectively.

(i) One mol KCl and 1 mol RbCl are ground together in a mortar and pestle to a very fine powder, and the X-ray diffraction pattern of the pulverized solid is measured. Two patterns are observed, each corresponding to a cubic unit cell—one with an edge length of 629 pm and one with an edge length of 658 pm. Call this Sample 1.

(ii) One mol KCl and 1 mol RbCl are heated until the entire mixture is molten and then cooled to room temperature. A single X-ray diffraction pattern indicates a cubic unit cell with an edge length of roughly 640 pm. Call this Sample 2.

(a) Suppose that Samples 1 and 2 were analyzed for their chloride content. What fraction of each sample is chloride? Could the samples be distinguished by means of chemical analysis?

(b) Interpret the two X-ray diffraction results in terms of the structures of the crystal lattices of Samples 1 and 2.

(c) What chemical formula should you write for Sample 1? For Sample 2?

(d) Suppose that you dissolved 1.00 g Sample 1 in 100 mL water in a beaker and did the same with 1.00 g Sample 2. Which sample would conduct electricity better, or would both be the same? What ions would be present in each solution at what concentrations?

96. Sulfur dioxide, SO₂, is found in polluted air.

(a) What type of forces are responsible for binding SO₂ molecules to one another in the solid or liquid phase?

(b) Using the information below, place the compounds listed in order of increasing intermolecular attractions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Normal Boiling Point (°C)</th>
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<tbody>
<tr>
<td>SO₂</td>
<td>−10</td>
</tr>
<tr>
<td>NH₃</td>
<td>−33.4</td>
</tr>
<tr>
<td>CH₄</td>
<td>−161.5</td>
</tr>
<tr>
<td>H₂O</td>
<td>100</td>
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Applying Concepts

97. Refer to Figure 11.5 when answering these questions.

(a) What is the equilibrium vapor pressure for ethyl alcohol at room temperature?
(b) At what temperature does diethyl ether have an equilibrium vapor pressure of 400 mm Hg?
(c) If a pot of water were boiling at a temperature of 95 °C, what would be the atmospheric pressure?
(d) At 200 mm Hg and 60 °C, which of the three substances are gases?
(e) If you put a couple of drops of each substance on your hand, which would immediately evaporate, and which would remain as a liquid?
(f) Which of the three substances has the greatest intermolecular attractions?

98. The normal boiling point of SO\(_2\) is 263.1 K and that of NH\(_3\) is 239.7 K. At −40 °C, would you predict that ammonia has a vapor pressure greater than, less than, or equal to that of sulfur dioxide? Explain.

99. Butane is a gas at room temperature; however, if you look closely at a butane lighter you see it contains liquid butane. How is this possible?

100. While camping with a friend in the Rocky Mountains, you decide to cook macaroni for dinner. Your friend says the macaroni will cook faster in the Rockies because the lower atmospheric pressure will cause the water to boil at a lower temperature. Do you agree with your friend? Explain your reasoning.

101. Examine the nanoscale diagrams and the phase diagram below. Match each particulate diagram (1 through 7) to its corresponding point (A through H) on the phase diagram.

102. Consider the phase diagram below. Draw corresponding heating curves for \(T_1\) to \(T_2\) at pressures \(P_1\) and \(P_2\). Label each phase and phase change on your heating curves.

103. Consider three boxes of equal volume. One is filled with tennis balls, another with golf balls, and the third with marbles. If a closest-packing arrangement is used in each box, which one has the most occupied space? Which one has the least occupied space? (Disregard the difference in filling space at the walls, bottom, and top of the box.)

More Challenging Questions

104. If you get boiling water at 100 °C on your skin, it burns. If you get 100 °C steam on your skin, it burns much more severely. Explain why this is so.

105. If water at room temperature is placed in a flask that is connected to a vacuum pump and the vacuum pump then lowers the pressure in the flask, we observe that the volume of the water has decreased and the remaining water has turned into ice. Explain what has happened.

106. We hear reports from weather forecasters of ‘relative humidity,’ the ratio of the partial pressure of water in the air to the equilibrium vapor pressure of water at the same temperature. (The vapor pressure of water at 32.2 °C is 36 mm Hg.)

(a) On a sticky, humid day, the relative humidity may reach 90% with a temperature of 90 °F (32.2 °C). What is the partial pressure of water under these conditions? How many moles per liter are present in the air? How many water molecules per cm\(^3\) are present in such air?

(b) On a day in a desert, the relative humidity may be 5% with the same temperature of 90 °F. How many water molecules per cm\(^3\) are present in such air?
107. (a) In the diagram below, for a substance going from point F (initial state) to point G (final state), what changes in phase occur? (b) What does point A represent? (c) What does the curve from point A to point B represent?

108. Suppose that liquid A has stronger intermolecular forces than liquid B at room temperature. (a) Which substance will have the greater surface tension? (b) Which substance will have the greater vapor pressure? (c) Which substance will have the greater viscosity?

109. Use the vapor pressure curves shown in the figure below for methyl ethyl ether (CH\(_3\)OCH\(_2\)CH\(_3\)), carbon disulfide (CS\(_2\)), and benzene (C\(_6\)H\(_6\)) to answer the following questions. (a) What is the vapor pressure of methyl ethyl ether at 0 °C? (b) Which of these three liquids has the strongest intermolecular attractions? (c) At what temperature does benzene have a vapor pressure of 600 mm Hg? (d) What are the normal boiling points of these three liquids?

110. Will a closed container of water at 70 °C or an open container of water at the same temperature cool faster? Explain why.

111. Calculate the boiling point of water at 24 mm Hg. (The \(\Delta H_{\text{vap}}\) of water is 40.7 kJ/mol.)

112. What is the concentration in mol/L of water vapor in air at 25 °C at saturation?

113. Solid lithium has a body-centered cubic unit cell with the length of the edge of 351 pm at 20 °C. What is the density of lithium at this temperature?

114. Tungsten has a body-centered cubic unit cell and an atomic radius of 139 pm. What is the density of solid tungsten?

115. Copper is an important metal in the U.S. economy. Most of it is mined in the form of the mineral chalcopyrite, CuFeS\(_2\). (a) To obtain one metric ton (1000. kilograms) of copper metal, how many metric tons of chalcopyrite would you have to mine? (b) If the sulfur in chalcopyrite is converted to SO\(_2\), how many metric tons of the gas would you get from one metric ton of chalcopyrite? (c) Copper crystallizes as a face-centered cubic lattice. Knowing that the density of copper is 8.95 g/cm\(^3\), calculate the radius of the copper atom.

Conceptual Challenge Problems

CP11.A (Section 11.2) In Section 11.2 you read that the enthalpy of vaporization of water “is somewhat dependent on the temperature.” At 100 °C this value is 40.7 kJ/mol, but at 25 °C it is 44.0 kJ/mol, a difference of 3.3 kJ/mol. List four enthalpy changes whose sum would equal this difference. Remember, the sum of the changes for a cyclic process must be zero because the system is returned to its initial state.

CP11.B (Section 11.3) For what reasons would you propose that two of the substances listed in Table 11.2 be considered better refrigerants for use in household refrigerators than the others listed there?

CP11.C (Section 11.3) A table of enthalpies of sublimation is not given in Section 11.3, but the enthalpy of sublimation of ice at 0 °C is given as 51 kJ/mol. How was this value obtained? Tables 11.2 and 11.3 list the enthalpies of vaporization and fusion, respectively, for several substances. Determine from data in these tables the \(\Delta H_{\text{sub}}\) for ice. Using the same method, estimate the enthalpies of sublimation of HBr and HI at their melting points.