12 Intermolecular Forces: Liquids, Solids, and Phase Changes

Three Forms of One. Mist over a stream in winter completes this scene of the three phases of water. In this chapter we discuss the forces *between* molecules that give rise to the phases and phase changes.

Key Principles
to focus on while studying this chapter

- The relative magnitudes of the energy of motion *(kinetic)* of the particles and the energy of attraction *(potential)* among them determine whether a substance is a gas, a liquid, or a solid under a given set of conditions: in a gas, kinetic energy is much greater than potential energy; in a solid, the relative magnitudes are reversed. ***(Section 12.1)***
- The same factors determine changes of state *(vaporization–condensation, melting–freezing, sublimation–deposition),* and each type of change is associated with an enthalpy change that is positive in one direction and negative in the other. It takes more energy to convert a liquid to a gas than a solid to a liquid. ***(Section 12.1)***
- A *heating-cooling curve* shows the changes of state that occur when heat is added to or removed from a substance at a constant rate. Within a state *(phase)*, a change in temperature accompanies a change in heat (*kinetic energy*, that is, in molecular motion). A change in state *(phase change)* occurs at constant temperature and arises from a change in average interparticle distance, which relates to attractions *(potential energy)*. ***(Section 12.2)***
- In a closed system, a phase change is *reversible*, and the system reaches a state of *dynamic equilibrium.* As a liquid vaporizes in a closed container at a given temperature, the rates of vaporization and condensation become equal, so the pressure of the gas *(vapor pressure)* becomes constant. The vapor pressure increases with temperature and decreases with stronger intermolecular forces. The *Clausius-Clapeyron equation* relates vapor pressure to temperature. A *phase diagram* shows the range of pressure and temperature at which each phase is stable and at which phase changes occur. ***(Section 12.2)***
- Bonding forces are stronger than nonbonding forces. A charged region of one molecule attracts an oppositely charged region of another, and the strength of these *intermolecular forces* determines many physical properties. A charged region of one molecule can *induce* a region in another molecule to become charged, depending on the *polarizability* of the electron clouds. *Hydrogen bonding* requires an H atom bonded to N, O, or F; *dispersion forces* exist between all molecules. ***(Section 12.3)***
- Combinations of intermolecular forces determine the properties of liquids—*surface tension, capillarity*, and *viscosity.* ***(Section 12.4)***
- The physical properties of water—great solvent power, high specific heat capacity, high heat of vaporization, high surface tension, high capillarity, and lower density of the solid—emerge from its atomic and molecular properties and play vital roles in biology and the environment. ***(Section 12.5)***
- Crystalline solids consist of particles tightly packed into a regular array called a *lattice.* The simplest repeating portion of the lattice is the *unit cell.* Many substances crystallize in one of three *cubic* unit cells. These differ in the arrangement of the particles and, therefore, in the number of particles per unit cell and how efficiently they are packed. ***(Section 12.6)***
- The properties of five types of crystalline solids—*atomic, molecular, ionic, metallic,* and *network covalent*—depend on the type(s) of particles in the crystal and the resultant interparticle forces. ***(Section 12.6)***
- The *electron-sea model* explains that the properties of metals are due to highly *delocalized* valence electrons.
- *Band theory* explains many properties of metals *(conductors)*, metalloids *(semiconductors)*, and nonmetals *(insulators)* in terms of bands of overlapping molecular orbitals and the size of the *energy gap* between those filled with valence electrons and those that are unfilled.

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All the matter in and around you occurs in one or more of the three physical states—gas, liquid, or solid. Under different conditions, many substances can occur in any of the states. The three states were introduced in Chapter 1, and their properties were compared when we examined gases in Chapter 5. Now, we examine liquids and solids, which are called *condensed* states because, unlike in gases, their *particles are very close together*.

CONCEPTS & SKILLS TO REVIEW before studying this chapter

- properties of gases, liquids, and solids (Section 5.1)
- kinetic-molecular theory of gases (Section 5.5)
- kinetic and potential energy (Section 6.1)
- enthalpy change, heat capacity, and Hess's law (Sections 6.2, 6.3, and 6.5)
- diffraction of light (Section 7.1)
- Coulomb's law (Section 9.2)
- chemical bonding models (Chapter 9)
- molecular polarity (Section 10.3)
- molecular orbital treatment of diatomic molecules (Section 11.3)

12.1 • AN OVERVIEW OF PHYSICAL STATES AND PHASE CHANGES

Each physical state is called a **phase,** a physically distinct, homogeneous part of a system. The water in a closed container constitutes one phase; the water vapor above the liquid is a second phase; add some ice, and there are three.

In this section, you'll see that interactions between the potential energy and the kinetic energy of the particles give rise to the properties of each phase:

- The *potential energy*, in the form of **intermolecular forces** (or, more generally, *interparticle forces*), tends to draw the molecules together. According to Coulomb's law, the electrostatic potential energy depends on the charges of the particles and the distances between them (Section 9.2).
- The *kinetic energy* associated with the random motion of the molecules tends to disperse them. It is related to their average speed and is proportional to the absolute temperature (Section 5.5).

These interactions also explain **phase changes,** changes in physical state from one phase to another—liquid to solid, solid to gas, and so forth.

A Kinetic-Molecular View of the Three States Imagine yourself among the particles in any of the three states of water. Look closely and you'll discover two types of electrostatic forces at work:

1. *Intra*molecular (bonding) forces exist *within* each molecule. The *chemical* behavior of the three states is identical because each consists of the same bent, polar H—O—H molecules held together by identical covalent bonding forces.
2. *Inter*molecular (nonbonding) forces exist *between* the molecules. The *physical* behavior of the states is different because the strengths of these forces differ from state to state.

Whether a substance occurs as a gas, liquid, or solid depends on the interplay of the potential and kinetic energy:

- *In a gas,* the potential energy (energy of attraction) is small relative to the kinetic energy (energy of motion); thus, on average, the particles are far apart. This large distance has several macroscopic consequences: a gas fills its container, is highly compressible, and flows easily through another gas (Table 12.1).
- *In a liquid,* attractions are stronger because the particles are touching, but they have enough kinetic energy to move randomly around each other. Thus, a liquid conforms to the shape of its container but has a surface; it resists an applied force and thus compresses very slightly; and it flows, but *much* more slowly than gases.

Table 12.1 A Macroscopic Comparison of Gases, Liquids, and Solids

State	Shape and Volume	Compressibility	Ability to Flow
Gas	Conforms to shape and volume of container	High	High
Liquid	Conforms to shape of container; volume limited by surface	Very low	Moderate
Solid	Maintains its own shape and volume	Almost none	Almost none

- *In a solid,* the attractions dominate the motion so much that the particles are fixed in position relative to one another, just jiggling in place. Thus, a solid has its own shape, compresses even less than liquids, and does not flow significantly.

THINK OF IT THIS WAY

Environmental Flow

The environment provides a perfect demonstration of these differences in ability to flow. Atmospheric gases mix so well that the lowest 80 km of air has a uniform composition. Much less mixing in the oceans allows the composition at various depths to support different species. And rocks intermingle so little that adjacent strata remain separated for millions of years.

Types of Phase Changes and Their Enthalpies When we consider phase changes, understanding the effect of temperature is critical:

- As *temperature increases,* the average kinetic energy does too, so the faster moving particles overcome attractions more easily.
- As *temperature decreases,* particles slow, so attractions can pull them together.

Each phase change has a name and an associated enthalpy change:

1. *Gas to liquid, and vice versa.* As the temperature drops, the molecules in the gas phase come together and form a liquid in the process of **condensation;** the opposite process, changing from a liquid to a gas, is **vaporization.**

2. *Liquid to solid, and vice versa*. As the temperature drops further, the particles move slower and become fixed in position in the process of **freezing;** the opposite change is called **melting,** or **fusion.** In common speech, *freezing* implies low temperature because we think of water. But, molten metals, for example, freeze (solidify) at much higher temperatures and have medical, industrial, and artistic applications, such as gold dental crowns, steel auto bodies, and bronze statues.

3. *Gas to solid, and vice versa.* All three states of water are familiar because they are stable under ordinary conditions. Carbon dioxide, on the other hand, is familiar as a gas and a solid (dry ice), but liquid CO_2 occurs only at pressures of 5.1 atm or greater. At ordinary conditions, solid CO_2 changes directly to a gas, a process called **sublimation.** Freeze-dried foods are prepared by sublimation. The opposite process, changing from a gas directly into a solid, is called **deposition**—ice crystals form on a cold window from the deposition of water vapor.

The accompanying enthalpy changes are either exothermic or endothermic:

- *Exothermic changes*. As the molecules of a gas attract each other into a liquid, and then become fixed in a solid, the system of particles *loses* energy, which is released as heat. Thus, *condensing, freezing, and depositing are exothermic changes.*
- *Endothermic changes*. Heat must be absorbed by the system to overcome the attractive forces that keep the particles fixed in place in a solid or near each other in a liquid. Thus, *melting, vaporizing, and subliming are endothermic changes.*

Sweating has a cooling effect because heat from your body vaporizes the water. To achieve this cooling, cats lick themselves and dogs pant.

For a pure substance, each phase change is accompanied by a standard enthalpy change, given in units of *kilojoules per mole* (measured at 1 atm and the temperature of the change). For vaporization, it is the **heat** (or *enthalpy*) **of vaporization (ΔH°_{vap}),** and for fusion (melting), it is the **heat** (or *enthalpy*) **of fusion (ΔH°_{fus}).** In the case of water, we have

$$H_2O(l) \longrightarrow H_2O(g) \qquad \Delta H = \Delta H^\circ_{vap} = 40.7 \text{ kJ/mol (at } 100°\text{C)}$$
$$H_2O(s) \longrightarrow H_2O(l) \qquad \Delta H = \Delta H^\circ_{fus} = 6.02 \text{ kJ/mol (at } 0°\text{C)}$$

The reverse processes, condensing and freezing, have enthalpy changes of the *same magnitude but opposite sign:*

$$H_2O(g) \longrightarrow H_2O(l) \qquad \Delta H = -\Delta H^\circ_{vap} = -40.7 \text{ kJ/mol}$$
$$H_2O(l) \longrightarrow H_2O(s) \qquad \Delta H = -\Delta H^\circ_{fus} = -6.02 \text{ kJ/mol}$$

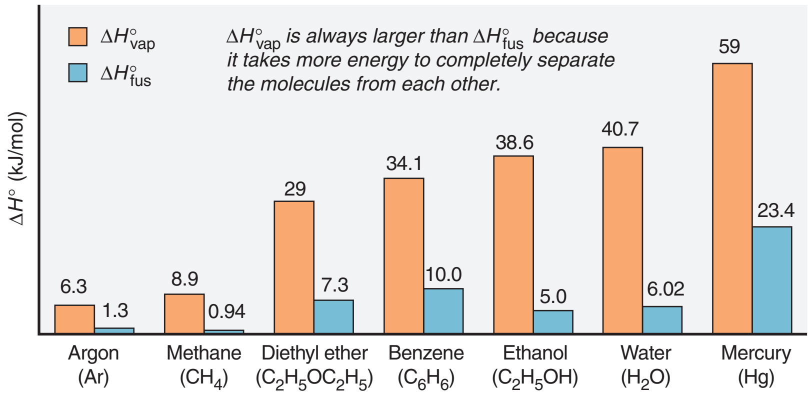


Figure 12.1 Heats of vaporization and fusion for several common substances.

Water behaves typically in that it takes much less energy to melt the solid than to vaporize the liquid: $\Delta H^\circ_{fus} < \Delta H^\circ_{vap}$; that is, it takes less energy to reduce the intermolecular forces enough for the molecules to move out of their fixed positions (melt a solid) than to separate them completely (vaporize a liquid) (Figure 12.1).

The **heat** (or *enthalpy*) **of sublimation** ($\boldsymbol{\Delta H^\circ_{subl}}$) is the enthalpy change when 1 mol of a substance sublimes, and the negative of this value is the change when 1 mol of the substance deposits. Since sublimation can be thought of as a combination of melting and vaporizing, Hess's law (Section 6.5) says that the heat of sublimation equals the sum of the heats of fusion and vaporization:

$$\begin{array}{lcl} \text{Solid} \longrightarrow \text{liquid} & & \Delta H^\circ_{fus} \\ \text{Liquid} \longrightarrow \text{gas} & & \Delta H^\circ_{vap} \\ \hline \text{Solid} \longrightarrow \text{gas} & & \Delta H^\circ_{subl} \end{array}$$

Figure 12.2 summarizes the phase changes and their enthalpy changes.

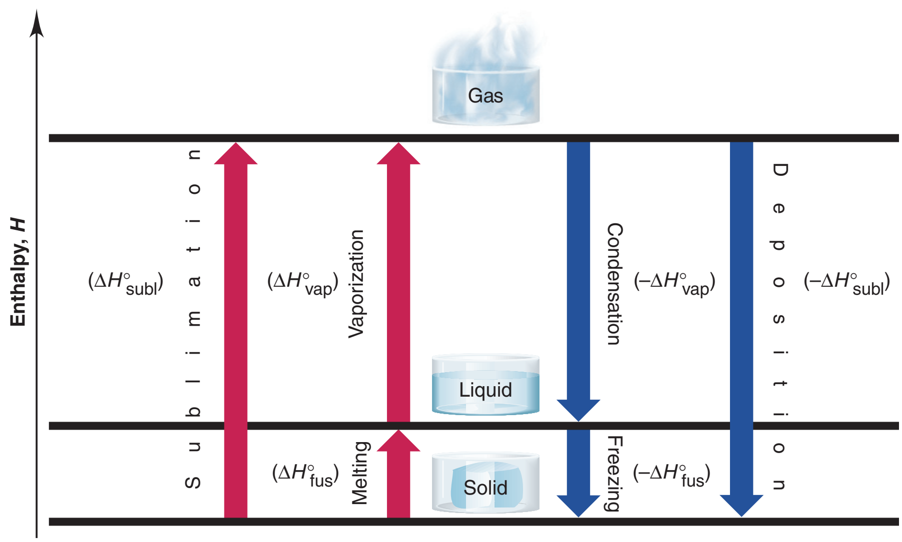


Figure 12.2 Phase changes and their enthalpy changes. Fusion (or melting), vaporization, and sublimation are endothermic changes (positive ΔH°), whereas freezing, condensation, and deposition are exothermic changes (negative ΔH°).

Summary of Section 12.1

- Because of the relative magnitudes of intermolecular forces (potential energy) and average speed (kinetic energy), the particles in a gas are far apart and moving randomly, those in a liquid are in contact and moving relative to each other, and those in a solid are in contact and in fixed positions. These molecular-level differences account for macroscopic differences in shape, compressibility, and ability to flow.
- When a solid becomes a liquid (melting, or fusion), a liquid becomes a gas (vaporization), or a solid becomes a gas (sublimation), energy is absorbed to overcome intermolecular forces and increase the average distance between particles. As particles come closer together in the reverse changes (freezing, condensation, and deposition), energy is released. Each phase change is associated with a given enthalpy change under specified conditions.

12.2 • QUANTITATIVE ASPECTS OF PHASE CHANGES

Many phase changes occur around you every day, accompanied by the release or absorption of heat. When it rains, water vapor has condensed to a liquid, which changes back to a gas as puddles dry up. In the spring, solid water melts, and in winter, it freezes again. And the same changes take place, but faster, whenever you make a pot of tea or a tray of ice cubes. In this section, we quantify the heat involved in a phase change and examine the equilibrium nature of the process.

Heat Involved in Phase Changes

We apply a kinetic-molecular approach to phase changes with a **heating-cooling curve,** which shows the changes in temperature of a sample when heat is absorbed or released at a constant rate. Let's examine what happens when 2.50 mol of gaseous water in a closed container undergoes a change from 130°C to −40°C at a constant pressure of 1 atm. We divide this process into five heat-releasing (exothermic) stages (Figure 12.3):

Stage 1. Gaseous water cools. Water molecules zoom chaotically at a range of speeds, smashing into each other and the container walls. At the starting temperature, the most probable speed of the molecules, and thus their average kinetic energy (E_k), is high enough to overcome the potential energy (E_p) of attractions. As the temperature falls, the average E_k decreases and attractions become more important. The change is

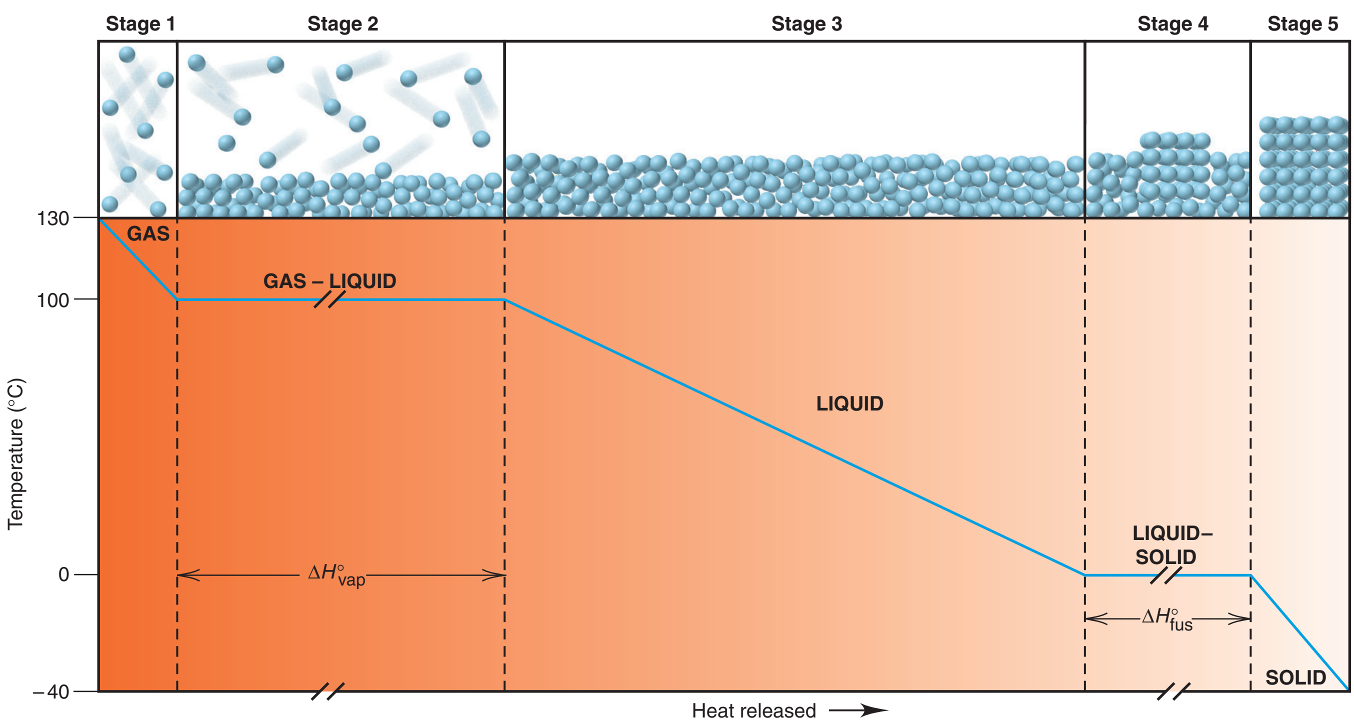
$$H_2O(g)\ [130°C] \longrightarrow H_2O(g)\ [100°C]$$

The heat (q) is the product of the amount (number of moles, n) of water, the molar heat capacity of *gaseous* water, $C_{water(g)}$, and the temperature change during this step, ΔT ($T_{final} - T_{initial}$):

$$q = n \times C_{water(g)} \times \Delta T = (2.50\ \text{mol})\ (33.1\ \text{J/mol·°C})\ (100°C - 130°C)$$
$$= -2482\ \text{J} = -2.48\ \text{kJ}$$

The minus sign indicates that heat is released. (For purposes of canceling, the units for molar heat capacity, C, include °C, rather than K, but this doesn't affect the magnitude of C because these two units represent the same temperature increment.)

Figure 12.3 A cooling curve for the conversion of gaseous water to ice. A plot of temperature vs. heat released as gaseous water changes to ice is shown, with a molecular-level depiction for each stage. The slopes of the lines in stages 1, 3, and 5 reflect the molar heat capacities of the phases. Although not drawn to scale, the line in stage 2 is longer than the line in stage 4 because $\Delta H°_{vap}$ of water is greater than $\Delta H°_{fus}$. A plot of temperature vs. heat absorbed starting at −40°C would have the same stages but in reverse order.



Stage 2. Gaseous water condenses. At the condensation point, intermolecular attractions cause the slowest of the molecules to aggregate into microdroplets and then a bulk liquid. Note that, during the phase change,

- The temperature of the sample, and thus its average E_k, is constant. At the same temperature, molecules move farther between collisions in a gas than in a liquid, but their *average* speed is the same.
- Releasing heat from the sample decreases the average E_p as the molecules approach each other.

Thus, at 100°C, gaseous and liquid water have the same average E_k, but the liquid has lower average E_p. The change is

$$H_2O(g)\,[100°C] \longrightarrow H_2O(l)\,[100°C]$$

The heat is the amount (n) times the negative of the heat of vaporization ($-\Delta H^\circ_{vap}$):

$$q = n(-\Delta H^\circ_{vap}) = (2.50\text{ mol})(-40.7\text{ kJ/mol}) = -102\text{ kJ}$$

This stage contributes the *greatest portion of the total heat released* because of the large decrease in E_p as the molecules become so much closer in the liquid than they were in the gas.

Stage 3. Liquid water cools. The molecules in the liquid state continue to lose heat, which appears as a decrease in temperature, that is, as a decrease in the most probable molecular speed and, thus, the average E_k. The temperature decreases as long as the sample remains liquid. The change is

$$H_2O(l)\,[100°C] \longrightarrow H_2O(l)\,[0°C]$$

The heat depends on amount (n), the molar heat capacity of *liquid* water, and ΔT:

$$q = n \times C_{water(l)} \times \Delta T = (2.50\text{ mol})(75.4\text{ J/mol·°C})(0°C - 100°C)$$
$$= -18{,}850\text{ J} = -18.8\text{ kJ}$$

Stage 4. Liquid water freezes. At 0°C, the sample loses E_p as increasing intermolecular attractions cause the molecules to align themselves into the crystalline structure of ice. Molecular motion continues only as random jiggling about fixed positions. As we saw during condensation, temperature and average E_k are constant during freezing. The change is

$$H_2O(l)\,[0°C] \longrightarrow H_2O(s)\,[0°C]$$

The heat is equal to n times the negative of the heat of fusion ($-\Delta H^\circ_{fus}$):

$$q = n(-\Delta H^\circ_{fus}) = (2.50\text{ mol})(-6.02\text{ kJ/mol}) = -15.0\text{ kJ}$$

Stage 5. Solid water cools. With motion restricted to jiggling in place, further cooling merely reduces the average speed of this jiggling. The change is

$$H_2O(s)\,[0°C] \longrightarrow H_2O(s)\,[-40°C]$$

The heat depends on n, the molar heat capacity of *solid* water, and ΔT:

$$q = n \times C_{water(s)} \times \Delta T = (2.50\text{ mol})(37.6\text{ J/mol·°C})(-40°C - 0°C)$$
$$= -3760\text{ J} = -3.76\text{ kJ}$$

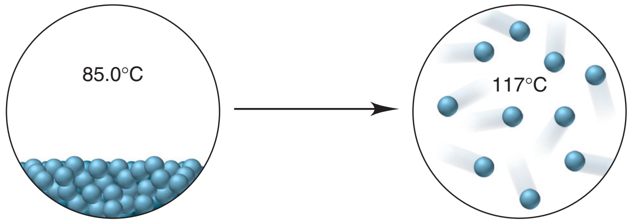
According to Hess's law, the total heat released is the sum of the heats released for the individual stages. The sum of q for stages 1 to 5 is -142 kJ. Two key points stand out for this or any similar process, whether exothermic or endothermic:

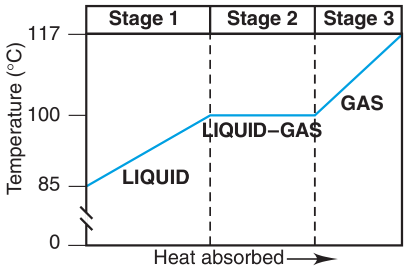
- *Within a phase,* heat flow is accompanied by *a change in temperature,* which is associated with a change in average E_k as *the most probable speed of the molecules changes.* The heat released or absorbed depends on the amount of substance, the molar heat capacity *for that phase,* and the change in temperature.
- *During a phase change,* heat flow occurs at a *constant temperature,* which is associated with a change in average E_p as *the average distance between molecules changes.* Both phases are present and (as you'll see below) are in equilibrium during the change. The heat released or absorbed depends on the amount of substance and the enthalpy change for that phase change.

Let's work a molecular-scene sample problem to make sure these ideas are clear.

Sample Problem 12.1 Finding the Heat of a Phase Change Depicted by Molecular Scenes

Problem The scenes below represent a phase change of water. Select data from the previous discussion to find the heat (in kJ) released or absorbed when 24.3 g of H_2O undergoes this change.





Plan From the molecular scenes, data in the text, and the given mass (24.3 g) of water, we have to find the heat that accompanies this change. The scenes show a disorderly, condensed phase at 85.0°C changing to separate molecules at 117°C. Thus, the phase change they depict is vaporization, an endothermic process. The text data are given per mole, so we first convert the mass (g) of water to amount (mol). There are three stages: (1) heating the liquid from 85.0°C to 100.°C, (2) converting liquid water at 100.°C to gaseous water at 100.°C, and (3) heating the gas from 100.°C to 117°C *(see margin)*. We add the values of q for these stages to obtain the total heat.

Solution Converting from mass (g) of H_2O to amount (mol):

$$\text{Amount (mol) of } H_2O = 24.3 \text{ g } H_2O \times \frac{1 \text{ mol}}{18.02 \text{ g } H_2O} = 1.35 \text{ mol}$$

Finding the heat accompanying stage 1, $H_2O(l)\,[85.0°C] \longrightarrow H_2O(l)\,[100.°C]$:

$$q = n \times C_{\text{water}(l)} \times \Delta T = (1.35 \text{ mol})(75.4 \text{ J/mol·°C})(100.°C - 85.0°C)$$
$$= 1527 \text{ J} = 1.53 \text{ kJ}$$

Finding the heat accompanying stage 2, $H_2O(l)\,[100.°C] \longrightarrow H_2O(g)\,[100.°C]$:

$$q = n(\Delta H^\circ_{\text{vap}}) = (1.35 \text{ mol})(40.7 \text{ kJ/mol}) = 54.9 \text{ kJ}$$

Finding the heat accompanying stage 3, $H_2O(g)\,[100.°C] \longrightarrow H_2O(g)\,[117°C]$:

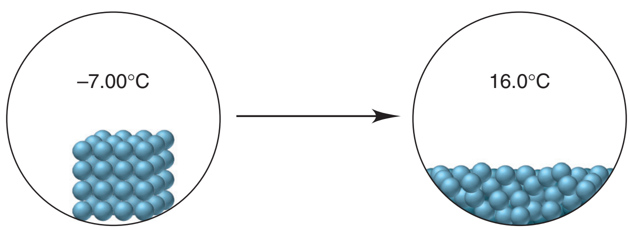
$$q = n \times C_{\text{water}(g)} \times \Delta T = (1.35 \text{ mol})(33.1 \text{ J/mol·°C})(117°C - 100.°C)$$
$$= 759.6 \text{ J} = 0.760 \text{ kJ}$$

Adding the three heats together to find the total heat of the process:

$$\text{Total heat (kJ)} = 1.53 \text{ kJ} + 54.9 \text{ kJ} + 0.760 \text{ kJ} = \boxed{57.2 \text{ kJ}}$$

Check The heat should have a positive value because it is absorbed. Be sure to round to check each value of q; for example, in stage 1, 1.33 mol × 75 J/mol·°C × 15°C = 1500 J. Note that the phase change itself (stage 2) requires the most energy and, thus, dominates the final answer. The $\Delta H^\circ_{\text{vap}}$ units include kJ, whereas the molar heat capacity units include J, which is a thousandth as large.

FOLLOW-UP PROBLEM 12.1 The scenes below represent a phase change of water. Select data from the text discussion to find the heat (in kJ) released or absorbed when 2.25 mol of H_2O undergoes this change.



The Equilibrium Nature of Phase Changes

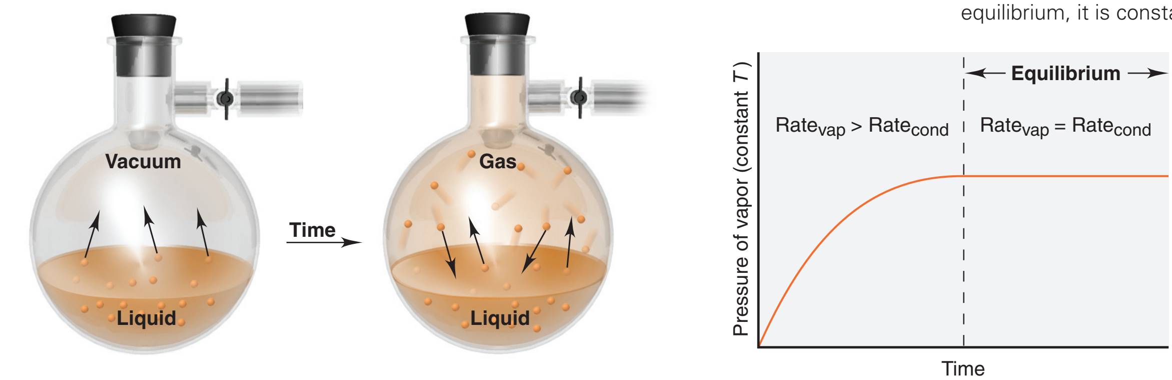
In everyday experience, phase changes take place in *open* containers—the outdoors, a pot on a stove, the freezer compartment of a refrigerator—so they are not reversible. But, in a *closed* container, *phase changes* ***are*** *reversible and reach equilibrium,* just as chemical changes do. In this discussion, we examine the three phase equilibria.

Liquid-Gas Equilibria Vaporization and condensation are familiar events. Let's see how these processes differ in open and closed systems of a liquid in a flask:

1. *Open system: nonequilibrium process*. Picture an *open* flask containing a pure liquid at constant temperature. Within their range of speeds, some molecules at the surface have a high enough E_k to overcome attractions and vaporize. Nearby molecules fill the gap, and with heat supplied by the constant-temperature surroundings, the process continues until the entire liquid phase is gone.

2. *Closed system: equilibrium process*. Now picture a *closed* flask at constant temperature and assume a vacuum exists above a liquid (Figure 12.4A). Two processes take place: Some molecules at the surface have a high enough E_k to *vaporize*. After a short time, molecules in the vapor collide with the surface, and the slower ones are attracted strongly enough to *condense.*

At first, these two processes occur at different rates. The number of molecules in a given surface area is constant, so the number of molecules leaving the surface per unit time—the rate of vaporization—is also constant, and the pressure increases. With time, the number of molecules colliding with and entering the surface—the rate of condensation—increases as the vapor becomes more populated, so the increase in pressure slows. Eventually, the rate of condensation equals the rate of vaporization; from this time onward, *the pressure is constant* (Figure 12.4B).



A Molecules in the liquid vaporize. **B** Molecules vaporize and condense at the same rate. **C** Plot of pressure vs. time.

Figure 12.4 Liquid-gas equilibrium. **A,** Molecules leave the surface at a constant rate and the pressure rises. **B,** At equilibrium, the same number of molecules leave and enter the liquid in a given time. **C,** Pressure increases until, at equilibrium, it is constant.

Macroscopically, the situation at this point seems static, but at the molecular level, molecules are entering and leaving the liquid at equal rates. The system has reached a state of **dynamic equilibrium:**

$$\text{liquid} \rightleftharpoons \text{gas}$$

The pressure exerted by the vapor at equilibrium is called the *equilibrium vapor pressure,* or just the **vapor pressure,** of the liquid at that temperature. Figure 12.4C depicts the entire process graphically. (In later chapters, beginning with Chapter 17, you'll see that reactions also reach a state of equilibrium, in which reactants are changing into products and products into reactants at the same rate. Thus, the yield of product becomes constant, and no further changes in concentration occur.)

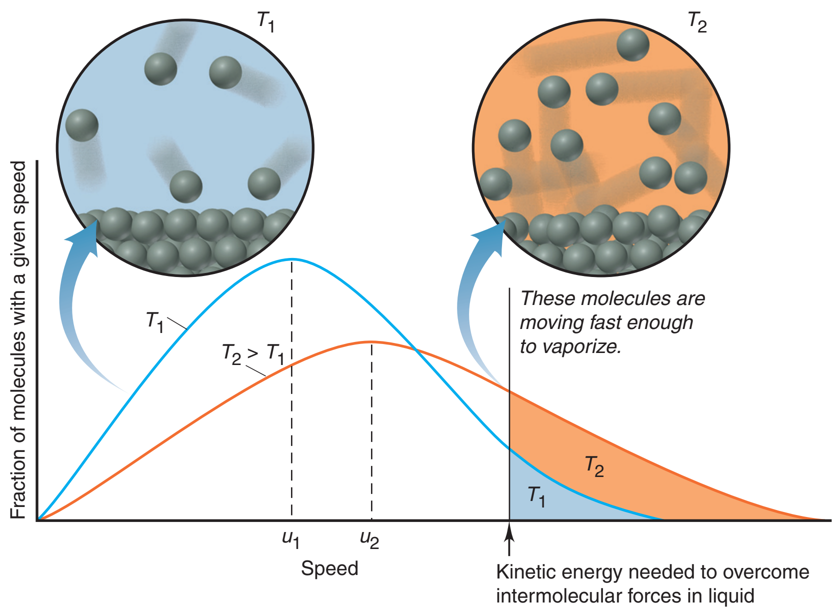
The Effects of Temperature and Intermolecular Forces on Vapor Pressure

The vapor pressure is affected by two factors—a change in temperature and a change in the gas itself, that is, in the type and/or strength of intermolecular forces:

1. *Effect of temperature*. Temperature has a major effect on vapor pressure because it changes the fraction of molecules moving fast enough to escape the liquid and, by the same token, the fraction moving slowly enough to be recaptured (Figure 12.5; see also Figure 5.5). At the higher temperature, T_2, more molecules have enough energy to leave the surface. Thus, in general, *the higher the temperature is, the higher the vapor pressure:*

$$\text{higher } T \Longrightarrow \text{higher } P$$

Figure 12.5 The effect of temperature on the distribution of molecular speeds.



2. *Effect of intermolecular forces*. At a given *T*, all substances have the same average E_k. Therefore, molecules with weaker intermolecular forces are held less tightly at the surface and vaporize more easily. In general, *the weaker the intermolecular forces are, the higher the vapor pressure:*

$$\text{weaker forces} \Longrightarrow \text{higher } P$$

Figure 12.6 shows the vapor pressure of three liquids as a function of temperature:

- The effect of temperature is seen in the steeper rise as the temperature increases.
- The effect of intermolecular forces is seen in the values of the vapor pressure, the short, horizontal dashed lines intersecting the vertical (pressure) axis at a given temperature *(vertical dashed line at 20°C):* the intermolecular forces in diethyl ether (highest vapor pressure) are weaker than those in ethanol, which are weaker than those in water (lowest vapor pressure).

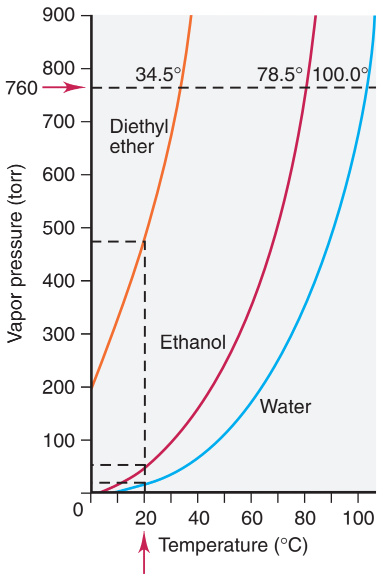


Figure 12.6 Vapor pressure as a function of temperature and intermolecular forces.

Quantifying the Effect of Temperature The nonlinear relationship between *P* and *T* is converted to a linear one with the **Clausius-Clapeyron equation:**

$$\ln P = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C$$
$$y \quad = \quad m \quad x \quad + b$$

where ln *P* is the natural logarithm of the vapor pressure, ΔH_{vap} is the heat of vaporization, *R* is the universal gas constant (8.314 J/mol·K), *T* is the absolute temperature, and *C* is a constant (not related to heat capacity). The equation is often used to find the heat of vaporization. The equation for a straight line is shown under it in blue, with $y = \ln P$, $x = 1/T$, *m* (the slope) $= -\Delta H_{vap}/R$, and *b* (the *y*-axis intercept) $= C$.

A plot of ln P vs. $1/T$ gives a straight line, as shown for diethyl ether and water in Figure 12.7.

A two-point version of the Clausius-Clapeyron equation allows us to calculate ΔH_{vap} if the vapor pressures at two temperatures are known:

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \textbf{(12.1)}$$

If ΔH_{vap} and P_1 at T_1 are known, we can also calculate the vapor pressure (P_2) at any other temperature (T_2) or the temperature at any other pressure.

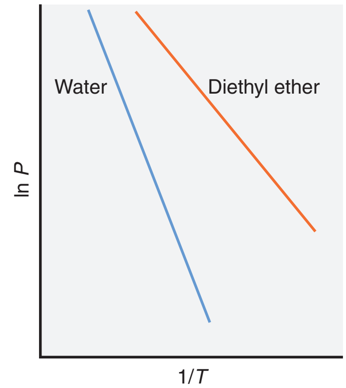


Figure 12.7 **Linear plots of the relationship between vapor pressure and temperature.** The slope is steeper for water because its ΔH_{vap} is greater.

Sample Problem 12.2 Applying the Clausius-Clapeyron Equation

Problem The vapor pressure of ethanol is 115 torr at 34.9°C. If ΔH_{vap} of ethanol is 38.6 kJ/mol, calculate the temperature (in °C) when the vapor pressure is 760 torr.

Plan We are given ΔH_{vap}, P_1, P_2, and T_1 and substitute them into Equation 12.1 to solve for T_2. The value of R here is 8.314 J/mol·K, so we must convert T_1 to K to obtain T_2, and then convert T_2 back to °C.

Solution Substituting the values into Equation 12.1 and solving for T_2:

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

$$T_1 = 34.9°\text{C} + 273.15 = 308.0\ \text{K}$$

$$\ln \frac{760\ \text{torr}}{115\ \text{torr}} = \left(-\frac{38.6\times10^3\ \text{J/mol}}{8.314\ \text{J/mol·K}}\right)\left(\frac{1}{T_2} - \frac{1}{308.0\ \text{K}}\right)$$

$$1.888 = (-4.64\times10^3)\left[\frac{1}{T_2} - (3.247\times10^{-3})\right]$$

$$T_2 = 352\ \text{K}$$

Converting T_2 from K to °C:

$$T_2 = 352\ \text{K} - 273.15 = \boxed{79°\text{C}}$$

Check Round off to check the math. The change is in the right direction: higher P should occur at higher T. As we discuss next, a substance has a vapor pressure of 760 torr at its *normal boiling point.* Checking the *CRC Handbook of Chemistry and Physics* shows that the boiling point of ethanol is 78.5°C, very close to our answer.

FOLLOW-UP PROBLEM 12.2 At 34.1°C, the vapor pressure of water is 40.1 torr. What is the vapor pressure at 85.5°C? The ΔH_{vap} of water is 40.7 kJ/mol.

Vapor Pressure and Boiling Point Let's discuss what is happening when a liquid boils and then see the effect of pressure on boiling point.

1. *How a liquid boils.* In an *open* container, the weight of the atmosphere bears down on a liquid surface. As the temperature rises, molecules move more quickly throughout the liquid. At some temperature, the average E_k of the molecules in the liquid is great enough for them to form bubbles of vapor *in the interior,* and the liquid boils. At any lower temperature, the bubbles collapse as soon as they start to form because the external pressure is greater than the vapor pressure inside the bubbles. Thus, the **boiling point** *is the temperature at which the vapor pressure equals the external pressure,* which is usually that of the atmosphere. As in condensation and freezing, once boiling begins, the temperature of the liquid remains constant until all of the liquid is gone.

2. *Effect of pressure on boiling point.* The boiling point of a liquid varies with elevation. At high elevations, a lower atmospheric pressure is exerted on the liquid surface, so molecules in the interior need less kinetic energy to form bubbles. Thus, *the boiling point depends on the applied pressure.*

In mountainous regions, food takes *more* time to cook because the boiling point is lower and the boiling liquid is not as hot; for instance, in Boulder, Colorado (elevation 5430 ft, or 1655 m), water boils at 94°C. On the other hand, in a pressure cooker, food takes *less* time to cook because the boiling point is higher at the higher pressure. The *normal boiling point* is observed at standard atmospheric pressure (760 torr, or 101.3 kPa; *long, horizontal dashed line* in Figure 12.6).

Solid-Liquid Equilibria The particles in a crystal are continually jiggling about their fixed positions. As the temperature rises, the particles jiggle more vigorously, until some have enough kinetic energy to break free of their positions. At this point, melting begins. As more molecules enter the liquid (molten) phase, some collide with the solid and become fixed in position again. Because the phases remain in contact, a dynamic equilibrium is established when the melting rate equals the freezing rate. The temperature at which this occurs is called the **melting point.** The temperature remains fixed at the melting point until all the solid melts.

Because liquids and solids are nearly incompressible, pressure has little effect on the rates of melting and freezing: a plot of pressure vs. temperature for a solid-liquid phase change is typically a *nearly* vertical straight line.

Solid-Gas Equilibria Sublimation is not very familiar because solids have *much* lower vapor pressures than liquids. A substance sublimes rather than melts because the intermolecular attractions are not great enough to keep the molecules near each other when they leave the solid state. Some solids *do* have high enough vapor pressures to sublime at ordinary conditions, including dry ice (carbon dioxide), solid iodine, and moth repellants, all nonpolar molecules with weak intermolecular forces.

The plot of pressure vs. temperature for a solid-gas phase change reflects the large effect of temperature on vapor pressure; thus, it resembles the liquid-gas curve in rising steeply with higher temperatures.

Phase Diagrams: Effect of Pressure and Temperature on Physical State

The **phase diagram** of a substance combines the liquid-gas, solid-liquid, and solid-gas curves and gives the conditions of temperature and pressure at which each phase is stable and where phase changes occur.

The Phase Diagram for CO_2 and Most Substances The diagram for CO_2, which is typical of most substances, has four general features (Figure 12.8A):

1. *Regions of the diagram.* Each region presents the conditions of pressure and temperature for which the phase is stable. If another phase is placed under those conditions, it will change to the stable phase. In general, the solid is stable at low temperature and high pressure, the gas at high temperature and low pressure, and the liquid at intermediate conditions.

2. *Lines between regions.* The lines are the phase-transition curves discussed earlier. Any point along a line shows the pressure and temperature at which the phases are in equilibrium. The solid-liquid line has a slightly *positive* slope (slants to the *right* with increasing pressure) because, for most substances, the solid is more dense than the liquid: an increase in pressure converts the liquid to the solid. (Water is *the* major exception.)

3. *The triple point.* The three phase-transition curves meet at the **triple point,** at which all three phases are in equilibrium. As strange as it sounds, at the triple point in Figure 12.8A, CO_2 is subliming and depositing, melting and freezing, and vaporizing and condensing simultaneously! Substances with several solid and/or liquid forms can have more than one triple point.

The CO_2 phase diagram shows why dry ice (solid CO_2) doesn't melt under ordinary conditions. The triple-point pressure is 5.1 atm, so liquid CO_2 doesn't occur at 1 atm because it is not stable. The horizontal dashed line at 1.0 atm crosses the solid-gas line, so when solid CO_2 is heated, it sublimes at −78°C rather than melts. If our normal atmospheric pressure were 5.2 atm, liquid CO_2 *would* occur.

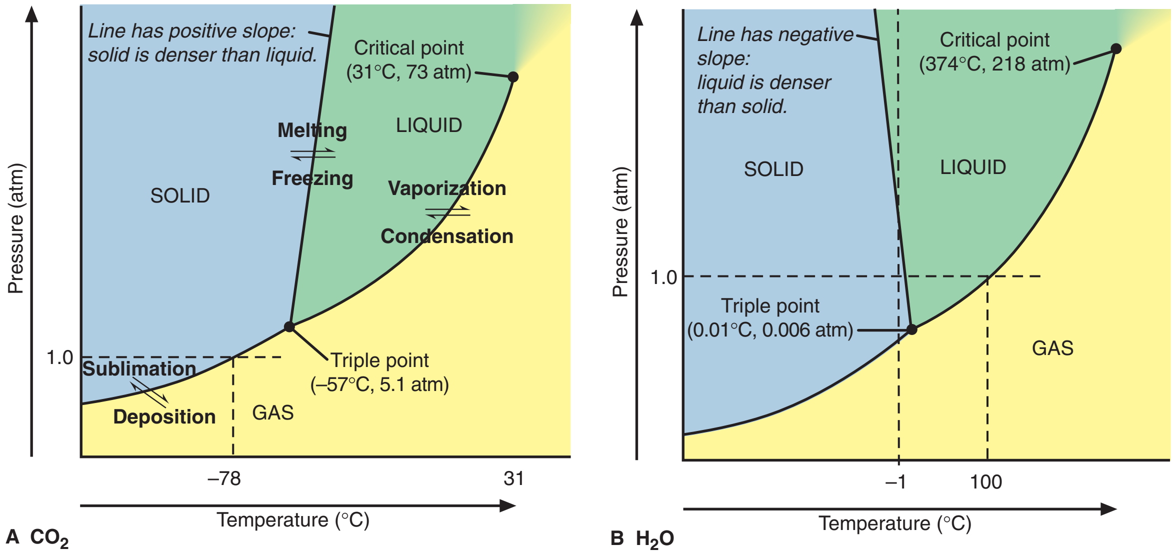


Figure 12.8 Phase diagrams for CO_2 and H_2O. (The slope of each solid-liquid line is exaggerated, and the axes are not linear.)

4. *The critical point.* Heat a liquid in a closed container and its density decreases. At the same time, more of the liquid vaporizes, so the density of the vapor increases. At the **critical point,** the two densities become equal and the phase boundary disappears. The temperature at the critical point is the *critical temperature* (T_c), and the pressure is the *critical pressure* (P_c). The average E_k is so high at this point that the vapor cannot be condensed at any pressure. The two most common gases in air have critical temperatures far below room temperature: O_2 cannot be condensed above −119°C, and N_2 above −147°C.

The Solid-Liquid Line for Water The phase diagram for water has the same four features but differs from others in one major respect that reveals a key property. Unlike almost any other substance, the solid form is *less dense* than the liquid; that is, *water expands upon freezing*. Thus, the solid-liquid line has a *negative* slope (slants to the *left* with increasing pressure): an increase in pressure converts the solid to the liquid, and the higher the pressure, the lower the temperature at which water freezes (Figure 12.8B). The vertical dashed line at −1°C crosses the solid-liquid line, which means that ice melts with only an increase in pressure.

The triple point of water occurs at low pressure (0.006 atm). Therefore, when solid water is heated at 1.0 atm *(horizontal dashed line),* the solid-liquid line is crossed at 0°C, the normal melting point. Thus, ice melts rather than sublimes. The horizontal dashed line then crosses the liquid-gas curve at 100°C, the normal boiling point.

Summary of Section 12.2

- A heating-cooling curve depicts the change in temperature when a substance absorbs or releases heat at a constant rate. Within a phase, temperature (and average E_k) changes. During a phase change, temperature (and average E_k) is constant, but E_p changes. The total enthalpy change for the system is found using Hess's law.
- In a closed container, the liquid and gas phases of a substance reach equilibrium. The vapor pressure, the pressure of the gas at equilibrium, is related directly to temperature and inversely to the strength of the intermolecular forces.
- The Clausius-Clapeyron equation relates the vapor pressure to the temperature and is often used to find ΔH_{vap}.
- A liquid in an open container boils when its vapor pressure equals the external pressure.
- Solid-liquid equilibrium occurs at the melting point. Some solids sublime because they have very weak intermolecular forces.
- The phase diagram of a substance shows the phase that is stable at any P and T, the conditions at which phase changes occur, and the conditions at the critical point and the triple point. Water differs from most substances in that its solid phase is less dense than its liquid phase, so its solid-liquid line has a negative slope.

12.3 • TYPES OF INTERMOLECULAR FORCES

In Chapter 9, we saw that bonding (*intra*molecular) forces are due to the attraction between cations and anions (ionic bonding) or between nuclei and electron pairs (covalent bonding). But the physical behavior of the phases and their changes are due primarily to *inter*molecular (nonbonding) forces, which arise from the attraction *between* molecules with partial charges or between ions and molecules. Coulomb's law explains why the two types of forces differ so much in magnitude:

- *Bonding forces are relatively strong* because larger charges are closer together.
- *Intermolecular forces are relatively weak* because smaller charges are farther apart.

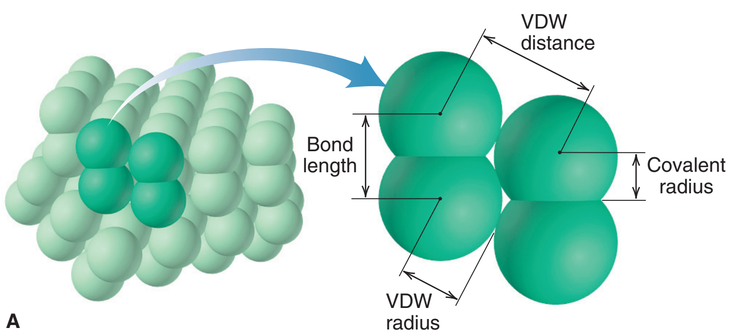
How Close Can Molecules Approach Each Other?

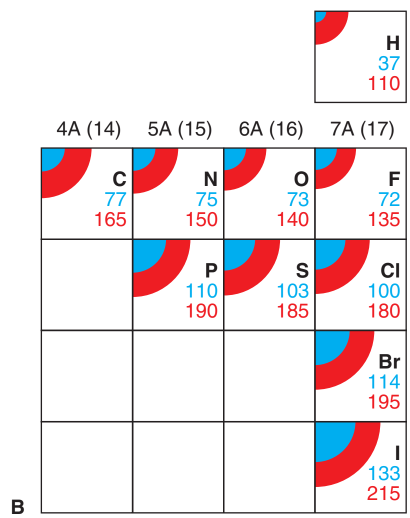
Because intermolecular forces arise from molecules being close but not bonding, we'd like to know how close molecules can get to each other. To see the minimum distance *between* molecules, consider solid Cl_2. When we measure the distances between two Cl nuclei, we obtain two different values (Figure 12.9A):

- *Bond length and covalent radius*. The shorter distance, called the *bond length,* is between *two bonded Cl atoms in the* ***same*** *molecule*. One-half this distance is the *covalent radius*.
- *Van der Waals distance and radius*. The longer distance is between *two nonbonded Cl atoms in* ***adjacent*** *molecules*. It is called the *van der Waals (VDW) distance*. At this distance, intermolecular attractions balance electron-cloud repulsions; thus, the VDW distance is as close as one Cl_2 molecule can approach another. The **van der Waals radius** is one-half the closest distance between nuclei of identical *nonbonded* atoms. The VDW radius of an atom is *always larger than its covalent radius.* Like covalent radii, VDW radii decrease across a period and increase down a group (Figure 12.9B).

As we discuss intermolecular forces (also called *van der Waals forces*), consult Table 12.2, which compares them with bonding forces.

Figure 12.9 Covalent and van der Waals radii and their periodic trends. **A,** The van der Waals (VDW) radius is one-half the distance between adjacent *nonbonded* atoms ($\frac{1}{2}$ × VDW distance). **B,** Like covalent radii *(blue quarter-circles and numbers),* VDW radii *(red quarter-circles and numbers)* increase down a group and decrease across a period.

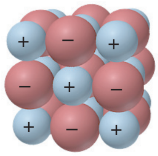
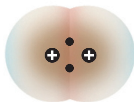
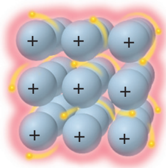
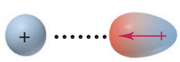
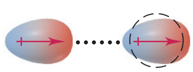
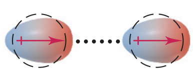




Ion-Dipole Forces

When an ion and a nearby polar molecule (dipole) attract each other, an **ion-dipole force** results. The most important example takes place when an ionic compound dissolves in water. The ions become separated because the attractions between the ions and the oppositely charged poles of the H_2O molecules are stronger than the attractions between the ions themselves. Ion-dipole forces in solutions and their associated energy are discussed fully in Chapter 13.

Table 12.2 Comparison of Bonding and Nonbonding (Intermolecular) Forces

Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Bonding				
Ionic		Cation–anion	400–4000	NaCl
Covalent		Nuclei–shared e^- pair	150–1100	H—H
Metallic		Cations–delocalized electrons	75–1000	Fe
Nonbonding (Intermolecular)				
Ion-dipole		Ion charge–dipole charge	40–600	$Na^{+}\cdots O{\genfrac{}{}{0pt}{}{H}{H}}$
H bond	$-\overset{\delta-}{A}-\overset{\delta+}{H}\cdots\cdots:\overset{\delta-}{B}-$	Polar bond to H–dipole charge (high EN of N, O, F)	10–40	$:\underset{H}{\underset{\vert}{\ddot{O}}}-H\cdots:\underset{H}{\underset{\vert}{\ddot{O}}}-H$
Dipole-dipole		Dipole charges	5–25	I—Cl···I—Cl
Ion–induced dipole		Ion charge–polarizable e^- cloud	3–15	$Fe^{2+}\cdots O_2$
Dipole–induced dipole		Dipole charge–polarizable e^- cloud	2–10	H—Cl···Cl—Cl
Dispersion (London)		Polarizable e^- cloud	0.05–40	F—F···F—F

Dipole-Dipole Forces

In Figure 10.11, you saw that an external electric field orients gaseous polar molecules. The polar molecules in liquids and solids lie near each other, and their partial charges act as tiny electric fields that give rise to **dipole-dipole forces:** the positive pole of one molecule attracts the negative pole of another (Figure 12.10). The orientation is more orderly in a solid than in a liquid because the average kinetic energy is lower.

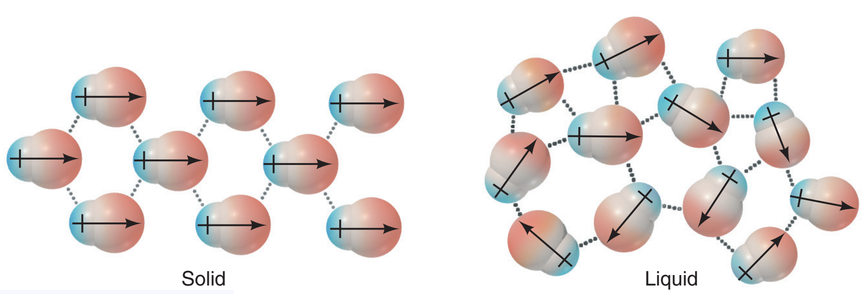


Figure 12.10 Polar molecules and dipole-dipole forces. (Spaces between the molecules are exaggerated.)

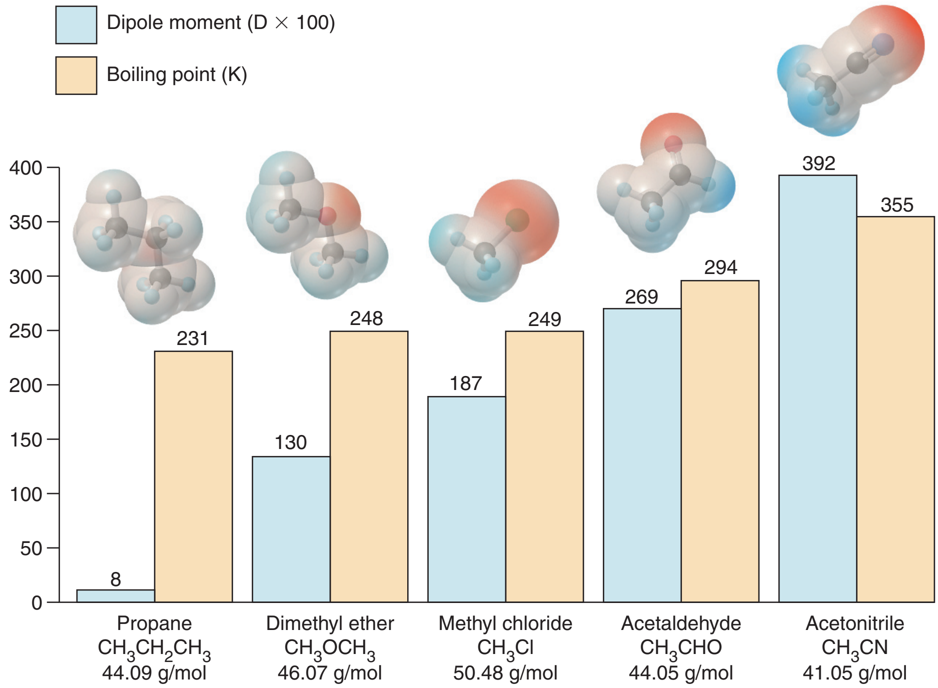
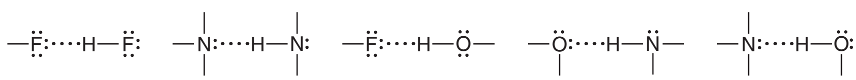


Figure 12.11 **Dipole moment and boiling point.** (Relative strength of the dipole moments is indicated by color intensities in the electron-density models.)

These forces depend on the magnitude of the molecular dipole moment. For compounds of similar molar mass, the greater the dipole moment, the greater the dipole-dipole forces, so the more energy it takes to separate the molecules; thus the boiling point is higher. Methyl chloride, for instance, has a smaller dipole moment than acetaldehyde and boils at a lower temperature (Figure 12.11).

The Hydrogen Bond

A special type of dipole-dipole force arises between molecules that have *an H atom bonded to a small, highly electronegative atom with lone electron pairs, specifically N, O, or F*. The basis of this force is that the H—N, H—O, and H—F bonds are very polar. When the partially positive H of one molecule is attracted to the partially negative lone pair on the N, O, or F of another molecule, a **hydrogen bond (H bond)** forms. Thus, the atom sequence of an H bond (dotted line) is —B:····H—A—, where A *and* B are N, O, or F. Some examples are



The first two are found in samples of pure HF and NH_3.

The small sizes of N, O, and F are essential to H bonding for two reasons:

1. The atoms are so electronegative that their covalently bonded H is highly positive.
2. The lone pair on the N, O, or F of the other molecule can come close to the H.

The Significance of Hydrogen Bonding Hydrogen bonding has a profound impact in many systems. We'll examine one effect on physical properties. Figure 12.12 shows the effect of H bonding on the boiling points of the binary hydrides of Groups 4A(14) through 7A(17). For reasons we'll discuss shortly, boiling points rise with molar mass,

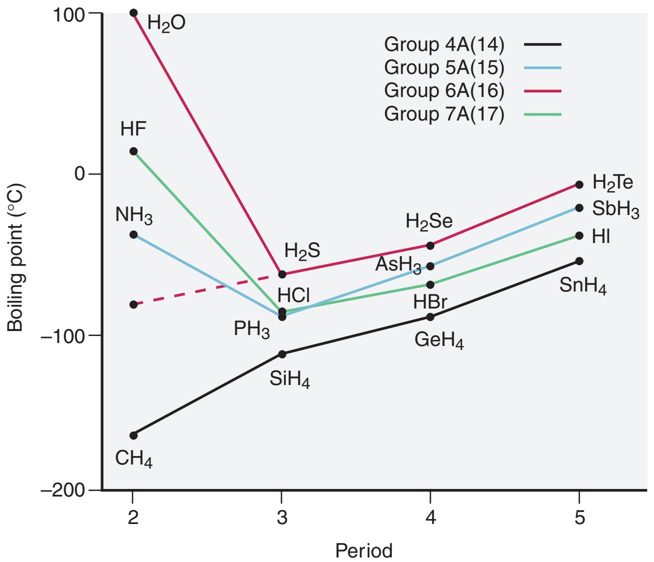


Figure 12.12 **Hydrogen bonding and boiling point.** NH_3, H_2O, and HF have exceptionally high boiling points because they form H bonds.

as the Group 4A(14) hydrides show. However, the first member in each of the other groups—NH_3, H_2O, and HF—deviates enormously from this expected trend. Within samples of these substances, the molecules form strong H bonds, so it takes more energy for the molecules to separate and enter the gas phase. For example, on the basis of molar mass alone, we would expect water to boil about 200°C lower than it actually does *(red dashed line).*

In Section 12.5, we'll discuss the effects that H bonds in water have in nature. In fact, the significance of hydrogen bonding in biological systems cannot be emphasized too strongly. It is a key feature in the structure and function of proteins and nucleic acids and is responsible for the action of many *enzymes,* the proteins that speed metabolic reactions, as well as for the functioning of genes.

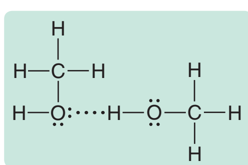
Sample Problem 12.3 Drawing Hydrogen Bonds Between Molecules of a Substance

Problem Which of the following substances exhibits H bonding? For any that do, show the H bonds between two of its molecules.

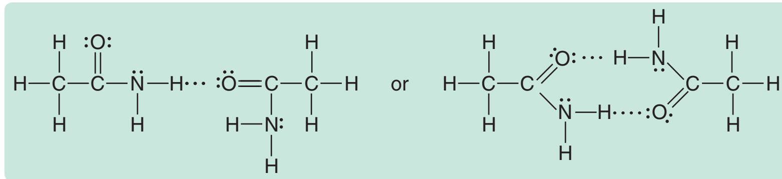
(a) C_2H_6 **(b)** CH_3OH **(c)** $CH_3\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2$

Plan If the molecule does *not* contain N, O, or F, it cannot form H bonds. If it contains any of these atoms covalently bonded to H, we draw two molecules in the —B:····H—A— pattern.

Solution **(a)** For C_2H_6. No N, O, or F, so no H bonds can form.
(b) For CH_3OH. The H covalently bonded to the O in one molecule forms an H bond to the lone pair on the O of an adjacent molecule:



(c) For $CH_3\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$. Two of these molecules can form one H bond between an H bonded to N and the O, or they can form two such H bonds:



A third possibility (not shown) is an H bond between an H attached to N in one molecule and the lone pair of N in another molecule.

Check The —B:····H—A— sequence (with A and B either N, O, or F) is present.

Comment Note that H covalently bonded to C *does not form H bonds* because carbon is not electronegative enough to make the C—H bond sufficiently polar.

FOLLOW-UP PROBLEM 12.3 Which of these substances exhibits H bonding? Draw the H bond(s) between two molecules of the substance where appropriate.

(a) $CH_3\overset{\overset{\displaystyle O}{\|}}{C}-OH$ **(b)** CH_3CH_2OH **(c)** $CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3$

Polarizability and Induced Dipole Forces

Even though electrons are attracted to nuclei and localized in bonding and lone pairs, we often picture them as "clouds" of negative charge because they are in constant motion. A nearby electric field can *induce* a distortion in the cloud, pulling electron density toward a positive pole of a field or pushing it away from a negative one:

- *For a nonpolar molecule,* the distortion induces a temporary dipole moment.
- *For a polar molecule,* it enhances the dipole moment already present.

In addition to charged plates connected to a battery, the source of the electric field can be the charge of an ion or the partial charges of a polar molecule.

How easily the electron cloud of an atom (or ion) can be distorted is called its **polarizability.** Smaller particles are less polarizable than larger ones because their electrons are closer to the nucleus and therefore held more tightly. Thus, we observe several trends:

- Polarizability *increases down a group* because atomic size increases and larger electron clouds are easier to distort.
- Polarizability *decreases across a period* because increasing Z_{eff} makes the atoms smaller and holds the electrons more tightly.
- Cations are *less* polarizable than their parent atoms because they are smaller; anions are *more* polarizable because they are larger.

Ion–induced dipole and dipole–induced dipole forces are the two types of charge-induced dipole forces; they are most important in solution, so we'll focus on them in Chapter 13. Nevertheless, *polarizability affects all intermolecular forces.*

Dispersion (London) Forces

So far, we've discussed forces that depend on the existing charge of an ion or a polar molecule. But what forces cause nonpolar substances like octane, chlorine, and argon to condense and solidify? As you'll see, polarizability plays the central role in the most universal intermolecular force.

The intermolecular force responsible for the condensed states of nonpolar substances is the **dispersion force** (or **London force,** named for Fritz London, the physicist who explained its quantum-mechanical basis around 1930). Dispersion forces *are present between all atoms, ions, and molecules* because they are caused by the *motion of electrons in atoms.* Let's examine their key aspects:

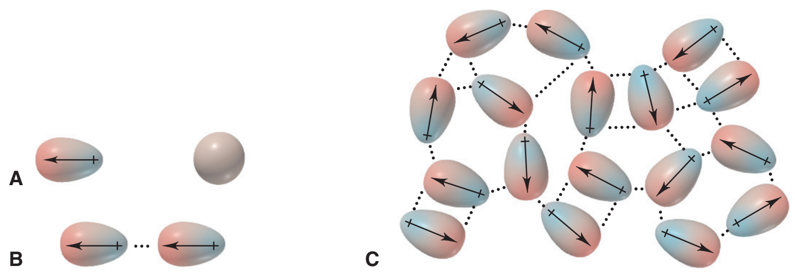


Figure 12.13 Dispersion forces among nonpolar particles. **A,** When atoms are far apart, an instantaneous dipole in one atom *(left)* doesn't influence another. **B,** But, when atoms are close together, the instantaneous dipole induces a dipole in the other. **C,** The process occurs through the sample.

1. *Source*. Picture one atom in a sample of, say, argon gas. Over time, its 18 electrons are distributed uniformly, so the atom is nonpolar. But at any instant, there may be more electrons on one side of the nucleus than the other, which gives the atom an *instantaneous dipole*. When a pair of argon atoms is far apart, they don't influence each other, but when close together, *the instantaneous dipole in one atom induces a dipole in its neighbor,* and they attract each other. This process spreads to other atoms and throughout the sample. At low temperatures, these attractions keep the atoms together (Figure 12.13). Thus, dispersion forces are *instantaneous dipole–induced dipole forces*.

2. *Prevalence*. While they are the *only* force existing between nonpolar particles, *dispersion forces contribute to the energy of attraction in all substances* because they exist between *all* particles. In fact, except for the forces between small, highly polar molecules or between molecules forming H bonds, the *dispersion force is the dominant intermolecular force.* Calculations show, for example, that 85% of the attraction between HCl molecules is due to dispersion forces and only 15% to dipole-dipole forces. Even for water, 75% of the intermolecular attraction comes from H bonds and 25% from dispersion forces.

3. *Relative strength*. The relative strength of dispersion forces depends on the polarizability of the particles, so they are weak for small particles, like H_2 and He, but stronger for larger particles, like I_2 and Xe. *Polarizability depends on the number of electrons, which correlates closely with molar mass* because heavier particles are either larger atoms or molecules with more atoms and, thus, more electrons. For this reason, as molar mass increases down the Group 4A(14) hydrides (see Figure 12.12) or down the halogens or the noble gases, dispersion forces increase and so do boiling points (Figure 12.14).

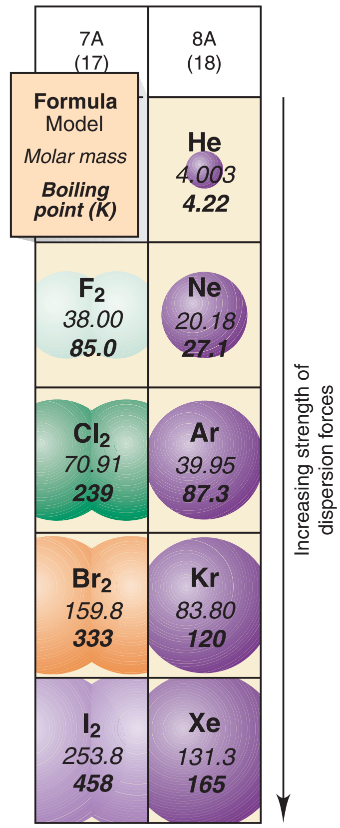


Figure 12.14 Molar mass and trends in boiling point.

4. *Effect of molecular shape*. For a pair of nonpolar substances with the same molar mass, stronger attractions occur for a molecular shape that has more area over which the electrons can be distorted. For example, the two five-carbon alkanes, *n*-pentane and neopentane (2,2-dimethylpropane) are structural isomers—same molecular formula (C_5H_{12}) but different properties. *n*-Pentane is more cylindrical and neopentane more spherical (Figure 12.15). Thus, two *n*-pentane molecules make more contact than do two neopentane molecules, so dispersion forces act at more points, and *n*-pentane has a higher boiling point.

Figure 12.16 *(next page)* shows how to determine the intermolecular forces in a sample.

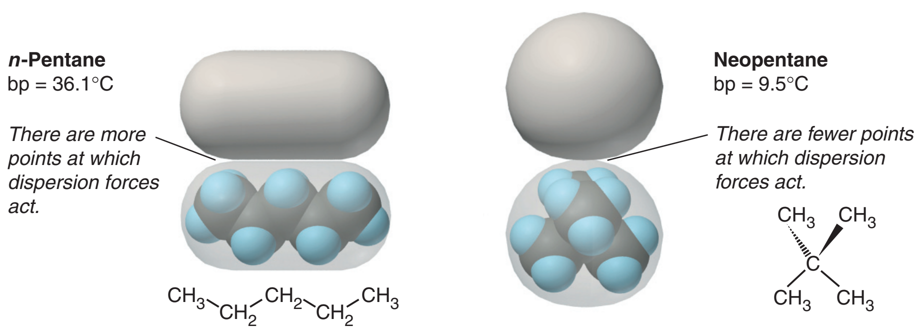


Figure 12.15 Molecular shape, intermolecular contact, and boiling point.

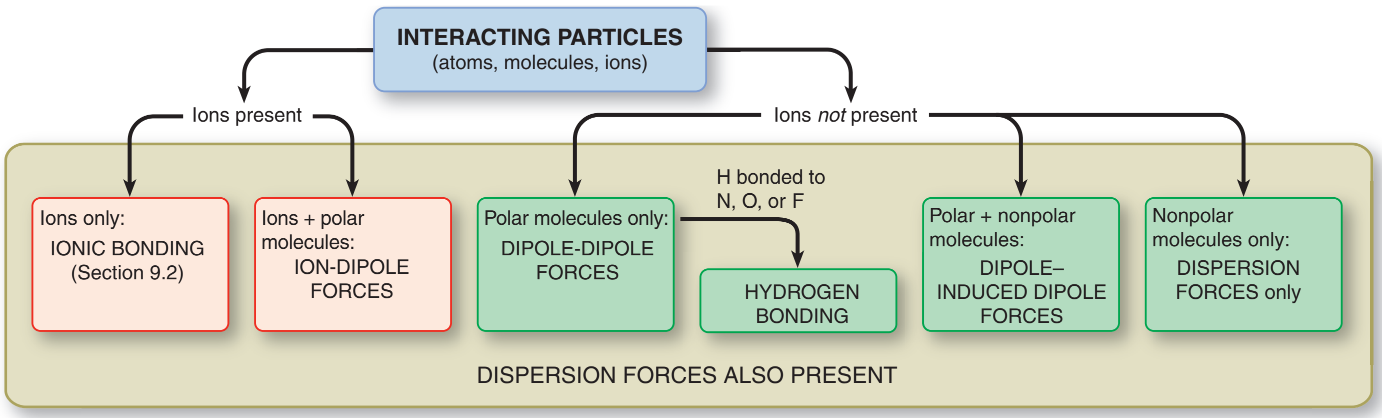


Figure 12.16 Determining the intermolecular forces in a sample.

Sample Problem 12.4 Predicting the Types of Intermolecular Forces

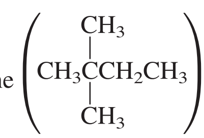
Problem For each substance, identify the key bonding and/or intermolecular force(s), and predict which one of the pair has the higher boiling point:

(a) $MgCl_2$ or PCl_3

(b) CH_3NH_2 or CH_3F

(c) CH_3OH or CH_3CH_2OH

(d) Hexane ($CH_3CH_2CH_2CH_2CH_2CH_3$) or 2,2-dimethylbutane



Plan We examine the formulas and structures for key differences between members of the pair: Are ions present? Are molecules polar or nonpolar? Is N, O, or F bonded to H? Do the molecules have different masses or shapes?

To rank boiling points, we consult Figure 12.16 and Table 12.2. Remember that

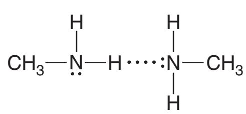
- Bonding forces are stronger than intermolecular forces.
- Hydrogen bonding is a strong type of dipole-dipole force.
- Dispersion forces are decisive when the difference is molar mass or molecular shape.

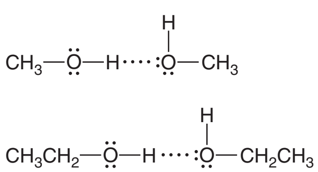
Solution **(a)** $MgCl_2$ consists of Mg^{2+} and Cl^- ions held together by ionic bonding forces; PCl_3 consists of polar molecules, so intermolecular dipole-dipole forces are present. The forces in $MgCl_2$ are stronger, so it should have a higher boiling point.

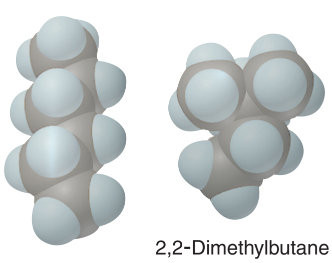
(b) CH_3NH_2 and CH_3F both consist of polar molecules of about the same molar mass. CH_3NH_2 has N—H bonds, so it can form H bonds *(see margin)*. CH_3F contains a C—F bond but no H—F bond, so dipole-dipole forces occur but not H bonds. Therefore, CH_3NH_2 should have the higher boiling point.

(c) CH_3OH and CH_3CH_2OH molecules both contain an O—H bond, so they can form H bonds *(see margin)*. CH_3CH_2OH has an additional —CH_2— group and thus a higher molar mass, which correlates with stronger dispersion forces; therefore, it should have a higher boiling point.

(d) Hexane and 2,2-dimethylbutane are nonpolar molecules of the same molar mass but different molecular shapes *(see margin)*. Cylindrical hexane molecules make more intermolecular contact than more compact 2,2-dimethylbutane molecules do, so hexane should have stronger dispersion forces and a higher boiling point.

(b) 

(c) 

(d) 

Hexane 2,2-Dimethylbutane

Check The actual boiling points show that our predictions are correct:

(a) $MgCl_2$ (1412°C) and PCl_3 (76°C)

(b) CH_3NH_2 (−6.3°C) and CH_3F (−78.4°C)

(c) CH_3OH (64.7°C) and CH_3CH_2OH (78.5°C)

(d) Hexane (69°C) and 2,2-dimethylbutane (49.7°C)

Comment Dispersion forces are *always* present, but in parts (a) and (b), they are much less significant than the other forces that occur.

FOLLOW-UP PROBLEM 12.4 In each pair, identify the intermolecular forces present for each substance, and predict which substance has the higher boiling point:

(a) CH_3Br or CH_3F **(b)** $CH_3CH_2CH_2OH$ or $CH_3CH_2OCH_3$ **(c)** C_2H_6 or C_3H_8

Summary of Section 12.3

- The van der Waals radius determines the shortest distance over which intermolecular forces operate; it is always larger than the covalent radius.
- Intermolecular forces are much weaker than bonding (intramolecular) forces.
- Ion-dipole forces occur between ions and polar molecules.
- Dipole-dipole forces occur between oppositely charged poles on polar molecules.
- Hydrogen bonding, a special type of dipole-dipole force, occurs when H bonded to N, O, or F is attracted to the lone pair of N, O, or F in another molecule.
- Electron clouds can be distorted (polarized) in an electric field.
- Ion– and dipole–induced dipole forces arise between a charge and the dipole it induces in another molecule.
- Dispersion (London) forces are instantaneous dipole–induced dipole forces that occur among all particles and increase with number of electrons (molar mass). Molecular shape determines the extent of contact between molecules and can be a factor in the strength of dispersion forces.

12.4 • PROPERTIES OF THE LIQUID STATE

Of the three states, only liquids combine the ability to flow with the effects of strong intermolecular forces. We understand this state least at the molecular level. Because of the *random* arrangement of the particles in a gas, any region of the sample is virtually identical to any other. And, different regions of a crystalline solid are identical because of the *orderly* arrangement of the particles (as you'll see in Section 12.6). Liquids, however, have regions that are orderly one moment and random the next. Despite this complexity, many macroscopic properties, such as surface tension, capillarity, and viscosity are well understood.

Surface Tension

Intermolecular forces have different effects on a molecule at the surface compared with one in the interior (Figure 12.17):

- An interior molecule is attracted by others on all sides.
- A surface molecule is attracted only by others below and to the sides, so it experiences a *net attraction downward.*

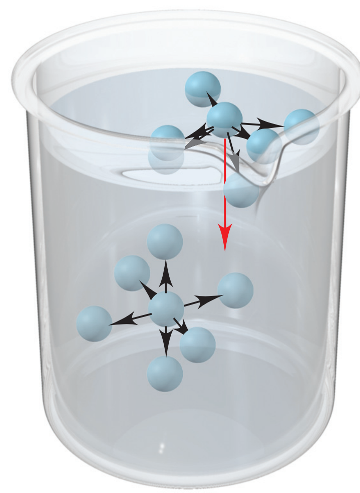


Figure 12.17 The molecular basis of surface tension.

Therefore, to increase attractions and become more stable, a surface molecule tends to move into the interior. For this reason, *a liquid surface has the fewest molecules and, thus, the smallest area possible*. In effect, the surface behaves like a "taut skin" covering the interior.

The only way to increase the surface area is for molecules to move up by breaking attractions in the interior, which requires energy. The **surface tension** is the energy required to increase the surface area and has units of J/m^2 (Table 12.3). In general, *the stronger the forces between particles, the more energy it takes to increase the surface area, so the greater the surface tension.* Water has a high surface tension because its molecules form multiple H bonds. *Surfactants* (*surf*ace-*act*ive *agents*), such as soaps, petroleum recovery agents, and fat emulsifiers, decrease the surface tension of water by congregating at the surface and disrupting the H bonds.

Table 12.3 Surface Tension and Forces Between Particles

Substance	Formula	Surface Tension (J/m^2) at 20°C	Major Force(s)
Diethyl ether	$CH_3CH_2OCH_2CH_3$	1.7×10^{-2}	Dipole-dipole; dispersion
Ethanol	CH_3CH_2OH	2.3×10^{-2}	H bonding
Butanol	$CH_3CH_2CH_2CH_2OH$	2.5×10^{-2}	H bonding; dispersion
Water	H_2O	7.3×10^{-2}	H bonding
Mercury	Hg	48×10^{-2}	Metallic bonding

Capillarity

The rising of a liquid against the pull of gravity through a narrow space, such as a thin tube, is called *capillary action,* or **capillarity.** Capillarity results from a competition between the intermolecular forces within the liquid (cohesive forces) and those between the liquid and the tube walls (adhesive forces). Let's look at the difference between the capillarities of water and mercury in glass:

1. *Water in glass*. When you place a narrow glass tube in water, why does the liquid rise up the tube and form a concave meniscus? Glass is mostly silicon dioxide (SiO_2), so water molecules form adhesive H bonding forces with the O atoms of the glass. As a result, a thin film of water creeps up the wall. At the same time, cohesive H bonding forces between water molecules, which give rise to surface tension, make the surface taut. These adhesive and cohesive forces combine to raise the water level and produce the concave meniscus (Figure 12.18A). The liquid rises until gravity pulling down is balanced by adhesive forces pulling up.

2. *Mercury in glass*. When you place a glass tube in a dish of mercury, why does the liquid drop below the level in the dish and form a convex meniscus? The cohesive forces among the mercury atoms are metallic bonds, so they are *much* stronger than the mostly dispersion adhesive forces between mercury and glass. As a result, the liquid pulls away from the walls. At the same time, the surface atoms are being pulled toward the interior by mercury's high surface tension, so the level drops. These combined forces produce the convex meniscus seen in a laboratory barometer (Figure 12.18B).

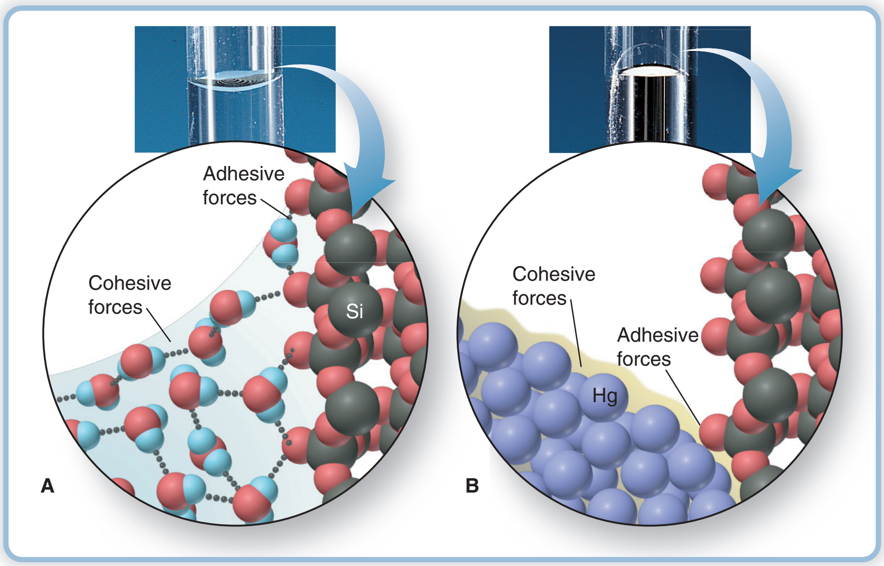


Figure 12.18 Capillary action and the shape of the water or mercury meniscus in glass. **A,** Water displays a concave meniscus. **B,** Mercury displays a convex meniscus.

Table 12.4 Viscosity of Water at Several Temperatures

Temperature (°C)	Viscosity ($N \cdot s/m^2$)*
20	1.00×10^{-3}
40	0.65×10^{-3}
60	0.47×10^{-3}
80	0.35×10^{-3}

*The units of viscosity are newton-seconds per square meter.

Viscosity

Viscosity is the resistance of a fluid to flow, and it results from intermolecular attractions that impede the movement of molecules around and past each other. Both gases and liquids flow, but liquid viscosities are *much* higher because the much shorter distances between their particles result in many more points for intermolecular forces to resist the flow of nearby molecules. Let's examine two factors—temperature and molecular shape—that influence viscosity:

- *Effect of temperature. Viscosity decreases with heating* (Table 12.4). Faster moving molecules overcome intermolecular forces more easily, so the resistance to flow decreases. Next time you heat cooking oil, watch the oil flow more easily and spread out in the pan as it warms.

- *Effect of molecular shape*. Small, spherical molecules make little contact and pour easily, like buckshot from a bowl. Long molecules make more contact and become entangled and pour slowly, like cooked spaghetti from a bowl. Thus, given the same types of intermolecular forces, liquids consisting of longer molecules have higher viscosities.

A striking example of a change in viscosity occurs during the making of syrup. Even at room temperature, a concentrated aqueous sugar solution has a higher viscosity than water because of H bonding among the many hydroxyl (—OH) groups on the ring-shaped sugar molecules. When the solution is slowly heated to boiling, the sugar molecules react with each other and link covalently, gradually forming long chains. Hydrogen bonds and dispersion forces occur at many points along the chains, and the resulting syrup is a viscous liquid that pours slowly and clings to a spoon. When a viscous syrup is cooled, it may become stiff enough to be picked up and stretched—into taffy candy.

Summary of Section 12.4

- Surface tension is a measure of the energy required to increase a liquid's surface area. Greater intermolecular forces within a liquid create higher surface tension.
- Capillarity, the rising of a liquid through a narrow space, occurs when the forces between a liquid and a surface (adhesive) are greater than those within the liquid (cohesive).
- Viscosity, the resistance to flow, depends on molecular shape and decreases with temperature. Stronger intermolecular forces create higher viscosity.

12.5 • THE UNIQUENESS OF WATER

Water is absolutely amazing stuff, with some of the most unusual properties of any substance, but it is so familiar we take it for granted. Like any substance, its properties arise inevitably from those of its atoms. Each O and H atom attains a filled outer level by sharing electrons in single bonds. With two bonding pairs and two lone pairs around O and a large electronegativity difference in each O—H bond, the H_2O molecule is bent and highly polar. This arrangement is crucial because it allows each molecule to engage in four H bonds with its neighbors (Figure 12.19). From these basic atomic and molecular facts emerges unique and remarkable macroscopic behavior.

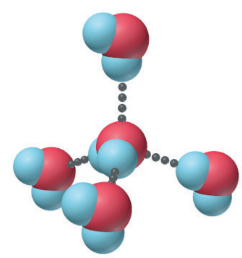


Figure 12.19 H-bonding ability of water. One H_2O molecule can form four H bonds to other molecules, resulting in a tetrahedral arrangement.

Solvent Properties of Water

The *great solvent power* of water results from its polarity and H-bonding ability:

- It dissolves ionic compounds through ion-dipole forces that separate the ions from the solid and keep them in solution (see Figure 4.2).
- It dissolves polar nonionic substances, such as ethanol (CH_3CH_2OH) and glucose ($C_6H_{12}O_6$), by H bonding.
- It dissolves nonpolar atmospheric gases to a limited extent through dipole–induced dipole and dispersion forces.

Water is the environmental and biological solvent, forming the complex solutions we know as oceans, lakes, and cellular fluid. From a chemical point of view, all organisms, from bacteria to humans, are highly organized systems of membranes enclosing and compartmentalizing complex aqueous solutions.

Thermal Properties of Water

When a substance is heated, some of the added energy increases average molecular speed, some increases vibration and rotation, and some overcomes intermolecular forces. The values for two of water's thermal properties have global impacts.

1. *Specific heat capacity*. Because water has so many strong H bonds, its *specific heat capacity* is higher than any common liquid. With oceans covering 70% of Earth's surface, daytime energy from the Sun causes relatively small changes in temperature, allowing life to survive. On the waterless, airless Moon, temperatures range from 100°C to −150°C during a complete lunar day. Even in Earth's deserts, day-night temperature differences of 40°C are common.

2. *Heat of vaporization*. Numerous strong H bonds give water a very *high heat of vaporization*. Two examples show why this is crucial. The average adult has 40 kg of body water and generates about 10,000 kJ of heat a day from metabolism. If this heat were used to increase the average E_k of water molecules in the body, the rise in body temperaure of tens of degrees would mean immediate death. Instead, the heat is converted to E_p as it breaks H bonds and evaporates sweat, resulting in a stable body temperature and minimal loss of body fluid. On a planetary scale, the Sun's energy vaporizes ocean water in warm latitudes, and the potential energy is released as heat to warm cooler regions when the vapor condenses to rain. This global-scale cycling of water powers many weather patterns.

Surface Properties of Water

Hydrogen bonding is also responsible for water's *high surface tension* and *high capillarity*. Except for some molten metals and salts, water has the highest surface tension of any liquid. It keeps plant debris resting on a pond surface, providing shelter and nutrients for fish and insects. High capillarity means water rises through the tiny spaces between soil particles, so plant roots can absorb deep groundwater during dry periods.

The Unusual Density of Solid Water

In the solid state, the tetrahedral arrangement of H-bonded water molecules (see Figure 12.19) leads to the hexagonal, *open structure* of ice (Figure 12.20A), and the symmetrical beauty of snowflakes (Figure 12.20B) reflects this hexagonal organization. The large spaces within ice make *the solid less dense than the liquid* and explain the negative slope of the solid-liquid line in the phase diagram for water (see Figure 12.8B). As pressure is applied, some H bonds break, so the ordered crystal structure is disrupted, and the ice liquefies. When ice melts at 0°C, the loosened molecules pack much more closely, filling spaces in the collapsing solid structure. As a result, liquid water is most dense (1.000 g/mL) at around 4°C (3.98°C). With more heating, the density decreases through normal thermal expansion.

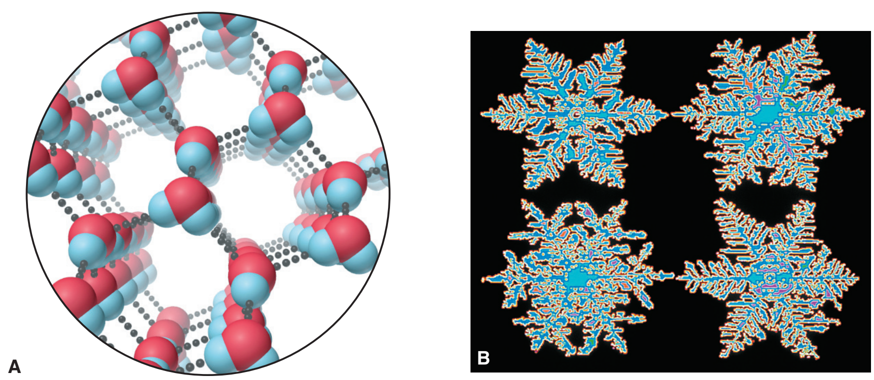


Figure 12.20 The hexagonal structure of ice. **A,** The open, hexagonal molecular structure of ice. **B,** The beauty of six-pointed snowflakes reflects this hexagonal structure.

This change in density is vital for freshwater life. When the surface of a lake freezes in winter, the ice floats. If the solid were denser than the liquid, as is true for nearly every other substance, the surface water would freeze and sink until the entire lake was solid. Aquatic life would not survive from year to year. As lake water becomes colder in the fall and early winter, it becomes more dense *before* it freezes. Similarly, in spring, less dense ice thaws to form more dense water *before* the water expands. During both of these seasonal density changes, the top layer of water reaches the high-density point first and sinks. The next layer of water rises because it is slightly less dense, reaches 4°C, and likewise sinks. This sinking and rising distribute nutrients and dissolved oxygen.

Summary of Section 12.5

- The atomic properties of H and O result in water's bent molecular shape, polarity, and H-bonding ability.
- These properties give water the ability to dissolve many ionic and polar compounds.
- Water's high specific heat capacity and heat of vaporization give Earth and its organisms a narrow temperature range.
- Water's exceptionally high surface tension and capillarity are essential to plants and animals.
- Because water expands on freezing, lake life survives in winter and nutrients mix from seasonal density changes.

12.6 • THE SOLID STATE: STRUCTURE, PROPERTIES, AND BONDING

Stroll through a museum's mineral collection, and you'll be struck by the variety and beauty of crystalline solids. In this section, we discuss the structural features of these and other solids and the intermolecular forces that create them. We also consider the main bonding model that explains many properties of solids.

Structural Features of Solids

We can divide solids into two broad categories:

- **Crystalline solids** have well defined shapes because their particles—atoms, molecules, or ions—occur in an orderly arrangement (Figure 12.21).
- **Amorphous solids** have poorly defined shapes because their particles lack an orderly arrangement throughout the sample. Examples are rubber and glass.

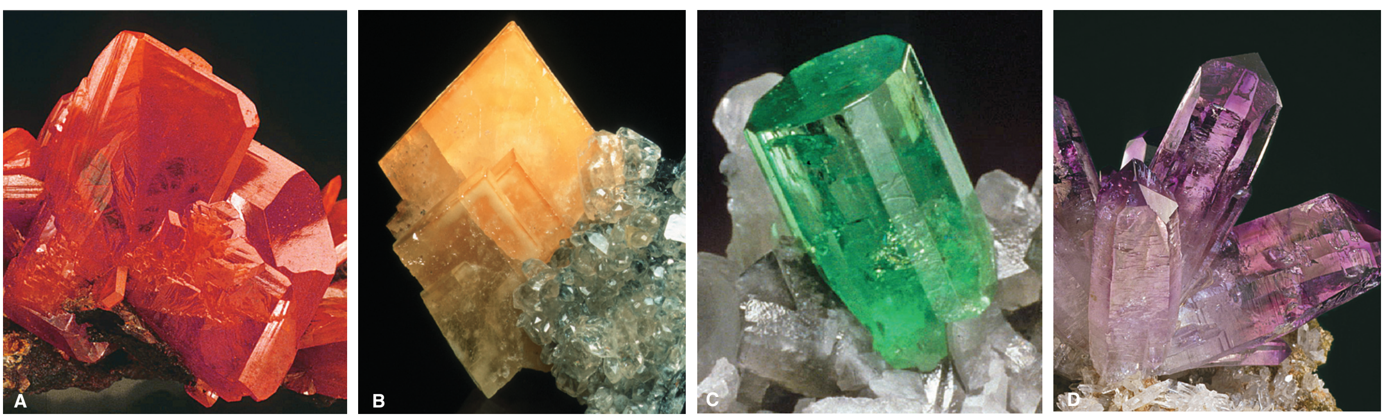


Figure 12.21 The beauty of crystalline solids. **A,** Wulfenite. **B,** Barite *(left)* on calcite *(right)*. **C,** Beryl (emerald). **D,** Quartz (amethyst).

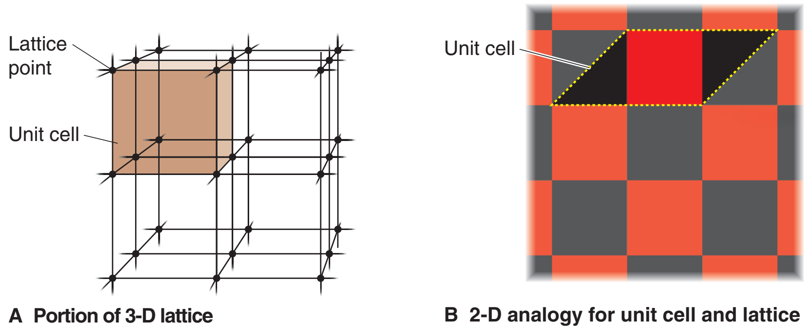


Figure 12.22 **The crystal lattice and the unit cell.** **A,** A small portion of a lattice is shown as points connected by lines, with a unit cell *(colored)*. **B,** A checkerboard analogy for a lattice.

The Crystal Lattice and the Unit Cell The particles in a crystal are packed tightly in an orderly, three-dimensional array. As the simplest case, consider the particles as *identical* spherical atoms, and imagine a point at the center of each. The collection of points forms a regular pattern called the crystal **lattice.** The lattice consists of *all points with identical surroundings;* that is, there would be no way to tell if you moved from one lattice point to another.

Figure 12.22A shows a portion of a lattice and the **unit cell,** the *smallest* portion that gives the crystal if it is repeated in all directions. A two-dimensional analogy for a unit cell and the resulting crystal lattice appears in a checkerboard (Figure 12.22B), a section of tiled floor, a strip of wallpaper, or any other pattern that is constructed from a repeating unit.

There are 7 crystal systems and 14 types of unit cells that occur in nature, but we will be concerned primarily with the *cubic system*. The solid states of a majority of metallic elements, some covalent compounds, and many ionic compounds occur as cubic lattices. A key parameter of any lattice is the **coordination number,** the number of *nearest* neighbors of a particle. There are three types of cubic unit cells:

1. In the **simple cubic unit cell** (Figure 12.23A), the centers of eight identical particles define the corners of a cube (shown in the expanded view, *top row*). The particles touch along the cube edges (see the space-filling view, *second row*), but they do not touch diagonally along the cube faces or through its center. An expanded portion of the crystal *(third row)* shows that the coordination number of each particle is 6: four in its own layer, one in the layer above, and one in the layer below.
2. In the **body-centered cubic unit cell** (Figure 12.23B), identical particles lie at each corner *and* in the center of the cube. Those at the corners do not touch each other, but they all touch the one in the center. Each particle is surrounded by eight nearest neighbors, four above and four below, so the coordination number is 8.
3. In the **face-centered cubic unit cell** (Figure 12.23C), identical particles lie at each corner *and* in the center of each face but not in the center of the cube. Particles at the corners touch those in the faces but not each other. The coordination number is 12.

How many particles make up a unit cell? For particles of the same size, *the higher the coordination number is, the greater the number of particles in a given volume.* Since one unit cell touches another, with no gaps, a particle at a corner or face is *shared* by adjacent cells. In the cubic unit cells, the particle at each corner is part of eight adjacent cells (Figure 12.23, *third row*), so one-eighth of each particle belongs to each cell *(bottom row).* There are eight corners in a cube, so

- A simple cubic unit cell contains $8 \times \frac{1}{8}$ particle $= 1$ particle.
- A body-centered cubic unit cell contains $8 \times \frac{1}{8}$ particle $= 1$ particle plus 1 particle in the center, for a total of 2 particles.
- A face-centered cubic unit cell contains $8 \times \frac{1}{8}$ particle $= 1$ particle plus one-half particle in each of the six faces, or $6 \times \frac{1}{2}$ particle $= 3$ particles, for a total of 4 particles.

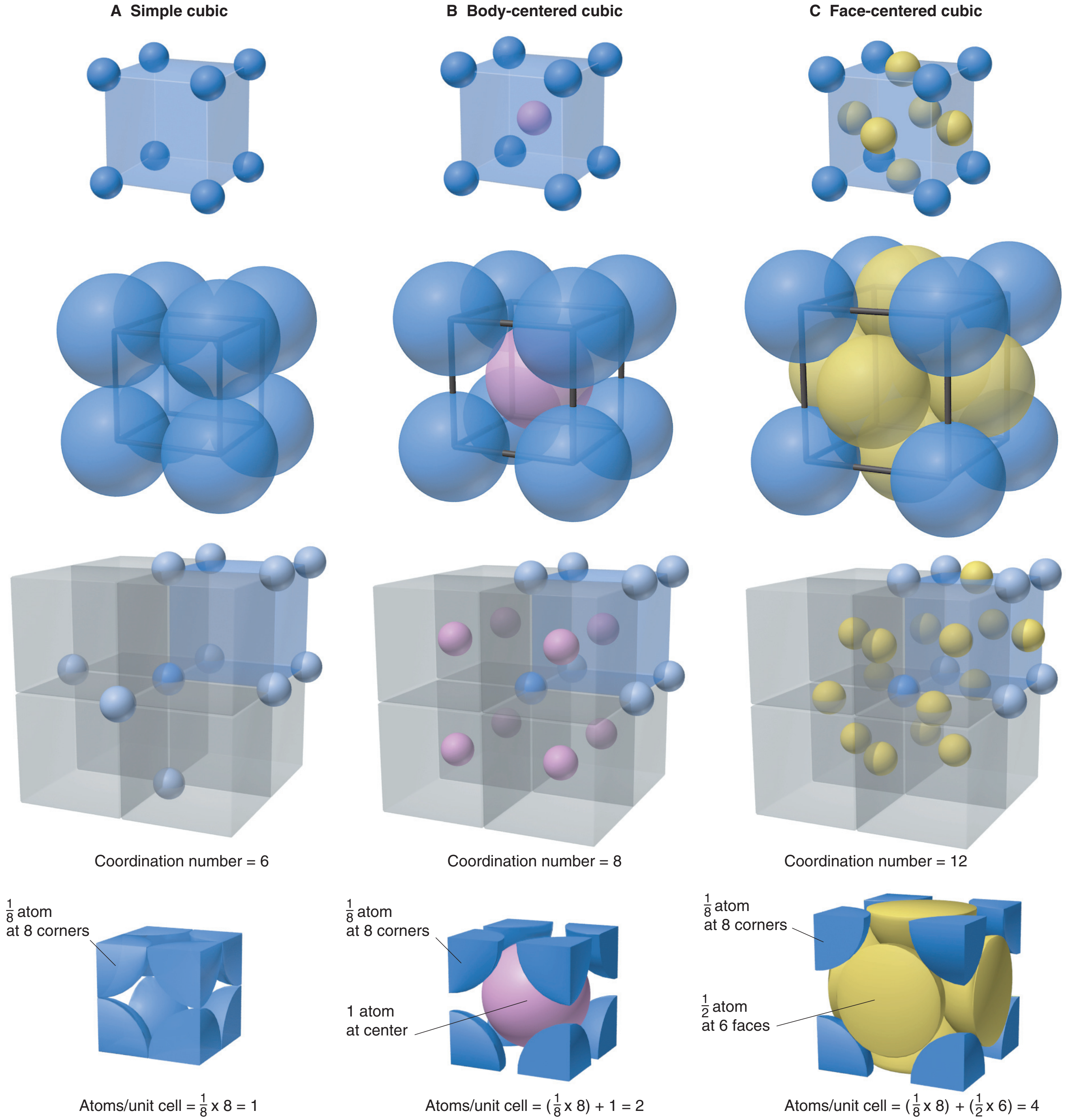


Figure 12.23 The three cubic unit cells. **A,** Simple cubic unit cell. **B,** Body-centered cubic unit cell. **C,** Face-centered cubic unit cell. *Top row:* Cubic arrangements of atoms in expanded view. *Second row:* Space-filling view of these cubic arrangements. All atoms are identical but, for clarity, corner atoms are blue, body-centered atoms pink, and face-centered atoms yellow. *Third row:* A unit cell *(shaded blue)* in an expanded portion of the crystal. The number of nearest neighbors around one particle *(dark blue in center)* is the coordination number. *Bottom row:* The total numbers of atoms in the actual unit cell. The simple cubic has one atom, the body-centered has two, and the face-centered has four.

The efficient packing of fruit.

Packing Efficiency and the Creation of Unit Cells Unit cells result from the ways atoms pack together, which are similar to the ways that macroscopic spheres—marbles, golf balls, fruit—are packed *(see photo)*. Let's pack *identical* spheres to create the three cubic unit cells and the hexagonal unit cell and determine the **packing efficiency,** the percentage of the total volume occupied by the spheres themselves:

1. *The simple cubic unit cell.* When we arrange the first layer of spheres in vertical and horizontal rows, large diamond-shaped spaces are formed (Figure 12.24A, *cutaway portion*). If we place the next layer of spheres *directly above* the first, we obtain an arrangement based on the *simple* cubic unit cell (Figure 12.24B). The spheres occupy only 52% of the unit-cell volume, so 48% is empty space between them. This is a very inefficient way to pack spheres, so neither fruit nor atoms are typically packed this way.

2. *The body-centered cubic unit cell.* Rather than placing the second layer (colored *green* for clarity) directly above the first, we use space more efficiently by placing it on the diamond-shaped spaces in the first layer (Figure 12.24C). Then we pack the third layer onto the diamond-shaped spaces in the second, which makes the first and third layers line up vertically. This arrangement is based on the *body-centered* cubic unit cell, and its packing efficiency is much higher at 68%. Several metallic elements, including chromium, iron, and all the Group 1A(1) elements, have a crystal structure based on this unit cell.

3. *The hexagonal and face-centered cubic unit cells*. Spheres are packed most efficiently in these cells. First, in the bottom layer (labeled *a, orange*), we shift every other row laterally so that the large diamond-shaped spaces become smaller triangular spaces. Then we place the second layer (labeled *b, green*) over these spaces (Figure 12.24D).

In layer *b,* notice that some spaces are orange because they lie above *spheres* in layer *a,* whereas other spaces are white because they lie above *spaces* in layer *a*. We can place the third layer in either of two ways, which gives rise to two different unit cells:

- *Hexagonal unit cell*. If we place the third layer of spheres *(orange)* over the orange spaces (look down and left to Figure 12.24E), they lie directly over the spheres in layer *a*. Every other layer is placed identically (an *abab. . .* layering pattern), and we obtain **hexagonal closest packing,** which is based on the *hexagonal* unit cell.
- *Face-centered unit cell*. If we place the third layer of spheres *(blue)* over the white spaces in layer *b* (look down and right to Figure 12.24F), the placement is different from layers *a* and *b* (an *abcabc. . .* pattern) and we obtain **cubic closest packing,** which is based on the *face-centered cubic* unit cell.

The packing efficiency of both hexagonal and cubic closest packing is 74%, and the coordination number of both is 12. Most metallic elements crystallize in one or the other of these arrangements. Magnesium, titanium, and zinc are some that adopt the hexagonal structure; nickel, copper, and lead adopt the cubic structure, as do many ionic compounds and other substances, such as CO_2, CH_4, and most noble gases.

Observing Crystal Structures: X-Ray Diffraction Analysis Our understanding of crystalline solids is based on the ability to "see" their crystal structures. One of the most powerful tools for doing this is **x-ray diffraction analysis.** In Chapter 7, we discussed wave diffraction and saw how interference patterns of bright and dark regions appear when light passes through closely spaced slits, especially those that are spaced at the distance of the light's wavelength (see Figure 7.5). Because x-ray wavelengths are about the same size as the spaces between layers of particles in many solids, the layers diffract x-rays.

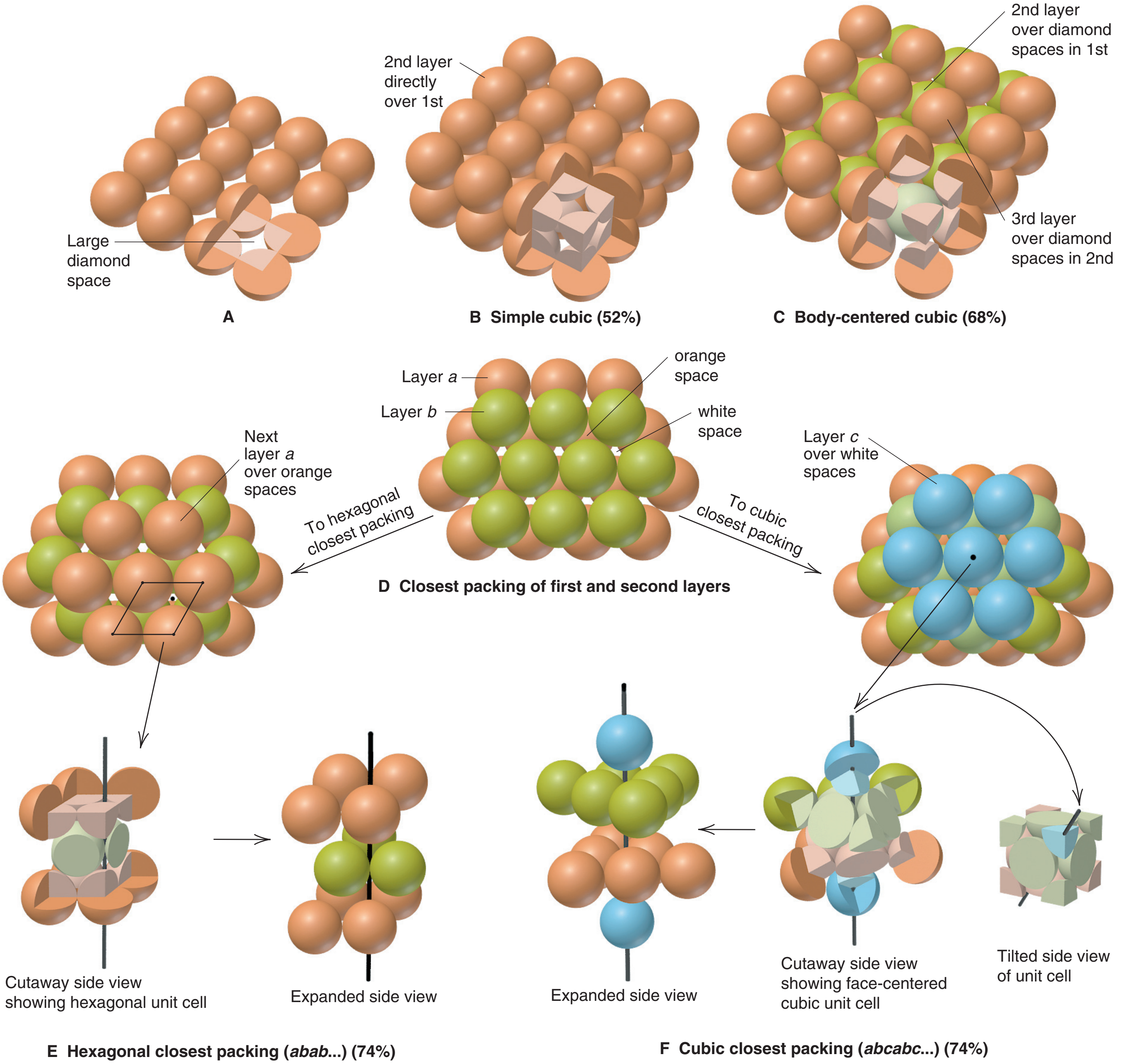


Figure 12.24 Packing spheres to obtain three cubic and hexagonal unit cells. **A,** In the first layer, each sphere lies next to another horizontally and vertically; note the large diamond-shaped spaces *(see cutaway)*. **B,** If the spheres in the next layer lie directly over those in the first, the packing is based on the simple cubic unit cell *(pale orange cube, lower right corner)*. **C,** If the spheres in the next layer lie in the diamond-shaped spaces of the first layer, the packing is based on the *body-centered cubic* unit cell *(lower right corner)*. **D,** The closest possible packing of the first layer *(layer a, orange)* is obtained by shifting every other row in part A to obtain smaller triangular spaces. The spheres of the second layer *(layer b, green)* are placed above these spaces; note the orange and white spaces that result. **E,** When the third layer *(next layer a, orange)* is placed over the orange spaces, we obtain an *abab*. . . pattern and the hexagonal unit cell. **F,** When the third layer *(layer c, blue)* covers the white spaces, we get an *abcabc*. . . pattern and the face-centered cubic unit cell.

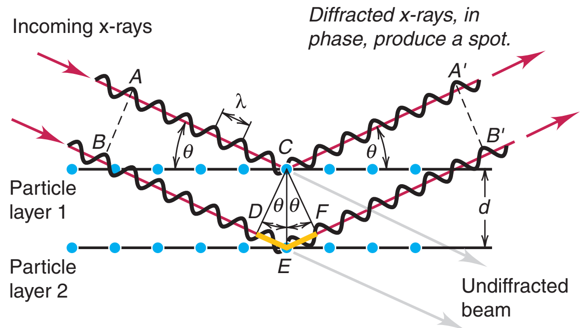


Figure 12.25 Diffraction of x-rays by crystal planes.

Let's see how this technique is used to measure a key parameter in a crystal structure: the distance (d) between layers of atoms. Figure 12.25 depicts a side view of two layers in a simplified lattice. Two waves impinge on the crystal at an angle θ and are diffracted at the same angle by adjacent layers. When the first wave strikes the top layer and the second strikes the next layer, the waves are *in phase* (peaks aligned with peaks and troughs with troughs). If they are still in phase after being diffracted, a spot appears on a nearby photographic plate. Note that this will occur only if the additional distance traveled by the second wave ($DE + EF$ in the figure) is a whole number of wavelengths, $n\lambda$, where n is an integer (1, 2, 3, and so on). From trigonometry, we find that

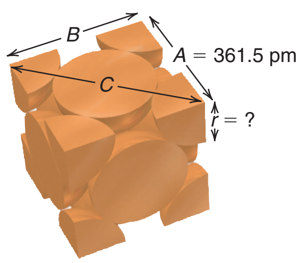
$$n\lambda = 2d \sin \theta$$

where θ is the known angle of incoming light, λ is its known wavelength, and d is the unknown distance between the layers in the crystal. This relationship is the *Bragg equation,* named for W. H. Bragg and his son W. L. Bragg, who shared the Nobel Prize in physics in 1915 for their work on crystal structure analysis.

Rotating the crystal changes the angle of incoming radiation and produces a different set of spots. Modern x-ray diffraction equipment automatically rotates the crystal and measures thousands of diffractions, and a computer calculates the distances and angles within the lattice.

In addition to the distance between layers, another piece of data obtained from x-ray crystallography is the edge length of the unit cell. Figure 12.26 shows how the edge length and basic geometry are used to find the atomic (or ionic) radii in the three cubic unit cells. Sample Problem 12.5 demonstrates this approach.

Sample Problem 12.5 Determining Atomic Radius from the Unit Cell



Problem Copper adopts cubic closest packing, and the edge length of the unit cell is 361.5 pm. What is the atomic radius of copper?

Plan Cubic closest packing gives a face-centered cubic unit cell, and we know the edge length. With Figure 12.26 and $A = 361.5$ pm, we solve for r *(see margin).*

Solution Using the Pythagorean theorem to find C, the diagonal of the cell's face:

$$C = \sqrt{A^2 + B^2}$$

The unit cell is a cube, so $A = B$. Therefore,

$$C = \sqrt{2A^2} = \sqrt{2(361.5 \text{ pm})^2} = 511.2 \text{ pm}$$

Finding r: $C = 4r$. Therefore, $r = 511.2 \text{ pm}/4 = 127.8$ pm.

Check Rounding and quickly checking the math gives

$$C = \sqrt{2(4\times10^2 \text{ pm})^2} = \sqrt{2(16\times10^4 \text{ pm}^2)}$$

or ~500–600 pm; thus, $r \approx 125$–150 pm. The actual value for copper is 128 pm (see Figure 8.10).

FOLLOW-UP PROBLEM 12.5 Iron crystallizes in a body-centered cubic structure. If the atomic radius of Fe is 126 pm, find the edge length (in nm) of the unit cell.

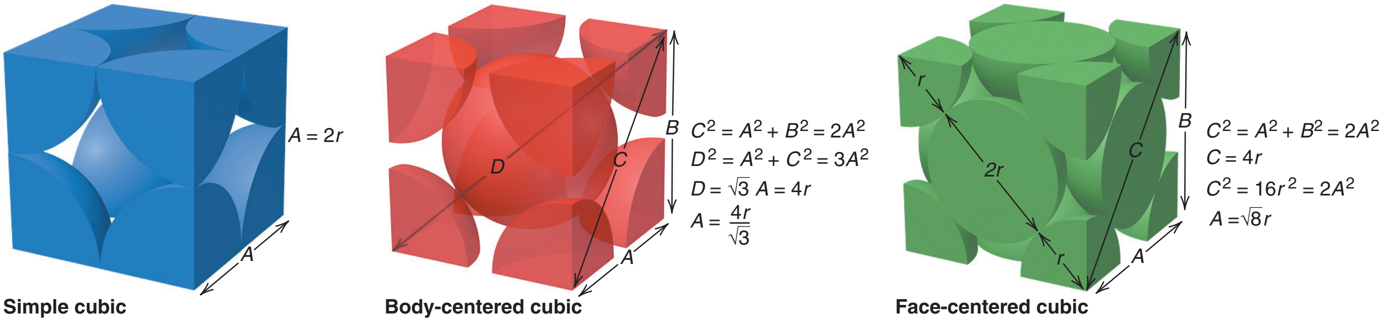


Figure 12.26 Edge length and atomic (ionic) radius in the three cubic unit cells.

Types and Properties of Crystalline Solids

The five most important types of solids are defined by the type(s) of particle(s) in the crystal (Table 12.5). We'll highlight interparticle forces and physical properties.

Atomic Solids Individual atoms held together only by *dispersion forces* form an **atomic solid,** and the noble gases [Group 8A(18)] are the only substances that form such solids. The very weak forces among the atoms mean melting and boiling points and heats of vaporization and fusion are all very low, rising smoothly with increasing molar mass. Argon crystallizes in a cubic closest packed structure (Figure 12.27), as do the other noble gases.

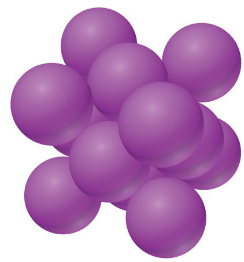


Figure 12.27 Cubic closest packing of frozen argon (face-centered cubic unit cell).

Molecular Solids In the many thousands of **molecular solids,** individual molecules occupy the lattice points. Various combinations of dipole-dipole, dispersion, and H-bonding forces account for a wide range of physical properties. Dispersion forces in nonpolar substances lead to melting points that generally increase with molar mass

Table 12.5 Characteristics of the Major Types of Crystalline Solids

Type	Particle(s)	Interparticle Forces	Physical Properties	Examples [mp, °C]
Atomic	Atoms	Dispersion	Soft, very low mp, poor thermal and electrical conductors	Group 8A(18) (Ne [−249] to Rn [−71])
Molecular	Molecules	Dispersion, dipole-dipole, H bonds	Fairly soft, low to moderate mp, poor thermal and electrical conductors	*Nonpolar** O_2 [−219], C_4H_{10} [−138] Cl_2 [−101], C_6H_{14} [−95], P_4 [44.1] *Polar* SO_2 [−73], $CHCl_3$ [−64], HNO_3 [−42], H_2O [0.0], CH_3COOH [17]
Ionic	Positive and negative ions	Ion-ion attraction	Hard and brittle, high mp, good thermal and electrical conductors when molten	NaCl [801] CaF_2 [1423] MgO [2852]
Metallic	Atoms	Metallic bond	Soft to hard, low to very high mp, excellent thermal and electrical conductors, malleable and ductile	Na [97.8] Zn [420] Fe [1535]
Network covalent	Atoms	Covalent bond	Very hard, very high mp, usually poor thermal and electrical conductors	SiO_2 (quartz) [1610] C (diamond) [~4000]

*Nonpolar molecular solids are arranged in order of increasing molar mass. Note the correlation with increasing melting point (mp).

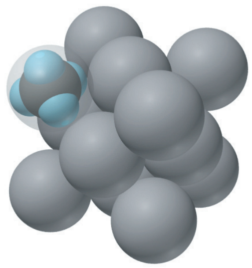


Figure 12.28 Cubic closest packing (face-centered unit cell) of frozen CH_4.

(Table 12.5). Among polar molecules, dipole-dipole forces and, where possible, H bonding occur. Most molecular solids have much higher melting points than atomic solids (noble gases) but much lower melting points than other types of solids. Methane crystallizes with a face-centered cubic unit cell, and the center of each carbon is the lattice point (Figure 12.28).

Ionic Solids: The Example of Sodium Chloride In crystalline **ionic solids,** the unit cell contains particles with whole, rather than partial, charges. As a result, the interparticle forces (ionic bonds) are *much* stronger than the van der Waals forces in atomic or molecular solids. To maximize attractions, cations are surrounded by as many anions as possible, and vice versa, with *the smaller of the two ions lying in the spaces (holes) formed by the packing of the larger.* Because the unit cell is the smallest portion of the crystal that maintains the overall spatial arrangement, it is also the smallest portion that maintains the overall chemical composition. In other words, *the unit cell has the same cation/anion ratio as the empirical formula.*

Ionic compounds adopt several different crystal structures, but many use cubic closest packing. As an example, let's consider a structure that has a 1/1 ratio of ions. The *sodium chloride structure* is found in many compounds, including most of the alkali metal [Group 1A(1)] halides and hydrides, the alkaline earth metal [Group 2A(2)] oxides and sulfides, several transition-metal oxides and sulfides, and most of the silver halides. To visualize this structure, first imagine Cl^- anions and Na^+ cations organized separately in face-centered cubic (cubic closest packed) arrays. The crystal structure arises when these two arrays penetrate each other such that the smaller Na^+ ions end up in the holes between the larger Cl^- ions, as shown in Figure 12.29A. Thus, each Na^+ is surrounded by six Cl^-, and vice versa (coordination number = 6). Figure 12.29B is a space-filling depiction of the unit cell showing a face-centered cube of Cl^- ions with Na^+ ions between them. Note the four Cl^- $[(8 \times \frac{1}{8}) + (6 \times \frac{1}{2}) = 4\ Cl^-]$ and four Na^+ $[(12 \times \frac{1}{4}) + 1$ in the center $= 4\ Na^+]$, giving a 1/1 ion ratio.

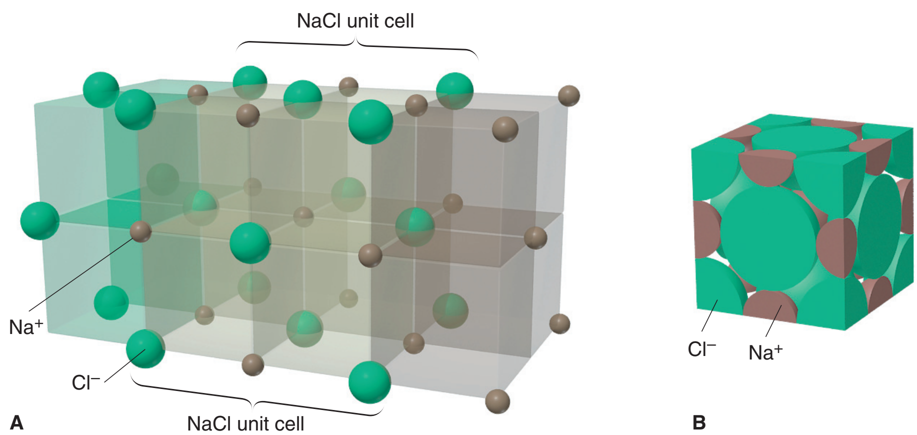


Figure 12.29 The sodium chloride structure. **A,** Expanded view. **B,** Space-filling model of the NaCl unit cell.

The properties of ionic solids are a direct consequence of the *fixed ion positions* and *very strong interionic forces,* which create a high lattice energy. Thus, ionic solids typically have high melting points and low electrical conductivities. When a large amount of heat is supplied and the ions gain enough kinetic energy to break free of their positions, the solid melts and the mobile ions conduct a current. Ionic compounds are hard because only a strong external force can change the relative positions of many trillions of interacting ions. If enough force *is* applied to move them, ions of like charge are brought near each other, and their repulsions crack the crystal (see Figure 9.8).

Metallic Solids Most metallic elements crystallize in one of the two closest packed structures (Figure 12.30). In contrast to the weak dispersion forces in atomic solids, powerful metallic bonding forces hold atoms together in **metallic solids.** The properties of metals—high electrical and thermal conductivity, luster, and malleability—result from their delocalized electrons (Section 9.1). Melting points and hardnesses of metallic solids are also related to packing efficiency and number of valence electrons. We discuss bonding models that explain these metallic properties in the next two subsections.

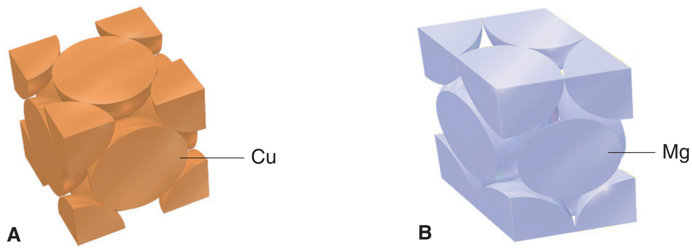


Figure 12.30 Crystal structures of metals. **A,** Copper adopts cubic closest packing. **B,** Magnesium adopts hexagonal closest packing.

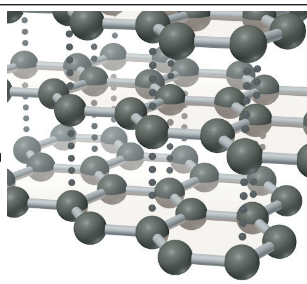
Network Covalent Solids Strong covalent bonds link the atoms together in a **network covalent solid;** thus, separate particles are not present. These substances adopt a variety of crystal structures depending on the details of their bonding.

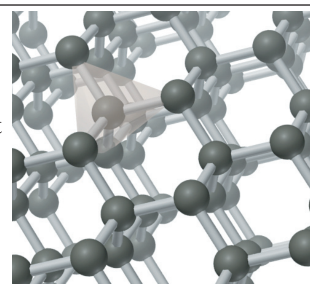
As a consequence of strong bonding, all network covalent solids have extremely high melting and boiling points, but their conductivity and hardness vary. Two examples with the same composition but strikingly different properties are the two common crystalline forms of elemental carbon, graphite and diamond (Table 12.6):

- *Graphite* occurs as stacked flat sheets of hexagonal carbon rings with a strong σ-bond framework and delocalized π bonds, reminiscent of benzene (Section 10.1); the arrangement looks like chicken wire or honeycomb. Whereas the π-bonding electrons of benzene are delocalized over one ring, those of graphite are delocalized over the entire sheet. Thus, graphite conducts electricity well—it is a common electrode material—but only in the plane of the sheets. The sheets interact via dispersion forces, and impurities, such as O_2, between the sheets allow them to slide past each other, which explains why graphite is soft and used as a lubricant.
- *Diamond* adopts a face-centered cubic unit cell, with each C tetrahedrally bonded to four others in an endless array. Throughout the crystal, strong single bonds make diamond the hardest natural substance known. Like most network covalent solids, diamond does not conduct electricity because the bonding electrons are localized.

Table 12.6 Comparison of the Properties of Diamond and Graphite

Property	Graphite	Diamond
Density (g/cm^3)	2.27	3.51
Hardness	<1 (very soft)	10 (hardest)
Melting point (K)	4100	4100
Color	Shiny black	Colorless transparent
Electrical conductivity	High (along sheet)	None
ΔH°_{rxn} for combustion (kJ/mol)	−393.5	−395.4
ΔH°_f (kJ/mol)	0 (standard state)	1.90





The most important network covalent solids are the *silicates,* which consist of extended arrays of covalently bonded silicon and oxygen atoms. Quartz (SiO_2) is a common example. We'll discuss silicates, which form the structure of clays, rocks, and many minerals, when we consider the chemistry of silicon in Chapter 14.

Bonding in Solids I: The Electron-Sea Model of Metallic Bonding

The simplest model that accounts for the properties of metals is the **electron-sea model.** It proposes that all the metal atoms in a sample pool their valence electrons to form an electron "sea" that is delocalized throughout the piece. The metal ions (nuclei plus core electrons) are submerged within this electron sea in an orderly array (see Figure 9.2C). They are not held in place as rigidly as the ions in an ionic solid, and no two metal atoms are bonded through a localized pair of electrons as in a covalent bond. Rather, *the valence electrons are shared among all the atoms in the sample,* and the piece of metal is held together by the mutual attraction of the metal cations for the mobile, highly delocalized valence electrons. The *regularity,* but not rigidity, of the metal-ion array and the *mobility* of the valence electrons account for three major physical properties of metals:

1. *Phase changes.* Metals have moderate to high melting points because the attractions between the cations and the delocalized electrons are not broken during melting, but boiling points are very high because each cation and its electron(s) must break away from the others. Gallium provides a striking example: it melts in your hand (mp 29.8°C) but doesn't boil until 2403°C. The alkaline earth metals [Group 2A(2)] have higher melting points than the alkali metals [Group 1A(1)] because of greater attraction between their 2+ cations and twice the number of valence electrons.

2. *Mechanical properties.* When struck by a hammer, metals usually bend or dent rather than crack or shatter. Instead of repelling each other, the metal cations slide past each other through the electron sea and end up in new positions (Figure 12.31). Compare this behavior with that of an ionic solid (see Figure 9.8). As a result, many metals can be flattened into sheets (malleable) and pulled into wires (ductile). Gold is in a class by itself: 1 g of gold (a cube 0.37 cm on a side) can be hammered into a 1.0-m^2 sheet that is only 230 atoms (50 nm) thick or drawn into a wire 165 m long and 20 μm thick!

3. *Conductivity.* Metals are good electrical conductors because the mobile electrons carry current. Metals conduct heat well because the mobile electrons disperse heat more quickly than do the localized electron pairs or fixed ions in other materials.

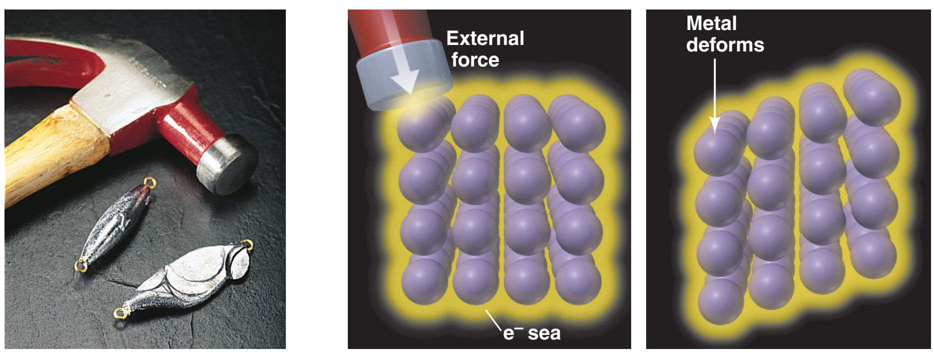


Figure 12.31 Why metals dent and bend rather than crack.

Bonding in Solids II: Band Theory

Molecular orbital (MO) theory offers another explanation of bonding in solids. It is a more quantitative, and therefore more useful, model called **band theory.** We'll focus on bonding in metals and the conductivity of metals, metalloids, and nonmetals.

Formation of Valence and Conduction Bands Recall from Section 11.3 that when two atoms form a diatomic molecule, their atomic orbitals (AOs) combine to

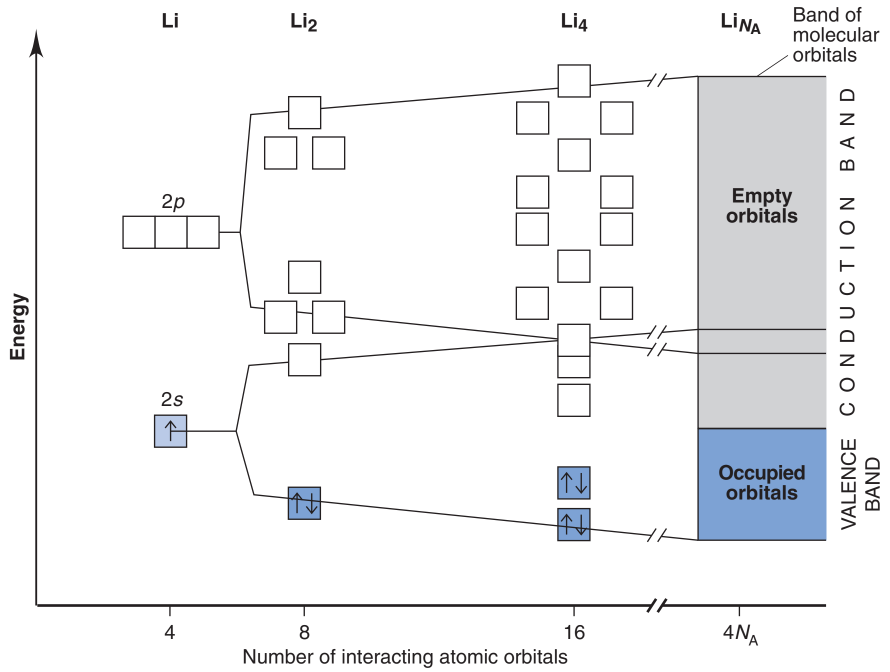


Figure 12.32 The band of molecular orbitals in lithium metal.

form an equal number of molecular orbitals (MOs). Figure 12.32 shows the formation of MOs in lithium. To form Li_2, each Li atom has four valence orbitals (one 2*s* and three 2*p*) that combine to form eight MOs, four bonding and four antibonding. The order of MOs shows 2*s*-2*p* mixing (Figure 11.19B). Two more Li atoms form Li_4, a slightly larger aggregate, with 16 delocalized MOs. As more Li atoms join the cluster, more MOs are created, and their energy levels lie closer and closer together. Extending this process to 7 g (1 mol) of lithium results in 6×10^{23} Li atoms (Li_{N_A}) combining to form an extremely large number (4 × Avogadro's number) of delocalized MOs. *The energies of the MOs are so close that they form a continuum, or band, of MOs.*

The lower energy MOs are occupied by the $2s^1$ valence electrons and make up the **valence band.** The empty MOs that are higher in energy make up the **conduction band.** In Li metal, the valence band is derived from the 2*s* AOs, and the conduction band is derived from 2*s* and mostly 2*p* AOs. In Li_2, two valence electrons fill the lowest energy bonding MO and leave the antibonding MO empty. In Li metal, 1 mol of valence electrons fills the valence band and leaves the conduction band empty.

How Band Theory Explains Metallic Properties The key to understanding the properties of metals is that *the valence and conduction bands are contiguous,* that is, the highest level of one touches the lowest of the other. This means that, given an infinitesimal quantity of energy, electrons jump from the filled valence band to the unfilled conduction band: *the electrons are completely delocalized and thus free to move throughout the piece of metal.*

- *Electrical conductivity*. Metals conduct so well because an applied field easily excites the highest energy valence electrons into empty conduction orbitals, allowing them to move through the sample.
- *Luster*. With so many closely spaced levels available, electrons absorb and release photons of many frequencies as they move between the valence and conduction bands.
- *Malleability*. Under an applied force, layers of positive metal ions move past each other, always protected from mutual repulsions by the delocalized electrons (see Figure 12.31).
- *Thermal conductivity.* When a metal wire is heated, the highest energy electrons are excited and their extra energy is transferred as kinetic energy along the wire's length.

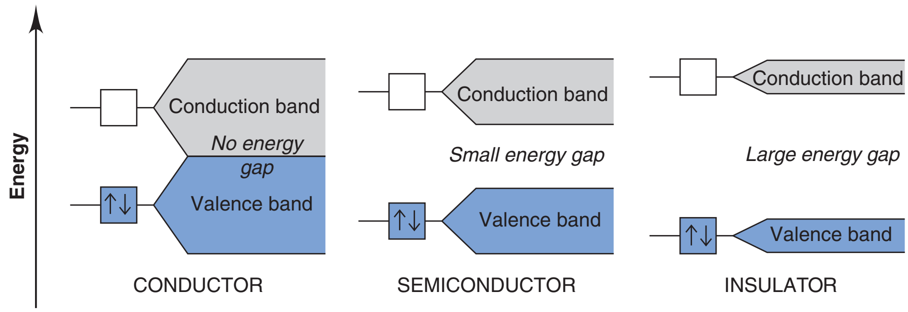


Figure 12.33 Electrical conductivity in a conductor, semiconductor, and insulator.

Conductivity of Solids and the Size of the Energy Gap Like metal atoms, large numbers of nonmetal and metalloid atoms can form bands of MOs. Band theory explains differences in electrical conductivity and the effect of temperature among these three classes of substances in terms of the presence of an energy gap between their valence and conduction bands (Figure 12.33):

1. *Conductors (metals).* The valence and conduction bands of a **conductor** have *no energy gap* between them, so electrons flow when a tiny electrical potential difference is applied. When the temperature is raised, greater random motion of the atoms hinders electron movement: conductivity *decreases* when a metal is heated.
2. *Semiconductors (metalloids).* In a **semiconductor,** a *small energy gap* exists between the valence and conduction bands. Thermally excited electrons can cross the gap, allowing a small current to flow: in contrast to a conductor, conductivity *increases* when a semiconductor is heated.
3. *Insulators (nonmetals).* In an **insulator,** a *large energy gap* exists between the bands: no current is observed even when the substance is heated.

Another type of electrical conductivity, called **superconductivity,** has been the focus of intensive research for the past few decades. When metals conduct at ordinary temperatures, moving electrons collide with vibrating atoms; the reduction in their flow appears as resistive heating and represents a loss of energy. For many years, to conduct with no energy loss—to superconduct—required minimizing this vibrational movement by cooling with liquid helium (bp $= 4$ K; price $\approx$ \$11/L). Then, in 1986, certain ionic oxides that superconduct near the boiling point of liquid nitrogen (bp $= 77$ K; price $=$ \$0.20/L) were prepared.

Like metal conductors, oxide superconductors, such as $YBa_2Cu_3O_7$, have no gap between bands. In 1989, oxides with Bi and Tl instead of Y and Ba were synthesized and found to superconduct at 125 K; and in 1993, an oxide with Hg, Ba, and Ca, in addition to Cu and O, superconducted at 133 K. Such materials could transmit electricity with no loss of energy, allowing power plants to be located far from cities. They could be part of ultrasmall microchips for ultrafast computers, electromagnets to levitate superfast trains, and inexpensive medical diagnostic equipment with superb image clarity. However, the oxides are brittle and not easy to machine, and when warmed, the superconductivity may disappear and not return on cooling. These and related problems will involve chemists, physicists, and engineers for many years.

Summary of Section 12.6

- Particles in crystalline solids lie at points that form a structure of repeating unit cells.
- The three types of unit cells of the cubic system are simple, body-centered, and face-centered. The highest packing efficiency occurs with cubic (face-centered) and hexagonal closest packing.
- Bond angles and distances in a crystal are determined with x-ray diffraction analysis. These data are used to determine atomic radii.
- Atomic [Group 8A(18)] solids adopt cubic closest packing, with atoms held together by weak dispersion forces.
- Molecular solids have molecules at the lattice points and often adopt cubic closest packing. Combinations of intermolecular forces (dispersion, dipole-dipole, and H bonding) result in physical properties that vary greatly.

- Ionic solids crystallize with one ion filling holes in the cubic closest packed array of the other. High melting points, hardness, and low conductivity arise from strong ionic attractions.
- Most metals have a closest packed structure. Their physical properties result from the high packing efficiency and the presence of delocalized electrons.
- Atoms of network covalent solids are covalently bonded throughout the sample, so these substances have very high melting and boiling points.
- The electron-sea model of metallic bonding pictures metal atom cores aligned in a "sea" of delocalized electrons. The model accounts for phase changes, mechanical behavior, and electrical and thermal conductivity of metals.
- Band theory proposes that atomic orbitals of many atoms combine to form a continuum, or band, of molecular orbitals. Metals are electrical conductors because electrons move freely from the filled (valence) band to the empty (conduction) band. Insulators have a large energy gap between the two bands, and semiconductors have a small gap, which can be bridged by heating. Superconductors conduct with no loss of energy.

CHAPTER REVIEW GUIDE

The following sections provide many aids to help you study this chapter. (Numbers in parentheses refer to pages, unless noted otherwise.)

Learning Objectives

These are concepts and skills to review after studying this chapter.

Related section (§), sample problem (SP), and upcoming end-of-chapter problem (EP) numbers are listed in parentheses.

1. Explain how kinetic energy and potential energy determine the properties of the three states and phase changes, what occurs when heat is added or removed from a substance, and how to calculate the enthalpy change (§12.1, §12.2) (SP 12.1) (EPs 12.1–12.9, 12.15, 12.16)
2. Understand that phase changes are equilibrium processes and how vapor pressure and boiling point are related (§12.2) (SP 12.2) (EPs 12.10, 12.11, 12.13, 12.17, 12.18, 12.21)
3. Use a phase diagram to show the phases and phase changes of a substance at different conditions of pressure and temperature (§12.2) (EPs 12.12, 12.14, 12.19, 12.20, 12.22)
4. Distinguish between bonding and molecular forces, predict the relative strengths of intermolecular forces acting in a substance, and understand the impact of H bonding on physical properties (§12.3) (SPs 12.3, 12.4) (EPs 12.23–12.45)
5. Define surface tension, capillarity, and viscosity, and describe how intermolecular forces influence their magnitudes (§12.4) (EPs 12.46–12.52)
6. Understand how the macroscopic properties of water arise from its molecular properties (§12.5) (EPs 12.53–12.58)
7. Describe the three types of cubic unit cells and explain how to find the number of particles in each and how packing of spheres gives rise to each; calculate the atomic radius of an element from its crystal structure; distinguish the types of crystalline solids; explain how the electron-sea model and band theory account for the properties of metals and how the size of the energy gap explains the conductivity of substances (§12.6) (SP 12.5) (EPs 12.59–12.79)

Key Terms

These important terms appear in boldface in the chapter and are defined again in the Glossary.

Section 12.1
phase (351)
intermolecular forces (351)
phase change (351)
condensation (352)
vaporization (352)
freezing (352)
melting (fusion) (352)
sublimation (352)
deposition (352)
heat of vaporization (ΔH°_{vap}) (352)
heat of fusion (ΔH°_{fus}) (352)
heat of sublimation (ΔH°_{subl}) (353)

Section 12.2
heating-cooling curve (354)
dynamic equilibrium (357)
vapor pressure (357)
Clausius-Clapeyron equation (358)
boiling point (359)
melting point (360)
phase diagram (360)
triple point (360)
critical point (361)

Section 12.3
van der Waals radius (362)
ion-dipole force (362)
dipole-dipole force (363)
hydrogen bond (H bond) (364)
polarizability (366)
dispersion (London) force (366)

Section 12.4
surface tension (369)
capillarity (370)
viscosity (370)

Section 12.6
crystalline solid (373)
amorphous solid (373)
lattice (374)
unit cell (374)
coordination number (374)
simple cubic unit cell (374)
body-centered cubic unit cell (374)
face-centered cubic unit cell (374)
packing efficiency (376)
hexagonal closest packing (376)
cubic closest packing (376)
x-ray diffraction analysis (376)
atomic solid (379)
molecular solid (379)
ionic solid (380)
metallic solid (381)
network covalent solid (381)
electron-sea model (382)
band theory (382)
valence band (383)
conduction band (383)
conductor (384)
semiconductor (384)
insulator (384)
superconductivity (384)

Key Equations and Relationships

Numbered and screened concepts are listed for you to refer to or memorize.

12.1 Using the vapor pressure at one temperature to find the vapor pressure at another temperature (two-point form of the Clausius-Clapeyron equation) (359):

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

BRIEF SOLUTIONS TO FOLLOW-UP PROBLEMS

Compare your own solutions to these calculation steps and answers.

12.1 The scenes represent solid water at −7.00°C melting to liquid water at 16.0°C, so there are three stages.

Stage 1, $H_2O(s)$ [−7.00°C] $\longrightarrow$ $H_2O(s)$ [0.00°C]:

$q = n \times C_{water(s)} \times \Delta T = (2.25\ mol)(37.6\ J/mol{\cdot}°C)(7.00°C)$
$= 592\ J = 0.592\ kJ$

Stage 2, $H_2O(s)$ [0.00°C] $\longrightarrow$ $H_2O(l)$ [0.00°C]:

$q = n(\Delta H^\circ_{fus}) = (2.25\ mol)(6.02\ kJ/mol) = 13.5\ kJ$

Stage 3, $H_2O(l)$ [0.00°C] $\longrightarrow$ $H_2O(l)$ [16.0°C]:

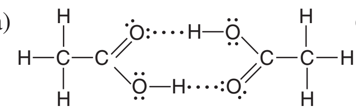
$q = n \times C_{water(l)} \times \Delta T = (2.25\ mol)(75.4\ J/mol{\cdot}°C)(16.0°C)$
$= 2714\ J = 2.71\ kJ$

Total heat (kJ) = 0.592 kJ + 13.5 kJ + 2.71 kJ = 16.8 kJ

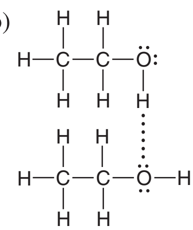
12.2
$$\ln \frac{P_2}{P_1} = \left(\frac{-40.7\times10^3\ J/mol}{8.314\ J/mol{\cdot}K}\right) \times \left(\frac{1}{273.15 + 85.5\ K} - \frac{1}{273.15 + 34.1\ K}\right)$$
$$= (-4.90\times10^3\ K)(-4.6\times10^{-4}\ K^{-1}) = 2.28$$

$\frac{P_2}{P_1} = 9.8$; thus, $P_2 = 40.1\ torr \times 9.8 = 3.9\times10^2\ torr$

12.3 (a)



(b)

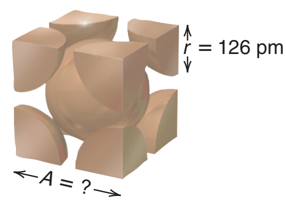


(c) No H bonding

12.4 (a) Dipole-dipole, dispersion; CH_3Br
(b) H bonds, dipole-dipole, dispersion; $CH_3CH_2CH_2OH$
(c) Dispersion; C_3H_8

12.5 From Figure 12.26 *(middle)*,

$$A = \frac{4r}{\sqrt{3}} = \frac{4(126\ pm)}{\sqrt{3}} = 291\ pm$$



PROBLEMS

Problems with **colored** numbers are answered in Appendix E. Sections match the text and provide the numbers of relevant sample problems. Bracketed problems are grouped in pairs (indicated by a short rule) that cover the same concept. Comprehensive Problems are based on material from any section or previous chapter.

An Overview of Physical States and Phase Changes

12.1 How does the energy of attraction between particles compare with their energy of motion in a gas and in a solid? As part of your answer, identify two macroscopic properties that differ between a gas and a solid.

12.2 (a) Why are gases more easily compressed than liquids? (b) Why do liquids have a greater ability to flow than solids?

12.3 What type of forces, intramolecular or intermolecular:
(a) Prevent ice cubes from adopting the shape of their container?
(b) Are overcome when ice melts?
(c) Are overcome when liquid water is vaporized?
(d) Are overcome when gaseous water is converted to hydrogen gas and oxygen gas?

12.4 (a) Why is the heat of fusion (ΔH_{fus}) of a substance smaller than its heat of vaporization (ΔH_{vap})?
(b) Why is the heat of sublimation (ΔH_{subl}) of a substance greater than its ΔH_{vap}?
(c) At a given temperature and pressure, how does the magnitude of the heat of vaporization of a substance compare with that of its heat of condensation?

12.5 Name the phase change in each of these events: (a) Dew appears on a lawn in the morning. (b) Icicles change into liquid water. (c) Wet clothes dry on a summer day.

12.6 Name the phase change in each of these events: (a) A diamond film forms on a surface from gaseous carbon atoms in a vacuum. (b) Mothballs in a bureau drawer disappear over time. (c) Molten iron from a blast furnace is cast into ingots ("pigs").

12.7 Liquid propane, a widely used fuel, is produced by compressing gaseous propane. During the process, approximately 15 kJ of energy is released for each mole of gas liquefied. Where does this energy come from?

12.8 Many heat-sensitive and oxygen-sensitive solids, such as camphor, are purified by warming under vacuum. The solid vaporizes directly, and the vapor crystallizes on a cool surface. What phase changes are involved in this method?

Quantitative Aspects of Phase Changes

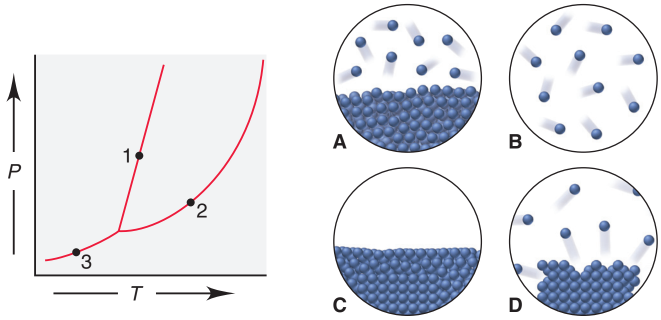
(Sample Problems 12.1 and 12.2)

12.9 Describe the changes (if any) in potential energy and in kinetic energy among the molecules when gaseous PCl_3 condenses to a liquid at a fixed temperature.

12.10 When benzene is at its melting point, two processes occur simultaneously and balance each other. Describe these processes on the macroscopic and molecular levels.

12.11 Liquid hexane (bp = 69°C) is placed in a closed container at room temperature. At first, the pressure of the vapor phase increases, but after a short time, it stops changing. Why?

12.12 Match each numbered point in the phase diagram for compound Q with the correct molecular scene:



12.13 At 1.1 atm, will water boil at 100.°C? Explain.

12.14 The phase diagram for substance A has a solid-liquid line with a positive slope, and that for substance B has a solid-liquid line with a negative slope. What macroscopic property can distinguish A from B?

12.15 From the data below, calculate the total heat (in J) needed to convert 22.00 g of ice at −6.00°C to liquid water at 0.500°C:

mp at 1 atm:	0.0°C	ΔH°_{fus}:	6.02 kJ/mol
c_{liquid}:	4.21 J/g·°C	c_{solid}:	2.09 J/g·°C

12.16 From the data below, calculate the total heat (in J) needed to convert 0.333 mol of gaseous ethanol at 300°C and 1 atm to liquid ethanol at 25.0°C and 1 atm:

bp at 1 atm:	78.5°C	ΔH°_{vap}:	38.6 kJ/mol
c_{gas}:	1.43 J/g·°C	c_{liquid}:	2.45 J/g·°C

12.17 A liquid has a ΔH°_{vap} of 35.5 kJ/mol and a boiling point of 122°C at 1.00 atm. What is its vapor pressure at 113°C?

12.18 What is the ΔH°_{vap} of a liquid that has a vapor pressure of 621 torr at 85.2°C and a boiling point of 95.6°C at 1 atm?

12.19 Use these data to draw a qualitative phase diagram for ethylene (C_2H_4). Is $C_2H_4(s)$ more or less dense than $C_2H_4(l)$?

bp at 1 atm:	−103.7°C
mp at 1 atm:	−169.16°C
Critical point:	9.9°C and 50.5 atm
Triple point:	−169.17°C and 1.20×10^{-3} atm

12.20 Use these data to draw a qualitative phase diagram for H_2. Does H_2 sublime at 0.05 atm? Explain.

mp at 1 atm:	13.96 K
bp at 1 atm:	20.39 K
Triple point:	13.95 K and 0.07 atm
Critical point:	33.2 K and 13.0 atm
Vapor pressure of solid at 10 K:	0.001 atm

12.21 Butane is a common fuel used in cigarette lighters and camping stoves. Normally supplied in metal containers under pressure, the fuel exists as a mixture of liquid and gas, so high temperatures may cause the container to explode. At 25.0°C, the vapor pressure of butane is 2.3 atm. What is the pressure in the container at 135°C (ΔH°_{vap} = 24.3 kJ/mol)?

12.22 Use Figure 12.8A, p. 361, to answer the following:
(a) Carbon dioxide is sold in steel cylinders under pressures of approximately 20 atm. Is there liquid CO_2 in the cylinder at room temperature (~20°C)? At 40°C? At −40°C? At −120°C?
(b) Carbon dioxide is also sold as solid chunks, called *dry ice,* in insulated containers. If the chunks are warmed by leaving them in an open container at room temperature, will they melt?
(c) If a container is nearly filled with dry ice and then sealed and warmed to room temperature, will the dry ice melt?
(d) If dry ice is compressed at a temperature below its triple point, will it melt?

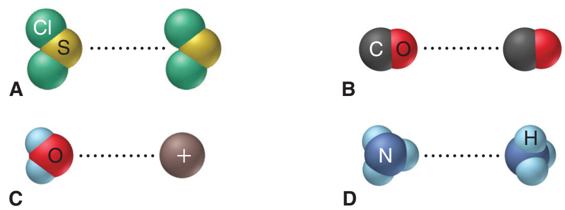
Types of Intermolecular Forces

(Sample Problems 12.3 and 12.4)

12.23 Why are covalent bonds typically much stronger than intermolecular forces?

12.24 Even though molecules are neutral, the dipole-dipole force is an important interparticle force that exists among them. Explain.

12.25 (a) Name the type of force depicted in each scene below. (b) Rank the forces in order of increasing strength.



12.26 Oxygen and selenium are members of Group 6A(16). Water forms H bonds, but H_2Se does not. Explain.

12.27 Polar molecules exhibit dipole-dipole forces. Do they also exhibit dispersion forces? Explain.

12.28 Distinguish between *polarizability* and *polarity*. How does each influence intermolecular forces?

12.29 How can one nonpolar molecule induce a dipole in a nearby nonpolar molecule?

12.30 What is the strongest interparticle force in each substance?
(a) CH_3OH (b) CCl_4 (c) Cl_2

12.31 What is the strongest interparticle force in each substance?
(a) H_3PO_4 (b) SO_2 (c) $MgCl_2$

12.32 What is the strongest interparticle force in each substance?
(a) CH_3Cl (b) CH_3CH_3 (c) NH_3

12.33 What is the strongest interparticle force in each substance?
(a) Kr (b) BrF (c) H_2SO_4

12.34 Which member of each pair of compounds forms intermolecular H bonds? Draw the H-bonded structures in each case:
(a) $CH_3\underset{\substack{|\\ OH}}{C}HCH_3$ or CH_3SCH_3 (b) HF or HBr

12.35 Which member of each pair of compounds forms intermolecular H bonds? Draw the H-bonded structures in each case:
(a) $(CH_3)_2NH$ or $(CH_3)_3N$ (b) $HOCH_2CH_2OH$ or FCH_2CH_2F

12.36 Which has the greater polarizability? Explain.
(a) Br^- or I^- (b) $CH_2{=}CH_2$ or $CH_3{-}CH_3$ (c) H_2O or H_2Se

12.37 Which has the greater polarizability? Explain.
(a) Ca^{2+} or Ca (b) CH_3CH_3 or $CH_3CH_2CH_3$ (c) CCl_4 or CF_4

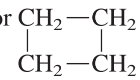
12.38 Which member in each pair of liquids has the *higher* vapor pressure at a given temperature? Explain.
(a) C_2H_6 or C_4H_{10} (b) CH_3CH_2OH or CH_3CH_2F
(c) NH_3 or PH_3

12.39 Which member in each pair of liquids has the *lower* vapor pressure at a given temperature? Explain.
(a) $HOCH_2CH_2OH$ or $CH_3CH_2CH_2OH$
(b) CH_3COOH or $(CH_3)_2C{=}O$ (c) HF or HCl

12.40 Which substance has the *lower* boiling point? Explain.
(a) LiCl or HCl (b) NH_3 or PH_3 (c) Xe or I_2

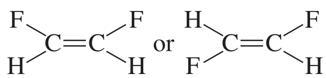
12.41 Which substance has the *higher* boiling point? Explain.
(a) CH_3CH_2OH or $CH_3CH_2CH_3$ (b) NO or N_2
(c) H_2S or H_2Te

12.42 Which substance has the *lower* boiling point? Explain.
(a) $CH_3CH_2CH_2CH_3$ or



(b) NaBr or PBr_3
(c) H_2O or HBr

12.43 Which substance has the *higher* boiling point? Explain.
(a) CH_3OH or CH_3CH_3
(b) FNO or ClNO
(c)



12.44 Dispersion forces are the only intermolecular forces present in motor oil, yet it has a high boiling point. Explain.

12.45 Why does the antifreeze ingredient ethylene glycol ($HOCH_2CH_2OH$; $\mathcal{M} = 62.07$ g/mol) have a boiling point of 197.6°C, whereas propanol ($CH_3CH_2CH_2OH$; $\mathcal{M} = 60.09$ g/mol), a compound with a similar molar mass, has a boiling point of only 97.4°C?

Properties of the Liquid State

12.46 Before the phenomenon of surface tension was understood, physicists described the surface of water as being covered with a "skin." What causes this skinlike phenomenon?

12.47 Small, equal-sized drops of oil, water, and mercury lie on a waxed floor. How does each liquid behave? Explain.

12.48 Does the *strength* of the intermolecular forces in a liquid change as the liquid is heated? Explain. Why does liquid viscosity decrease with rising temperature?

12.49 Rank the following in order of *increasing* surface tension at a given temperature, and explain your ranking:
(a) $CH_3CH_2CH_2OH$ (b) $HOCH_2CH(OH)CH_2OH$
(c) $HOCH_2CH_2OH$

12.50 Rank the following in order of *decreasing* surface tension at a given temperature, and explain your ranking:
(a) CH_3OH (b) CH_3CH_3 (c) $H_2C{=}O$

12.51 Use Figure 12.1, p. 353 to answer the following: (a) Does it take more heat to melt 12.0 g of CH_4 or 12.0 g of Hg? (b) Does it take more heat to vaporize 12.0 g of CH_4 or 12.0 g of Hg? (c) What is the principal intermolecular force in each sample?

12.52 Pentanol ($C_5H_{11}OH$; $\mathcal{M} = 88.15$ g/mol) has nearly the same molar mass as hexane (C_6H_{14}; $\mathcal{M} = 86.17$ g/mol) but is more than 12 times as viscous at 20°C. Explain.

The Uniqueness of Water

12.53 For what types of substances is water a good solvent? For what types is it a poor solvent? Explain.

12.54 A water molecule can engage in as many as four H bonds. Explain.

12.55 Warm-blooded animals have a narrow range of body temperature because their bodies have a high water content. Explain.

12.56 A drooping plant can be made upright by watering the ground around it. Explain.

12.57 Describe the molecular basis of the property of water responsible for the presence of ice on the surface of a frozen lake.

12.58 Describe in molecular terms what occurs when ice melts.

The Solid State: Structure, Properties, and Bonding

(Sample Problem 12.5)

12.59 What is the difference between an amorphous solid and a crystalline solid on the macroscopic and molecular levels? Give an example of each.

12.60 How are a solid's unit cell and crystal structure related?

12.61 For structures consisting of identical atoms, how many atoms are contained in the simple, body-centered, and face-centered cubic unit cells? Explain how you obtained the values.

12.62 List four physical characteristics of a solid metal.

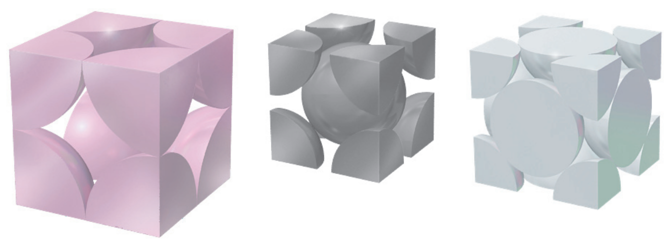
12.63 Briefly account for the following relative values:
(a) The melting point of sodium is 89°C, whereas that of potassium is 63°C.
(b) The melting points of Li and Be are 180°C and 1287°C, respectively.
(c) Lithium boils more than 1100°C higher than it melts.

12.64 Magnesium metal is easily deformed by an applied force, whereas magnesium fluoride is shattered. Why do these two solids behave so differently?

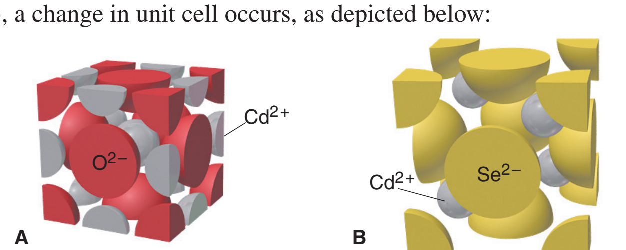
12.65 What is the energy gap in band theory? Compare its size in superconductors, conductors, semiconductors, and insulators.

12.66 What type of crystal lattice does each metal form? (The number of atoms per unit cell is given in parentheses.)
(a) Ni (4) (b) Cr (2) (c) Ca (4)

12.67 What is the number of atoms per unit cell for each metal?
(a) Polonium, Po (b) Manganese, Mn (c) Silver, Ag

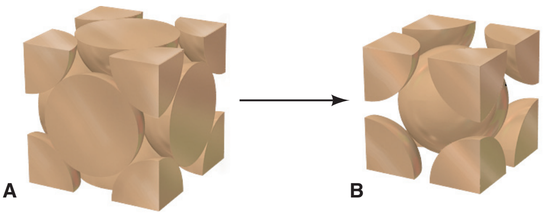


12.68 When cadmium oxide (A) reacts to form cadmium selenide (B), a change in unit cell occurs, as depicted below:



(a) What is the change in unit cell?
(b) Does the coordination number of cadmium change? Explain.

12.69 As molten iron cools to 1674 K, it adopts one type of cubic unit cell (A); then, as the temperature drops below 1181 K, it changes to another (B), as depicted below:



(a) What is the change in unit cell?
(b) Which crystal structure has the greater packing efficiency?

12.70 Of the five major types of crystalline solid, which does each of the following form, and why: (a) Ni; (b) F_2; (c) CH_3OH; (d) Sn; (e) Si; (f) Xe?

12.71 Of the five major types of crystalline solid, which does each of the following form, and why: (a) SiC; (b) Na_2SO_4; (c) SF_6; (d) cholesterol ($C_{27}H_{45}OH$); (e) KCl; (f) BN?

12.72 Zinc oxide adopts the zinc blende crystal structure (Figure P12.72). How many Zn^{2+} ions are in the ZnO unit cell?

12.73 Calcium sulfide adopts the sodium chloride crystal structure (Figure P12.73). How many S^{2-} ions are in the CaS unit cell?

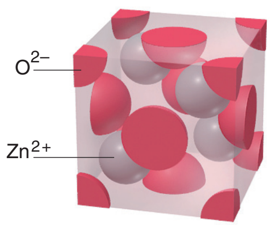


Figure P12.72

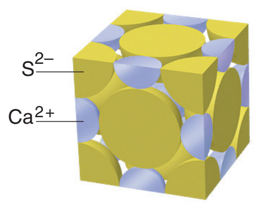


Figure P12.73

12.74 Zinc selenide (ZnSe) crystallizes in the zinc blende structure (see Figure P12.72) and has a density of 5.42 g/cm^3.
(a) How many Zn and Se ions are in each unit cell?
(b) What is the mass of a unit cell?
(c) What is the volume of a unit cell?
(d) What is the edge length of a unit cell?

12.75 An element crystallizes in a face-centered cubic lattice and has a density of 1.45 g/cm^3. The edge of its unit cell is 4.52×10^{-8} cm.
(a) How many atoms are in each unit cell?
(b) What is the volume of a unit cell?
(c) What is the mass of a unit cell?
(d) Calculate an approximate atomic mass for the element.

12.76 Classify each of the following as a conductor, insulator, or semiconductor: (a) phosphorus; (b) mercury; (c) germanium.

12.77 Predict the effect (if any) of an increase in temperature on the electrical conductivity of (a) antimony; (b) tellurium; (c) bismuth.

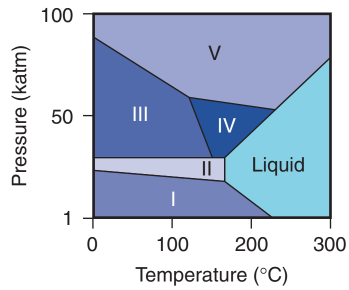
12.78 Use condensed electron configurations to predict the relative hardnesses and melting points of rubidium ($Z = 37$), vanadium ($Z = 23$), and cadmium ($Z = 48$).

12.79 One of the most important enzymes in the world—nitrogenase, the plant protein that catalyzes nitrogen fixation—contains active clusters of iron, sulfur, and molybdenum atoms. Crystalline molybdenum (Mo) has a body-centered cubic unit cell (d of Mo $= 10.28$ g/cm^3). (a) Determine the edge length of the unit cell. (b) Calculate the atomic radius of Mo.

12.80 Barium is the largest nonradioactive alkaline earth metal. It has a body-centered cubic unit cell and a density of 3.62 g/cm^3. What is the atomic radius of barium? (*Hint:* The reciprocal of a metal's density multiplied by its molar mass gives cm^3/mol of the metal, which includes the space between atoms; volume of a sphere: $V = \frac{4}{3}\pi r^3$.)

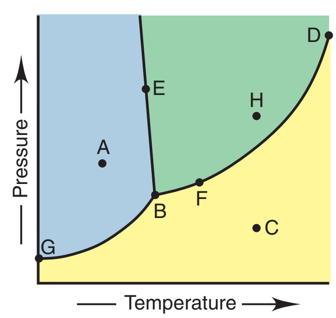
Comprehensive Problems

12.81 Bismuth is used to calibrate instruments employed in high-pressure studies because it has several well-characterized crystalline phases. Its phase diagram *(right)* shows the liquid phase and five solid phases that are stable above 1 katm (1000 atm) and up to 300°C. (a) Which solid phases are stable at 25°C? (b) Which phase is stable at 50 katm and 175°C? (c) As the pressure is reduced from 100 to 1 katm at 200°C, what phase transitions does bismuth undergo? (d) What phases are present at each of the triple points?



12.82 Mercury (Hg) vapor is toxic and readily absorbed from the lungs. At 20.°C, mercury ($\Delta H_{vap} = 59.1$ kJ/mol) has a vapor pressure of 1.20×10^{-3} torr, which is high enough to be hazardous. To reduce the danger to workers in processing plants, Hg is cooled to lower its vapor pressure. At what temperature would the vapor pressure of Hg be at the safer level of 5.0×10^{-5} torr?

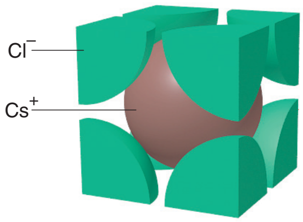
12.83 Consider the phase diagram shown for substance X.
(a) What phase(s) is (are) present at point A? E? F? H? B? C?
(b) Which point corresponds to the critical point? Which point corresponds to the triple point?
(c) What curve corresponds to conditions at which the solid and gas are in equilibrium?
(d) Describe what happens when you start at point A and increase the temperature at constant pressure.
(e) Describe what happens when you start at point H and decrease the pressure at constant temperature.
(f) Is liquid X more or less dense than solid X?



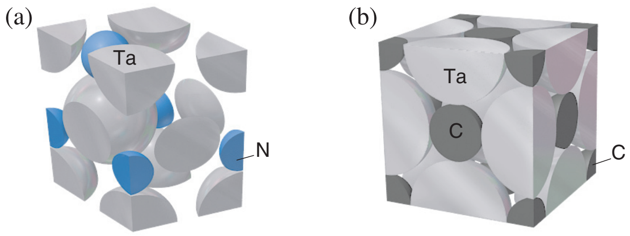
12.84 Some oxide superconductors adopt a crystal structure similar to that of *perovskite* ($CaTiO_3$). The unit cell is cubic with a Ti^{4+} ion in each corner, a Ca^{2+} ion in the body center, and O^{2-} ions at the midpoint of each edge. (a) Is this unit cell simple, body-centered, or face-centered? (b) If the unit cell edge length is 3.84 Å, what is the density of perovskite (in g/cm^3)?

12.85 Iron crystallizes in a body-centered cubic structure. The volume of one Fe atom is 8.38×10^{-24} cm^3, and the density of Fe is 7.874 g/cm^3. Find an approximate value for Avogadro's number.

12.86 The only alkali metal halides that do not adopt the NaCl structure are CsCl, CsBr, and CsI, formed from the largest alkali metal cation and the three largest halide ions. These crystallize in the *cesium chloride structure* (shown here for CsCl). This structure has been used as an example of how dispersion forces can dominate in the presence of ionic forces. Use the ideas of coordination number and polarizability to explain why the CsCl structure exists.

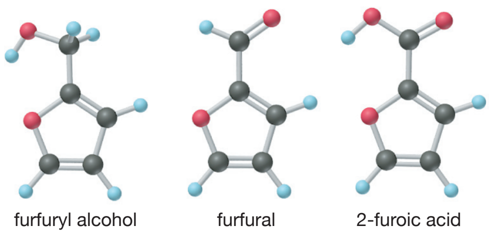


12.87 Like most transition metals, tantalum (Ta) exhibits several oxidation states. Give the formula of each tantalum compound whose unit cell is depicted below:



12.88 KF has the same type of crystal structure as NaCl. The unit cell of KF has an edge length of 5.39 Å. Find the density of KF.

12.89 Furfural, which is prepared from corncobs, is an important solvent in synthetic rubber manufacturing, and it is reduced to furfuryl alcohol, which is used to make polymer resins. Furfural can also be oxidized to 2-furoic acid.



(a) Which of these compounds can form H bonds? Draw structures in each case.
(b) The molecules of some substances can form an "internal" H bond, that is, an H bond *within* a molecule. This takes the form of a polygon with atoms as corners and bonds as sides and an H bond as one of the sides. Which of these molecules is (are) likely to form a stable internal H bond? Draw the structure. (*Hint:* Structures with 5 or 6 atoms as corners are most stable.)

12.90 A cubic unit cell contains atoms of element A at each corner and atoms of element Z on each face. What is the empirical formula of the compound?

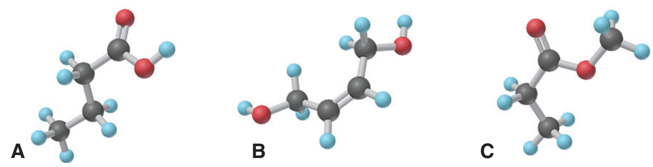
12.91 Is it possible for a salt of formula AB_3 to have a face-centered cubic unit cell of anions with cations in all eight of the available holes? Explain.

12.92 A 4.7-L sealed bottle containing 0.33 g of liquid ethanol, C_2H_6O, is placed in a refrigerator and reaches equilibrium with its vapor at -11°C. (a) What mass of ethanol is present in the vapor? (b) When the container is removed and warmed to room temperature, 20.°C, will all the ethanol vaporize? (c) How much liquid ethanol would be present at 0.0°C? The vapor pressure of ethanol is 10. torr at -2.3°C and 40. torr at 19°C.

12.93 In a body-centered cubic unit cell, the central atom lies on an internal diagonal of the cell and touches the corner atoms.

(a) Find the length of the diagonal in terms of *r*, the atomic radius. (b) If the edge length of the cube is *a*, what is the length of a *face* diagonal? (c) Derive an expression for *a* in terms of *r*. (d) How many atoms are in this unit cell? (e) What fraction of the unit cell volume is filled with spheres?

12.94 The ball-and-stick models below represent three compounds with the same molecular formula, $C_4H_8O_2$:



(a) Which compound(s) can form intermolecular H bonds?
(b) Which has the highest viscosity?