9 Liquids and Solids

The painting shows water in two of its physical states: liquid and solid.

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See plastic Nature working
to this end,
The single atoms each to
other tend,
Attract, attracted to, the
next in place
Form'd and impell'd its
neighbour to embrace.

—ALEXANDER POPE
From *An Essay on Man: Epistle III*

Chapter Outline

In Chapter 5, we pointed out that at ordinary temperatures and pressures, all gases follow the ideal gas law. In this chapter we will examine liquids and solids. Unfortunately, there are no simple relations analogous to the ideal gas law that correlate the properties of these two physical states.

- In Section 9-1 we will compare some of the properties of the three different phases and give two reasons for this difference in behavior.
- Section 9-2 will focus on the different phases of a pure substance. We will consider different phenomena related to gas-liquid equilibria, including *vapor pressure*, *boiling point behavior*, and *critical properties*.
- Section 9-3 deals with phase diagrams, which describe all these types of phase equilibria (gas-liquid, gas-solid, and liquid-solid).
- Section 9-4 explores the relationship between particle structure, interparticle forces, and physical properties in molecular substances.
- Section 9-5 extends the discussion to nonmolecular solids (network covalent, ionic, and metallic).
- Section 9-6 is devoted to the crystal structure of ionic and metallic solids.

9-1 Comparing Solids, Liquids, and Gases

Why are liquids and solids so different from gases? There are two reasons for this difference in behavior.

1. *Molecules are much closer to one another in liquids and solids.* In the gas state, particles are typically separated by ten molecular diameters or more; in liquids and solids, they touch one another. This explains why liquids and solids have densities so much larger than those of gases. At 100°C, 1 atm, water ($H_2O(l)$) has a density of 0.95 g/mL; that of steam ($H_2O(g)$) under the same condition is only 0.00059 g/mL (Table 9.1). Because of such small numbers for gas densities, they are usually given in g/L, whereas those of liquids and solids are in g/mL.

Table 9.1 Comparison of the Three Phases of Water

Phase	Molecular Spacing	Density	Volume of One Mole
Steam ($H_2O(g)$)		at 100°C, 1 atm 0.00059 g/mL	at 100°C, 1 atm 31 L
Water ($H_2O(l)$)		at 100°C, 1 atm 0.95 g/mL	19 mL
Ice ($H_2O(s)$)		at 0°C, 1 atm 0.92 g/mL	20 mL

Table 9.1 also shows that the volume of one mole of water and one mole of ice are similar, whereas that of steam is about 1500 times greater. The low density and large molar volume of steam result from the large separation between the water molecules.

For the same reason, liquids and solids are much less compressible than gases. When the pressure on liquid water is increased from 1 to 2 atm, the volume decreases by about 0.0045%. The same change in pressure reduces the volume of an equal amount of ideal gas by 50%.

2. *Intermolecular forces, which are essentially negligible with gases, play a much more important role in liquids and solids.* Among the effects of these forces is the phenomenon of *surface tension,* shown by liquids. Molecules at the surface are attracted inward by unbalanced intermolecular forces; as a result, liquids tend to form spherical drops, for which the ratio of surface area to volume is as small as possible (Figure 9.1). Water, in which there are relatively strong intermolecular forces, has a high surface tension. That of most organic liquids is lower, which explains why they tend to "wet" or spread out on solid surfaces more readily than water. The wetting ability of water can be increased by adding a soap or detergent, which drastically lowers the surface tension.

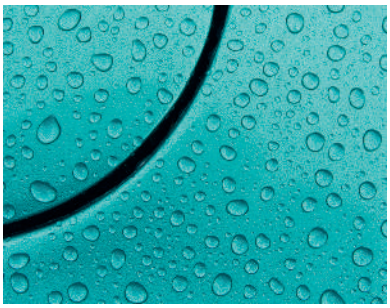

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Figure 9.1 Surface tension causes water to bead on the polished surface of a car.

9-2 Liquid-Vapor Equilibrium

All of us are familiar with the process of vaporization, in which a liquid is converted to a gas, commonly referred to as a *vapor.* In an open container, *evaporation* continues until all the liquid is gone. If the container is closed, the situation is quite different. At first, the movement of molecules is primarily in one direction, from liquid to vapor. Here, however, the vapor molecules cannot escape from the container. Some of them collide with the surface and re-enter the liquid. As time passes and the concentration of molecules in the vapor increases, so does the rate of condensation. When the rate of condensation becomes equal to the rate of vaporization, the liquid and vapor are in a state of dynamic **equilibrium**:

$$\text{liquid} \rightleftharpoons \text{vapor}$$

The double arrow implies that the forward and reverse processes are occurring at the same rate, which is characteristic of a dynamic equilibrium (Figure 9.2). The vapor, like any gas, can be assumed to obey the ideal gas law.

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Figure 9.2 Liquid-vapor equilibrium. Under the conditions shown, the bromine liquid and vapor have established a dynamic equilibrium.

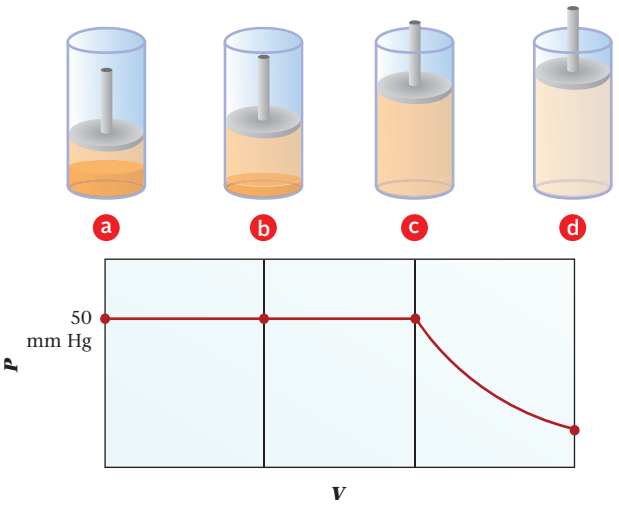


Figure 9.3 The pressure of a vapor in equilibrium with a liquid is independent of the volume of the container. The volumes of the cylinders in the figure are determined by the movable piston. In A and B, some liquid remains. In C all the liquid is just vaporized. A further increase in volume in D decreases the pressure in accordance with Boyle's law.

Vapor Pressure

Once equilibrium between liquid and vapor is reached, the number of molecules per unit volume in the vapor does not change with time. This means that ***the pressure exerted by the vapor over the liquid remains constant.*** The pressure of vapor in equilibrium with a liquid is called the **vapor pressure.** This quantity is a characteristic property of a given liquid at a particular temperature. It varies from one liquid to another, depending on the strength of the intermolecular forces. At 25°C, the vapor pressure of water is 24 mm Hg; that of ether, in which intermolecular forces are weaker, is 537 mm Hg.

It is important to realize that ***so long as both liquid and vapor are present, the pressure exerted by the vapor is independent of the volume of the container.*** If a small amount of liquid is introduced into a closed container, some of it will vaporize, establishing its equilibrium vapor pressure. The greater the volume of the container, the greater will be the amount of liquid that vaporizes to establish that pressure. The ratio n/V stays constant, so $P = nRT/V$ does not change. Only if all the liquid vaporizes will the pressure drop below the equilibrium value (Figure 9.3).

EXAMPLE 9.1 GRADED

A "cool-mist" vaporizer with capacity 2.00 L is used to add moisture to dry air in a room at 25°C. The room has dimensions 12 ft by 12 ft by 8 ft. The vapor pressure of water at 25°C is 24 mm Hg. Take the density of water at 25°C to be 1.00 g/mL.

a If the vaporizer runs until it is empty, what is the vapor pressure of water in the room?

ANALYSIS

Information given:	volume of vaporizer (2.00 L), T (25°C) room dimensions (12 ft × 12 ft × 8 ft) vapor pressure of water at 25°C (24 mm Hg) density of water (1.00 g/mL)
Information implied:	volume of water to be "vaporized" molar mass of H_2O ft^3 to L conversion factor R value
Asked for:	vapor pressure in the room when all the water is vaporized

STRATEGY

1. Assume that all the water in the vaporizer has been converted to vapor.
2. Find the volume of the room = volume of vapor (V).
3. Find the moles of water, n, from the vaporizer that will vaporize:

$$\text{Volume of water in vaporizer} \xrightarrow{\text{density}} \text{mass of water} \xrightarrow{\text{MM}} \text{mol water } (n)$$

4. Substitute into the ideal gas law and find P.
5. Check whether your assumption in (1) is correct.
   Calculated P from (3) > vapor pressure at 25°C: assumption wrong;
   Vapor pressure is vapor pressure of water at 25°C.
   Calculated P from (3) < vapor pressure at 25°C: assumption correct;
   Vapor pressure is calculated pressure from (3)

continued

SOLUTION

2. $V_{room} = V_{vapor}$	$(12 \times 12 \times 8)\ \text{ft}^3 \times \dfrac{28.32\ \text{L}}{1\ \text{ft}^3} = 3.3 \times 10^4\ \text{L}$
3. n_{vapor}	$2.00\ \text{L} \times \dfrac{1000\ \text{mL}}{1\ \text{L}} \times \dfrac{1.00\ \text{g}}{1\ \text{mL}} \times \dfrac{1\ \text{mol}}{18.02\ \text{g}} = 111\ \text{mol}$
4. P_{calc}	$P_{calc} = \dfrac{nRT}{V} = \dfrac{(111\ \text{mol})(0.0821\ \text{L} \cdot \text{atm/mol} \cdot \text{K})(298\ \text{K})}{3.3 \times 10^4\ \text{L}} = 0.082\ \text{atm} = 62\ \text{mm Hg}$
5. Check assumption	vapor pressure of water at 25°C = 24 mm Hg; P_{calc} = 62 mm Hg $P_{calc} > 24$ mm Hg; the assumption is wrong. The vapor pressure of water in the room is 24 mm Hg.

b How much water is required to completely saturate the air at 25°C?

ANALYSIS

Information given:	From part (a): P_{vapor} (24 mm Hg), V_{vapor} (3.3×10^4 L) T(25°C)
Information implied:	molar mass of H_2O R value
Asked for:	volume of water required to saturate the room

STRATEGY

1. Substitute into the ideal gas law to find n_{steam}.
2. Moles of vapor = moles of water. Convert to mass of water.

SOLUTION

1. n_{H_2O}	$n_{H_2O} = \dfrac{PV}{RT} = \dfrac{(24/760\ \text{atm})(3.3 \times 10^4\ \text{L})}{(0.0821\ \text{L} \cdot \text{atm/mol} \cdot \text{K})(298\ \text{K})} = 43\ \text{mol}$
2. mass_{H_2O}	$(43\ \text{mol})(18.02\ \text{g/mol}) = 7.7 \times 10^2\ \text{g}$

END POINTS

1. The volume of the room is the volume of the water vapor obtained from the vaporizer.
2. The volume of the water in the vaporizer cannot be used as V in the ideal gas law because it is the volume of a liquid, not a gas.
3. The calculations in part (b) show that about 770 grams (0.77 L) are required for saturation (100% relative humidity).

Vapor Pressure Versus Temperature

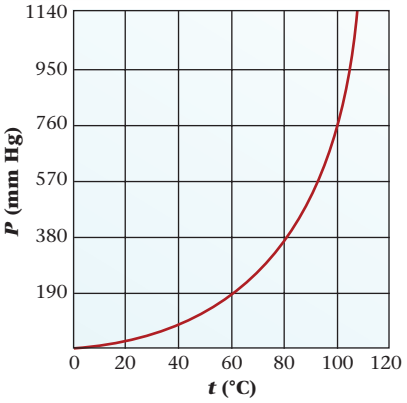
The vapor pressure of a liquid always increases as temperature rises. Water evaporates more readily on a hot, dry day. Stoppers in bottles of volatile liquids such as ether or gasoline pop out when the temperature rises.

The vapor pressure of water, which is 24 mm Hg at 25°C, becomes 92 mm Hg at 50°C and 1 atm (760 mm Hg) at 100°C. The data for water are plotted in Figure 9.4a. As you can see, the graph of vapor pressure versus temperature is not a straight line, as it would be if pressure were plotted versus temperature for an ideal gas. Instead, the slope increases steadily as temperature rises, reflecting the fact that more molecules vaporize at higher temperatures. At 100°C, the concentration of H_2O molecules in the vapor in equilibrium with liquid is 25 times as great as at 25°C.

In working with the relationship between two variables, such as vapor pressure and temperature, scientists prefer to deal with linear (straight-line) functions. Straight-line graphs are easier to construct and to interpret. In this case, it is possible to obtain a linear function by making a simple shift in variables. Instead of plotting vapor pressure (P) versus temperature (T), we plot the *natural logarithm** of the

*Many natural laws are most simply expressed in terms of natural logarithms, which are based on the number $e = 2.71828\ldots$. If $y = e^x$, then the natural logarithm of y, ln y, is equal to x (see Appendix 3).

A plot of vapor pressure vs. temperature (in °C) for a liquid is an exponentially increasing curve.



A plot of the logarithm of the vapor pressure vs. $1/T$ (in K) is a straight line. (To provide larger numbers, we have plotted $1000/T$.)

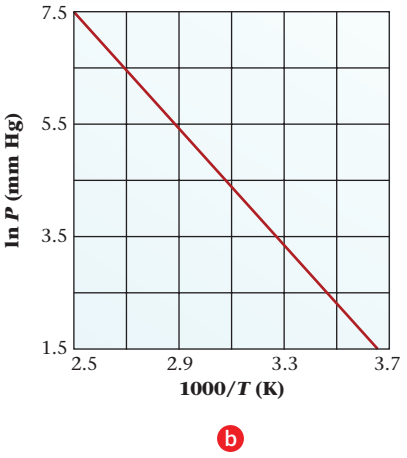


Figure 9.4 Vapor pressure versus temperature.

vapor pressure ($\ln P$) versus the reciprocal of the absolute temperature ($1/T$). Such a plot for water is shown in Figure 9.4b. As with all other liquids, a plot of $\ln P$ versus $1/T$ is a straight line.

The general equation of a straight line is

$$y = mx + b \qquad (m = \text{slope}, b = y\text{-intercept})$$

The y-coordinate in Figure 9.4b is $\ln P$, and the x-coordinate is $1/T$. The slope, which is a negative quantity, turns out to be $-\Delta H_{vap}/R$, where ΔH_{vap} is the molar heat of vaporization and R is the gas constant, in the proper units. Hence the equation of the straight line in Figure 9.4b is

$$\ln P = \frac{-\Delta H_{vap}}{RT} + b$$

For many purposes, it is convenient to have a two-point relation between the vapor pressures (P_2, P_1) at two different temperatures (T_2, T_1). Such a relation is obtained by first writing separate equations at each temperature:

$$\text{at } T_2: \qquad \ln P_2 = b - \frac{\Delta H_{vap}}{RT_2}$$

$$\text{at } T_1: \qquad \ln P_1 = b - \frac{\Delta H_{vap}}{RT_1}$$

On subtraction, the constant b is eliminated, and we obtain

$$\ln P_2 - \ln P_1 = \ln \frac{P_2}{P_1} = -\frac{\Delta H_{vap}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] = \frac{\Delta H_{vap}}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad (9.1)$$

This equation is known as the **Clausius-Clapeyron equation.** Rudolph Clausius (1822–1888) was a prestigious nineteenth-century German scientist. B. P. E. Clapeyron (1799–1864), a French engineer, first proposed a modified version of the equation in 1834.

In using the Clausius-Clapeyron equation, the units of ΔH_{vap} and R must be consistent. If ΔH is expressed in joules, then R must be expressed in joules per mole per kelvin. Recall (Table 5.1) that

$$R = 8.31 \text{ J/mol} \cdot \text{K}$$

We'll use this value of R frequently in future chapters.

This equation can be used to calculate any one of the five variables (P_2, P_1, T_2, T_1, and ΔH_{vap}), knowing the values of the other four. For example, we can use it to find the vapor pressure (P_1) at temperature T_1, knowing P_2 at T_2 and the value of the heat of vaporization (Example 9.2).

EXAMPLE 9.2

Benzene has a vapor pressure of 183 mm Hg at 40°C. Taking its heat of vaporization to be 30.8 kJ/mol, calculate its vapor pressure at 25°C.

ANALYSIS

Information given:	vapor pressure at 40°C (183 mm Hg) temperature (25°C) ΔH_{vap} (30.8 kJ/mol)
Information implied:	R value with energy units
Asked for:	pressure at 25°C

continued

STRATEGY

1. Use subscript 2 for the higher temperature, pressure pair: $P_2 = 183$ mm Hg; $T_2 = 40°C$
2. Substitute into Equation 9.1 using the appropriate R value and T in K.

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

SOLUTION

Substitute into Equation 9.1

$$\ln 183 - \ln P_1 = \frac{30.8 \text{ kJ/mol}}{8.31 \times 10^{-3} \text{ kJ/mol} \cdot \text{K}}\left[\frac{1}{298 \text{ K}} - \frac{1}{313 \text{ K}}\right]$$

$$\ln 183 = 5.209$$

$$\frac{30.8 \text{ kJ/mol}}{8.31 \times 10^{-3} \text{ kJ/mol} \cdot \text{K}}\left[\frac{1}{298 \text{ K}} - \frac{1}{313 \text{ K}}\right] = 0.596$$

P_1

$5.209 - \ln P_1 = 0.596$; $\ln P_1 = 4.613$; $P_1 =$ 101 mm Hg

END POINT

This value is reasonable. Lowering the temperature (40°C to 25°C) should decrease the pressure. The answer shows that it does (183 mm Hg to 101 mm Hg)!

Boiling Point

When a liquid is heated in an open container, bubbles form, usually at the bottom, where heat is applied. The first small bubbles are air, driven out of solution by the increase in temperature. Eventually, at a certain temperature, large vapor bubbles form throughout the liquid. These vapor bubbles rise to the surface, where they break. When this happens, the liquid is said to be boiling. For a pure liquid, the temperature remains constant throughout the boiling process.

The temperature at which a liquid boils depends on the pressure above it. To understand why this is the case, consider Figure 9.5. This shows vapor bubbles rising in a boiling liquid. For a vapor bubble to form, the pressure within it, P_1, must be at least equal to the pressure above it, P_2. Because P_1 is simply the vapor pressure of the liquid, it follows that ***a liquid boils at a temperature at which its vapor pressure is equal to the pressure above its surface.*** If this pressure is 1 atm (760 mm Hg), the temperature is referred to as the **normal boiling point.** (When the term **"boiling point"** is used without qualification, normal boiling point is implied.) The normal boiling point of water is 100°C; its vapor pressure is 760 mm Hg at that temperature.

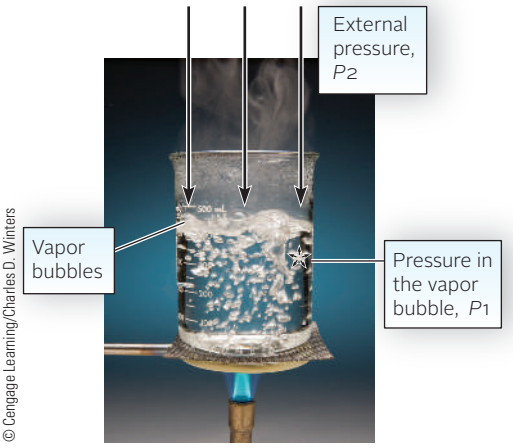


Figure 9.5 Boiling and vapor pressure. A liquid boils when it reaches the temperature at which the vapor pressure in its vapor bubbles (P_1) exceeds the pressure above the liquid (P_2).

As you might expect, the boiling point of a liquid can be reduced by lowering the pressure above it. Water can be made to boil at 25°C by evacuating the space above it. When a pressure of 24 mm Hg, the equilibrium vapor pressure at 25°C, is reached, the water starts to boil. Chemists often take advantage of this effect in purifying a high-boiling compound that might decompose or oxidize at its normal boiling point. They distill it at a reduced temperature under vacuum and condense the vapor.

If you have been fortunate enough to camp in the high Sierras or the Rockies, you may have noticed that it takes longer at high altitudes to cook foods in boiling water. The reduced pressure lowers the temperature at which water boils in an open container and thus slows down the physical and chemical changes that take place when foods like potatoes or eggs are cooked. In principle, this problem can be solved by using a pressure cooker. In that device, the pressure that develops is high enough to raise the boiling point of water

The vapor pressure of a substance at its normal bp is 760 mm Hg.

Or in the Presidential Range of New Hampshire (William L. Masterton), or in the Swiss Alps (CNH).

above 100°C. Pressure cookers are indeed used in places like Salt Lake City, Utah (elevation 1340 m, bp $H_2O(l)$ = 95°C), but not by mountain climbers, who have to carry all their equipment on their backs.

Critical Temperature and Pressure

Consider an experiment in which liquid carbon dioxide is introduced into an otherwise evacuated glass tube, which is then sealed (Figure 9.6). At 0°C, the pressure above the liquid is 34 atm, the equilibrium vapor pressure of $CO_2(l)$ at that temperature. As the tube is heated, some of the liquid is converted to vapor, and the pressure rises, to 44 atm at 10°C and 56 atm at 20°C. Nothing spectacular happens (unless there happens to be a weak spot in the tube) until 31°C is reached, where the vapor pressure is 73 atm. Suddenly, as the temperature goes above 31°C, the meniscus between the liquid and vapor disappears! The tube now contains only one phase.

It is impossible to have liquid carbon dioxide at temperatures above 31°C, no matter how much pressure is applied. Even at pressures as high as 1000 atm, carbon dioxide gas does not liquefy at 35 or 40°C. This behavior is typical of all substances. There is a temperature, called the **critical temperature,** above which the liquid phase of a pure substance cannot exist. The pressure that must be applied to cause condensation at that temperature is called the **critical pressure.** Quite simply, the critical pressure is the vapor pressure of the liquid at the critical temperature.

Table 9.2 lists the critical temperatures of several common substances. The species in the column at the left all have critical temperatures below 25°C. They are often referred to as "permanent gases." Applying pressure at room temperature will not condense a permanent gas. It must be cooled as well. When you see a truck labeled "liquid nitrogen" on the highway, you can be sure that the cargo trailer is refrigerated to at least −147°C, the critical temperature of N_2.

"Permanent gases" are most often stored and sold in steel cylinders under high pressures, often 150 atm or greater. When the valve on a cylinder of N_2 or O_2 is opened, gas escapes, and the pressure drops accordingly. The substances listed

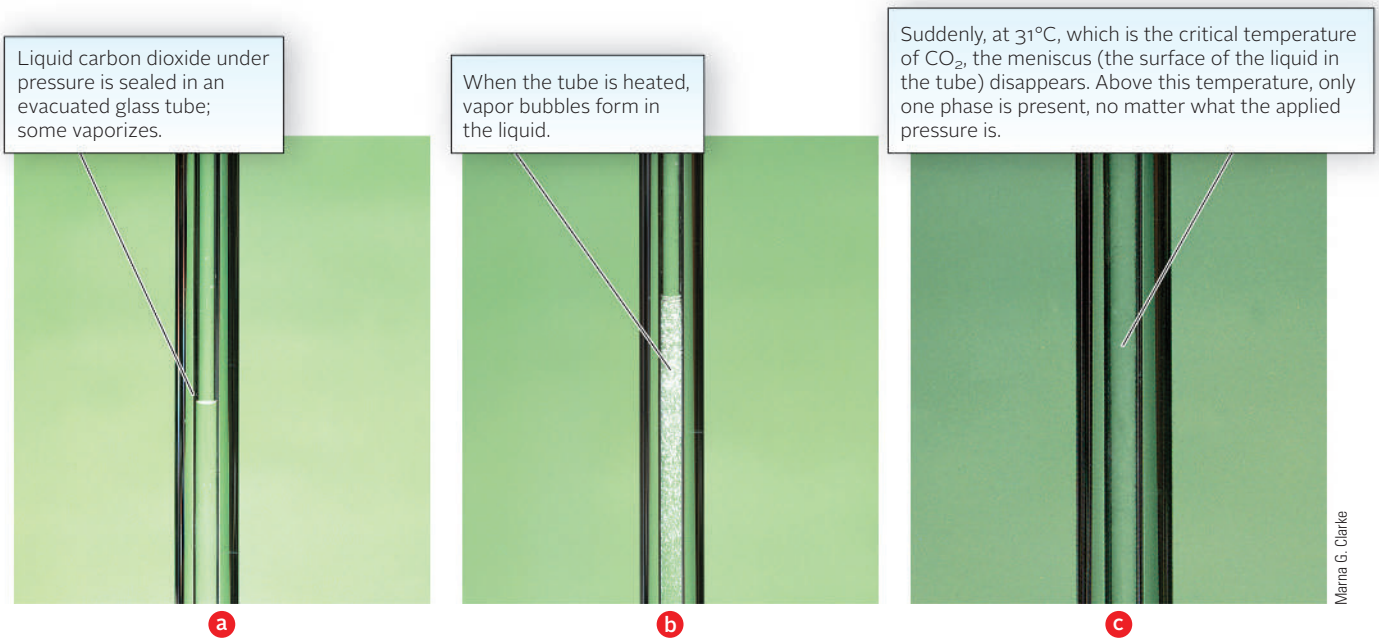


Figure 9.6 Critical temperature.

Table 9.2 Critical Temperatures (°C)

Permanent Gases		Condensable Gases		Liquids	
Helium	−268	Carbon dioxide	31	Ethyl ether	194
Hydrogen	−240	Ethane	32	Ethyl alcohol	243
Nitrogen	−147	Propane	97	Benzene	289
Argon	−122	Ammonia	132	Bromine	311
Oxygen	−119	Chlorine	144	Water	374
Methane	−82	Sulfur dioxide	158		

in the center column of Table 9.2, all of which have critical temperatures above 25°C, are handled quite differently. They are available commercially as liquids in high-pressure cylinders. When the valve on a cylinder of propane is opened, the gas that escapes is replaced by vaporization of liquid. The pressure quickly returns to its original value. Only when the liquid is completely vaporized does the pressure drop as gas is withdrawn. This indicates that almost all of the propane is gone, and it is time to recharge the tank.

A pressure gauge on a propane tank doesn't indicate how much gas you have left.

Above the critical temperature and pressure, a substance is referred to as a *supercritical fluid*. Such fluids have unusual characteristics. They can diffuse through a solid like a gas and dissolve materials like a liquid. Carbon dioxide and water are the most commonly used supercritical fluids and hold the promise of many practical new applications (see Beyond the Classroom at the end of this chapter).

9-3 Phase Diagrams

In the preceding section, we discussed several features of the equilibrium between a liquid and its vapor. For a pure substance, at least two other types of phase equilibria need to be considered. One is the equilibrium between a solid and its vapor, the other between solid and liquid at the **melting point** (also called the **freezing point**). Many of the important relations in all these equilibria can be shown in a **phase diagram.** A phase diagram is a graph that shows the pressures and temperatures at which different phases are in equilibrium with each other. The phase diagram of water is shown in Figure 9.7 (page 224). This figure, which covers a wide range of temperatures and pressures, is not drawn to scale.

To understand what a phase diagram implies, consider first curves **b** (in green) and **c** (in red) and line **a** (in blue) in Figure 9.7. Each of these shows the pressures and temperatures at which two adjacent phases are in equilibrium.

1. Curve **b** is a portion of the pressure-temperature curve of liquid water. At any temperature and pressure along this curve, liquid water is in equilibrium with water vapor. At point **X** on the curve, these two phases are in equilibrium at 0°C and about 5 mm Hg (more exactly, 0.01°C and 4.56 mm Hg). At point **Y** corresponding to 100°C, the pressure exerted by the vapor in equilibrium with liquid water is 1 atm; this is the normal boiling point of water. The extension of the curve **b** beyond point **Y** gives the equilibrium vapor pressure of water above the normal boiling point. The extension ends at 374°C, the critical temperature of water, where the pressure is 218 atm.
2. Curve **c** represents the vapor pressure curve of ice. At any point along this curve, such as point **X** (0°C, 5 mm Hg) or point **Z**, which might represent −3°C and 3 mm Hg, ice and water vapor are in equilibrium with each other.
3. Line **a** gives the temperatures and applied pressures at which liquid water is in equilibrium with ice.

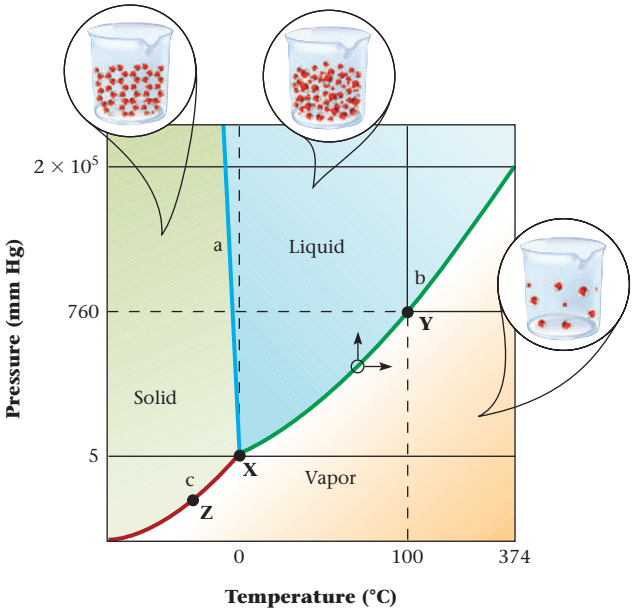


Figure 9.7 Phase diagram of water (not to scale). The curves and line represent the temperatures and pressures at which phases are in equilibrium. The triple point is at 0.01°C, 4.56 mm Hg; the critical point is at 374°C, 1.66×10^5 mm Hg (218 atm).

The equivalent of point **X** on any phase diagram is the only one at which all three phases, liquid, solid, and vapor, are in equilibrium with each other. It is called the **triple point.** For water, the triple point temperature is 0.01°C. At this temperature, liquid water and ice have the same vapor pressure, 4.56 mm Hg.

In the three areas of the phase diagram labeled solid, liquid, and vapor, only one phase is present. To understand this, consider what happens to an equilibrium mixture of two phases when the pressure or temperature is changed. Suppose we start at the point on the curve **b** indicated by an open circle. Here liquid water and vapor are in equilibrium with each other, let us say at 70°C and 234 mm Hg. If the pressure on this mixture is increased, condensation occurs. The phase diagram confirms this; increasing the pressure at 70°C *(vertical arrow)* puts us in the liquid region. In another experiment, the temperature might be increased at a constant pressure. This should cause the liquid to vaporize. The phase diagram shows that this is indeed what happens. An increase in temperature *(horizontal arrow)* shifts us to the vapor region.

EXAMPLE 9.3 CONCEPTUAL

Consider a sample of H_2O at point X in Figure 9.7.

(a) What phase(s) is (are) present?

(b) If the temperature of the sample were reduced at constant pressure, what would happen?

(c) How would you convert the sample to vapor without changing the temperature?

STRATEGY

1. Use the phase diagram in Figure 9.7.
2. Note that *P* increases moving up vertically; *T* increases moving to the right.

SOLUTION

(a) **X** is the triple point. Ice, liquid water, and water vapor are present.

(b) Move to the left to reduce *T*. This penetrates the solid area, which implies that the sample freezes completely.

(c) Reduce the pressure to below the triple point value, perhaps to 4 mm Hg.

Sublimation

The process by which a solid changes directly to vapor without passing through the liquid phase is called **sublimation.** The opposite of sublimation, the phase transition from the vapor phase to solid without passing through the liquid phase, is called **deposition.** The pressure of the solid in equilibrium with the gas is called the vapor pressure of the solid (analogous to the vapor pressure of the liquid). A solid can sublime only at temperatures below the triple point; above that temperature it will melt to liquid (Figure 9.7). At temperatures below the triple point, a solid can be made to sublime by reducing the pressure of the vapor above it to less than the equilibrium value. To illustrate what this means, consider the conditions under which ice sublimes. This happens on a cold, dry, winter day when the temperature is below 0°C and the pressure of water vapor in the air is less than the equilibrium value (4.5 mm Hg at 0°C). The rate of sublimation can be increased by evacuating the space above the ice. This is how foods are freeze-dried. The food is frozen, put into a vacuum chamber, and evacuated to a pressure of 1 mm Hg or less. The ice crystals formed on freezing sublime, which leaves a product whose mass is only a fraction of that of the original food.

Your freezer can have the conditions necessary for the sublimation of ice or the deposition of water vapor. Ice cubes left in the freezer after a period of time shrink. Ice crystals formed on meat (even in air-tight containers) provide an example of deposition. The crystals are a product of the deposition of the water vapor in the meat to ice, leaving the meat dehydrated.

Iodine sublimes more readily than ice because its triple-point pressure, 90 mm Hg, is much higher. Sublimation occurs on heating (Figure 9.8) below the triple-point temperature, 114°C. If the triple point is exceeded, the solid melts. Solid carbon dioxide (dry ice) has a triple-point pressure above 1 atm (5.2 atm at −57°C). Liquid carbon dioxide cannot exist at 1 atm pressure regardless of temperature. Solid CO_2 always passes directly to vapor if allowed to warm up in an open container.

Figure 9.8 Sublimation. Solid iodine passes directly to the vapor at any temperature below the triple point, 114°C. The vapor deposes back to a solid on a cold surface like that of the upper flask, which is filled with ice.

The white "smoke" around a piece of dry ice is $CO_2(g)$, formed by sublimation.

Melting Point

For a pure substance, the melting point is identical to the freezing point. It represents the temperature at which solid and liquid phases are in equilibrium. Melting points are usually measured in an open container, that is, at atmospheric pressure. For most substances, the melting point at 1 atm (the "normal" melting point) is virtually identical with the triple-point temperature. For water, the difference is only 0.01°C.

Although the effect of pressure on melting point is very small, its direction is still important. To decide whether the melting point will be increased or decreased by compression, a simple principle is applied. ***An increase in pressure favors the formation of the more dense phase.***

Two types of behavior are shown in Figure 9.9 (page 226).

1. *The solid is the more dense phase* (Figure 9.9a). The solid-liquid equilibrium line is inclined to the right, shifting away from the *y*-axis as it rises. At higher pressures, the solid becomes stable at temperatures above the normal melting point. In other words, the melting point is raised by an increase in pressure. This behavior is shown by most substances.

2. *The liquid is the more dense phase* (Figure 9.9b). The liquid-solid line is inclined to the left, toward the *y*-axis. An increase in pressure favors the formation of liquid; that is, the melting point is decreased by raising the pressure. Water is one of the few substances that behave this way; ice is less dense than liquid water. The effect is exaggerated for emphasis in Figure 9.9b. Actually, an increase in pressure of 134 atm is required to lower the melting point of ice by 1°C.

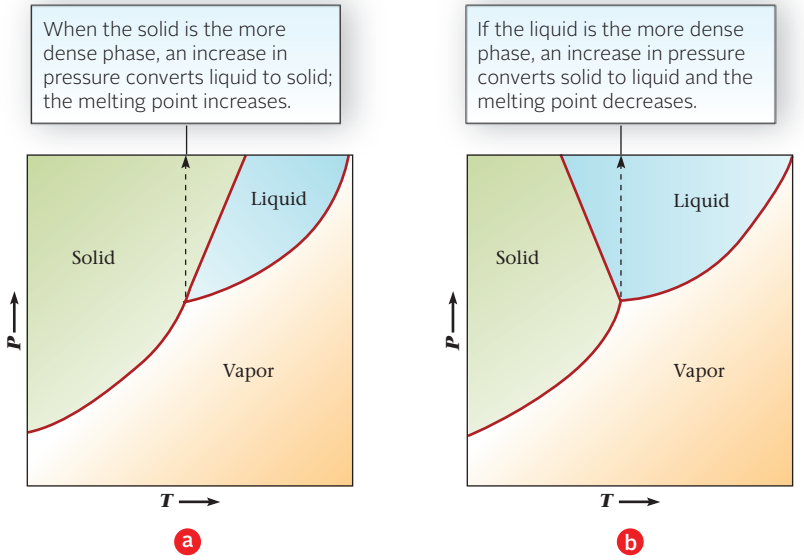


Figure 9.9 Effect of pressure on the melting point of a solid.

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Figure 9.10 Molecular liquids. The bottom layer, carbon tetrachloride (CCl_4), and the top layer, octane (C_8H_{18}), are nonpolar molecular liquids that are not soluble in water. The middle layer is a water solution of blue copper sulfate.

9-4 Molecular Substances; Intermolecular Forces

Molecules are the characteristic structural units of gases, most liquids, and many solids. As a class, molecular substances tend to have the following characteristics. They are:

1. ***Nonconductors of electricity when pure.*** Molecules are uncharged, so they cannot carry an electric current. In most cases (e.g., iodine, I_2, and ethyl alcohol, C_2H_5OH), water solutions of molecular substances are also nonconductors. A few polar molecules, including HCl, react with water to form ions:

$$HCl(g) \longrightarrow H^+(aq) + Cl^-(aq)$$

and hence produce a conducting water solution.

2. ***Insoluble in water but soluble in nonpolar solvents such as CCl_4 or benzene.*** Iodine is typical of most molecular substances; it is only slightly soluble in water (0.0013 mol/L at 25°C), much more soluble in benzene (0.48 mol/L). A few molecular substances, including ethyl alcohol, are very soluble in water. As you will see later in this section, such substances have intermolecular forces similar to those in water.

3. ***Low melting and boiling.*** Many molecular substances are gases at 25°C and 1 atm (e.g., N_2, O_2, and CO_2), which means that they have boiling points below 25°C. Others (such as octane and CCl_4) are liquids (Figure 9.10) with melting (freezing) points below room temperature. Of the molecular substances that are solids at ordinary temperatures, most are low-melting. For example, iodine melts at 114°C; the melting point of naphthalene, used in mothballs, is 80°C. The upper limit for melting and boiling points of most molecular substances is about 300°C.

The generally low melting and boiling points of molecular substances reflect the fact that the forces between molecules (**intermolecular forces**) are weak. To melt or boil a molecular substance, the molecules must be set free from one another. This requires only that enough energy be supplied to overcome the weak attractive forces between molecules. The strong covalent bonds within molecules remain intact when a molecular substance melts or boils.

It's much easier to separate two molecules than to separate two atoms within a molecule.

The boiling points of different molecular substances are directly related to the strength of the intermolecular forces involved. ***The stronger the intermolecular forces, the higher the boiling point of the substance.*** In the remainder of this section,

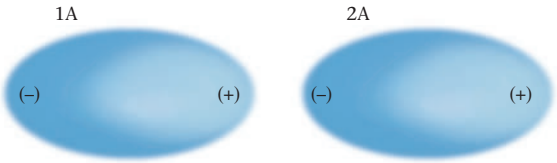


Figure 9.11 Dispersion force. Temporary dipoles in adjacent molecules line up to create an electrical attraction force known as the dispersion force. Deeply shaded areas indicate regions where the electron cloud is momentarily concentrated and creates partial charges, indicated by (+) and (−).

we examine the nature of the three different types of intermolecular forces: *dispersion forces, dipole forces,* and *hydrogen bonds.*

Dispersion (London) Forces

The most common type of intermolecular force, found in all molecular substances, is referred to as a **dispersion force.** It is basically electrical in nature, involving an attraction between temporary or *induced* dipoles in adjacent molecules. To understand the origin of dispersion forces, consider Figure 9.11.

On the average, electrons in a nonpolar molecule, such as H_2, are as close to one nucleus as to the other. However, at a given instant, the electron cloud may be concentrated at one end of the molecule (position 1A in Figure 9.11). This momentary concentration of the electron cloud on one side of the molecule creates a temporary dipole in H_2. One side of the molecule, shown in deeper color in Figure 9.11, acquires a partial negative charge; the other side has a partial positive charge of equal magnitude.

It is time to review the material in Chapter 7.

This temporary dipole induces a similar dipole (an induced dipole) in an adjacent molecule. When the electron cloud in the first molecule is at 1A, the electrons in the second molecule are attracted to 2A. These temporary dipoles, both in the same direction, lead to an attractive force between the molecules. This is the dispersion force.

All molecules have dispersion forces. The strength of these forces depends on two factors

In nonpolar molecules, dispersion is the only intermolecular force.

- the number of electrons in the atoms that make up the molecule.
- the ease with which electrons are *dispersed* to form temporary dipoles.

Both these factors increase with increasing molecular size. Large molecules are made up of more and/or larger atoms. The outer electrons in larger atoms are relatively far from the nucleus and are easier to disperse than the electrons in small atoms. In general, molecular size and molar mass parallel one another. Thus within a given class of substances (Table 9.3) we can say that ***as molar mass increases, dispersion forces become stronger and the boiling point of nonpolar molecular substances increases.***

Dispersion forces are weak in H_2, much stronger in I_2.

Table 9.3 Effect of Molar Mass on Boiling Points of Molecular Substances

Noble Gases*			Halogens			Hydrocarbons		
	MM (g/mol)	bp (°C)		MM (g/mol)	bp (°C)		MM (g/mol)	bp (°C)
He	4	−269	F_2	38	−188	CH_4	16	−161
Ne	20	−246	Cl_2	71	−34	C_2H_6	30	−88
Ar	40	−186	Br_2	160	59	C_3H_8	44	−42
Kr	84	−152	I_2	254	184	n-C_4H_{10}	58	0

*Strictly speaking, the noble gases are "atomic" rather than molecular. However, like molecules, the noble-gas atoms are attracted to one another by dispersion forces.

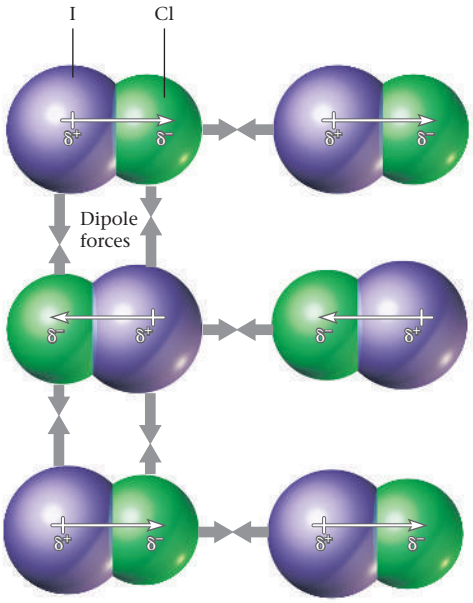


Figure 9.12 Dipole forces in the ICl crystal. The δ^+ and δ^- indicate partial charges on the I and Cl atoms in the polar molecules. The existence of these partial charges causes the molecules to line up in the pattern shown. Adjacent molecules are attracted to each other by the dipole forces between the δ^+ of one molecule and the δ^- of another molecule.

In most molecules, dispersion forces are stronger than dipole forces.

Dipole Forces

Polar molecules, like nonpolar molecules, are attracted to one another by dispersion forces. In addition, they experience **dipole forces** as illustrated in Figure 9.12, which shows the orientation of polar molecules, such as ICl, in a crystal. Adjacent molecules line up so that the negative pole of one molecule (small Cl atom) is as close as possible to the positive pole (large I atom) of its neighbor. Under these conditions, there is an electrical attractive force, referred to as a dipole force, between adjacent polar molecules.

When iodine chloride is heated to 27°C, the weak intermolecular forces are unable to keep the molecules rigidly aligned, and the solid melts. Dipole forces are still important in the liquid state, because the polar molecules remain close to one another. Only in the gas, where the molecules are far apart, do the effects of dipole forces become negligible. Hence boiling points as well as melting points of polar compounds such as ICl are somewhat higher than those of nonpolar substances of comparable molar mass. This effect is shown in Table 9.4.

Table 9.4 Boiling Points of Nonpolar Versus Polar Substances

Nonpolar			Polar		
Formula	MM (g/mol)	bp (°C)	Formula	MM (g/mol)	bp (°C)
N_2	28	−196	CO	28	−192
SiH_4	32	−112	PH_3	34	−88
GeH_4	77	−90	AsH_3	78	−62
Br_2	160	59	ICl	162	97

EXAMPLE 9.4 CONCEPTUAL

Explain, in terms of intermolecular forces, why the boiling point of O_2 (−183°C) is higher than that of N_2 (−196°C) and the boiling point of NO (−151°C) is higher than that of either O_2 or N_2.

STRATEGY

1. Draw the Lewis structure of the molecule.
2. Determine its polarity.
3. Identify the intermolecular forces present.
4. Remember that dispersion forces are always present and increase with molar mass.

SOLUTION

O_2 vs. N_2	
1. Lewis structures	:Ö=Ö: vs :N≡N:
2. Polarity	Both are nonpolar.
3. Intermolecular forces	Only dispersion forces for both O_2 and N_2
4. Strength of forces	MM_{O_2} = 32 g/mol; MM_{N_2} = 28 g/mol
	Dispersion forces of O_2 are larger.

continued

NO vs. O_2 and N_2	
1. Lewis structures	$\cdot\ddot{N}{=}\ddot{O}\cdot$; see above for O_2 and N_2
2. Polarity	NO is polar, O_2 and N_2 are nonpolar.
3. Intermolecular forces	NO: dispersion and dipole forces; O_2 and N_2 only have dispersion forces.
4. Strength of forces	MM_{O_2} = 32 g/mol; MM_{N_2} = 28 g/mol; MM_{NO} = 30 g/mol All have similar dispersion force strength. Only NO has dipole forces in addition to the dispersion forces.

Hydrogen Bonds

Ordinarily, polarity has a relatively small effect on boiling point. In the series HCl → HBr → HI, boiling point increases steadily with molar mass, even though polarity decreases moving from HCl to HI. However, when hydrogen is bonded to a small, highly electronegative atom (N, O, F), polarity has a much greater effect on boiling point. Hydrogen fluoride, HF, despite its low molar mass (20 g/mol), has the highest boiling point of all the hydrogen halides. Water (MM = 18 g/mol) and ammonia (MM = 17 g/mol) also have abnormally high boiling points (Table 9.5). In these cases, the effect of polarity reverses the normal trend expected from molar mass alone.

The unusually high boiling points of HF, H_2O, and NH_3 result from an unusually strong type of dipole force called a **hydrogen bond.** The hydrogen bond is a force exerted between an H atom bonded to an F, O, or N atom in one molecule and an unshared pair on the F, O, or N atom of a neighboring molecule:

$$:X{-}H\cdots:X{-}H \qquad X{=}N,\ O,\ \text{or}\ F$$

hydrogen bond

There are two reasons why hydrogen bonds are stronger than ordinary dipole forces:

1. The difference in electronegativity between hydrogen (2.2) and fluorine (4.0), oxygen (3.5), or nitrogen (3.0) is quite large. It causes the bonding electrons in molecules such as HF, H_2O, and NH_3 to be primarily associated with the more electronegative atom (F, O, or N). So the hydrogen atom, insofar as its interaction with a neighboring molecule is concerned, behaves almost like a bare proton.

2. The small size of the hydrogen atom allows the unshared pair of an F, O, or N atom of one molecule to approach the H atom in another very closely. It is significant that hydrogen bonding occurs only with these three nonmetals, all of which have small atomic radii.

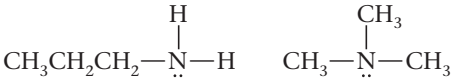
Table 9.5 Effect of Hydrogen Bonding on Boiling Point

	bp (°C)		bp (°C)		bp (°C)
NH_3	−33	H_2O	100	HF	19
PH_3	−88	H_2S	−60	HCl	−85
AsH_3	−63	H_2Se	−42	HBr	−67
SbH_3	−18	H_2Te	−2	HI	−35

Note: Molecules in blue show hydrogen bonding.

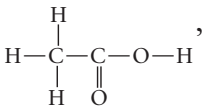
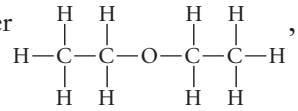
Hydrogen bonding is important in biochemistry, particularly with proteins.

Hydrogen bonds can exist in many molecules other than HF, H_2O, and NH_3. The basic requirement is simply that hydrogen be bonded to a fluorine, oxygen, or nitrogen atom with at least one unshared pair. Consider, for example, the two compounds whose condensed structural formulas are



Propylamine, in which two hydrogen atoms are bonded to nitrogen, can show hydrogen bonding; it is a liquid with a normal boiling point of 49°C. Trimethylamine, which like propylamine has the molecular formula C_3H_9N, cannot hydrogen bond to itself; it boils at 3°C.

EXAMPLE 9.5

Would you expect to find hydrogen bonds in acetic acid  , diethyl ether  , and hydrazine, N_2H_4?

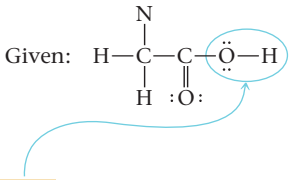
STRATEGY

1. Skeleton structures for acetic acid and diethyl ether are given; draw the Lewis structure for all three compounds.
2. For H-bonding to occur, one of the following bonds has to be present in the molecule: H—F, H—O, or H—N

SOLUTION

Acetic acid

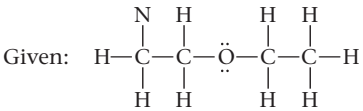
1. Lewis structure:



2. H—F, H—O, or H—N? Yes; hydrogen bonding is present.

Diethyl ether

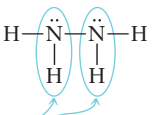
1. Lewis structure:



2. H—F, H—O, or H—N? No. The presence of O and H atoms in the molecule does not mean that H-bonding can occur.

Hydrazine

1. Lewis structure:



2. H—F, H—O, or H—N? Yes; H-bonding can occur.

END POINT

In acetic acid, the H atom bonded to oxygen in one molecule forms a hydrogen bond with an oxygen in an adjacent molecule. The same situation applies in hydrazine if you substitute nitrogen for oxygen.

Water has many unusual properties in addition to its high boiling point. As pointed out in Chapter 8, it has a very high specific heat, 4.18 J/g · °C. Its heat of vaporization per gram, 2.26 kJ/g, is the highest of all molecular substances. Both of these properties reflect the hydrogen-bonded structure of the liquid. Many of these bonds have to be broken when the liquid is heated; all of them disappear on boiling.

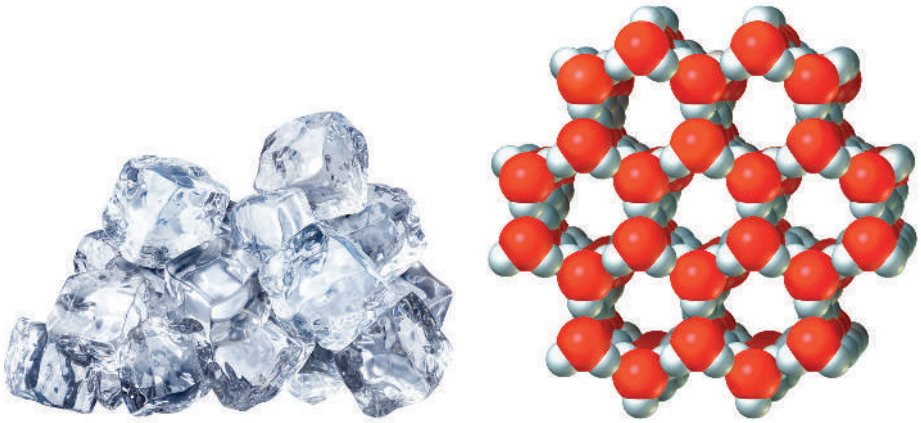


Figure 9.13 The structure of ice. In ice, the water molecules are arranged in an open pattern that gives ice its low density. Each oxygen atom (red) is bonded covalently to two hydrogen atoms (gray) and forms hydrogen bonds with two other hydrogen atoms.

In contrast to most substances, water expands on freezing. Ice is one of the very few solids that has a density less than that of the liquid from which it is formed (*d* ice at 0°C = 0.917 g/cm^3; *d* water at 0°C = 1.000 g/cm^3). This behavior is an indirect result of hydrogen bonding. When water freezes to ice, an open hexagonal pattern of molecules results (Figure 9.13). Each oxygen atom in an ice crystal is bonded to four hydrogens. Two of these are attached by ordinary covalent bonds at a distance of 0.099 nm. The other two form hydrogen bonds 0.177 nm in length. The large proportion of empty space in the ice structure explains why ice is less dense than water.

If ice were more dense than water, skating would be a lot less popular.

EXAMPLE 9.6 CONCEPTUAL

What types of intermolecular forces are present in nitrogen, N_2, chloroform, $CHCl_3$, carbon dioxide, CO_2, and ammonia, NH_3?

STRATEGY

1. Write the Lewis structure for each molecule.
2. Determine polarity. Polar molecules have dipole forces.
3. Check for the presence of H—N, H—O, and H—F bonds. The presence of these bonds indicates hydrogen bonding.
4. All molecules have dispersion forces.

SOLUTION

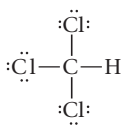
N_2

1. Lewis structure: $\ddot{N}\equiv\ddot{N}$
2. Polarity: Nonpolar—no dipole forces present
3. H—N, H—O, and H—F bonds? No. Hydrogen bonding not possible.

Intermolecular forces: dispersion forces

$CHCl_3$

1. Lewis structure:



2. Polarity: Polar—dipole forces present

continued

3. H—N, H—O, and H—F bonds?	No. Hydrogen bonding not possible.
	Intermolecular forces: dispersion and dipole forces
CO_2	
1. Lewis structure:	:Ö=C=Ö:
2. Polarity:	Nonpolar—no dipole forces present
3. H—N, H—O, and H—F bonds?	No. Hydrogen bonding not possible
	Intermolecular forces: dispersion forces
NH_3	
1. Lewis structure:	H—N—H (N bears a lone pair; H below)
2. Polarity:	Polar—dipole forces present
3. H—N, H—O, and H—F bonds?	Yes. Hydrogen bonding possible.
	Intermolecular forces: dispersion, hydrogen bonds, and dipole forces

We have now discussed three types of intermolecular forces: dispersion forces, dipole forces, and hydrogen bonds. You should bear in mind that **all these forces are relatively weak compared with ordinary covalent bonds.** Consider, for example, the situation in H_2O. The total intermolecular attractive energy in ice is about 50 kJ/mol. In contrast, to dissociate one mole of water vapor into atoms requires the absorption of 928 kJ of energy, that is, 2(OH bond energy). This explains why it is a lot easier to boil water than to decompose it into the elements. Even at a temperature of 1000°C and 1 atm, only about one H_2O molecule in a billion decomposes to hydrogen and oxygen atoms.

9-5 Network Covalent, Ionic, and Metallic Solids

Virtually all substances that are gases or liquids at 25°C and 1 atm are molecular. In contrast, there are three types of nonmolecular solids (Figure 9.14). These are

- **network covalent** solids, in which atoms are joined by a continuous network of covalent bonds. The entire crystal, in effect, consists of one huge molecule.
- **ionic solids,** held together by strong electrical forces (ionic bonds) between oppositely charged ions adjacent to one another.
- **metals,** in which the structural units are electrons (e^-) and cations, which may have charges of +1, +2, or +3.

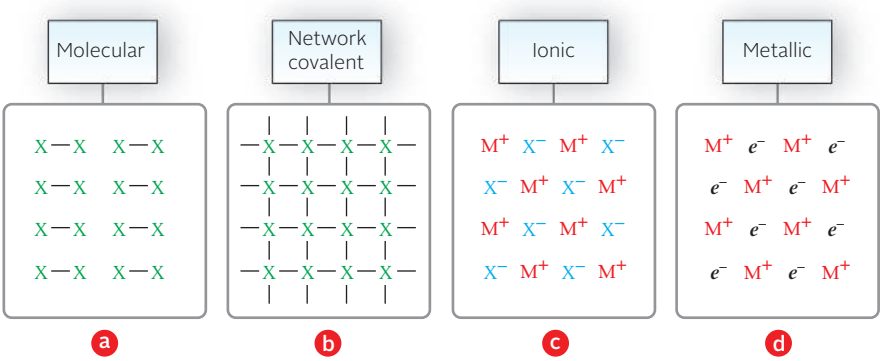


Figure 9.14 Diagrams of four types of substances (see text discussion). X represents a nonmetal atom, — represents a covalent bond, M^+ a cation, X^- an anion, and e^- an electron.

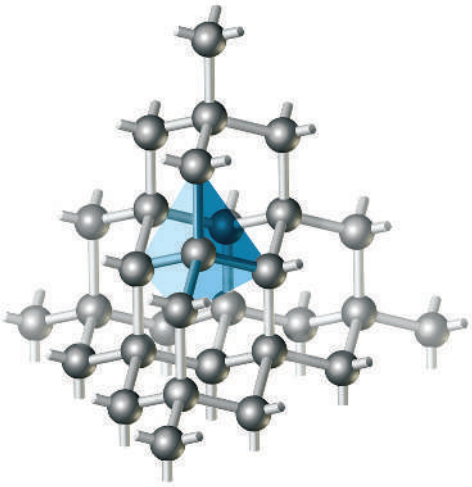


Figure 9.15 The structure of a diamond. Diamond has a three-dimensional structure in which each carbon atom is surrounded tetrahedrally by four other carbon atoms.

Network Covalent Solids

As a class, network covalent solids

- ***have high melting points, often about 1000°C.*** To melt the solid, covalent bonds between atoms must be broken. In this respect, solids of this type differ markedly from molecular solids, which have much lower melting points.
- ***are insoluble in all common solvents.*** For solution to occur, covalent bonds throughout the solid have to be broken.
- ***are poor electrical conductors.*** In most network covalent substances (graphite is an exception), there are no mobile electrons to carry a current.

Graphite and Diamond

Several nonmetallic elements and metalloids have a network covalent structure. The most important of these is carbon, which has two different crystalline forms of the network covalent type. Both graphite and diamond have high melting points, above 3500°C. However, the bonding patterns in the two solids are quite different.

In diamond, each carbon atom forms single bonds with four other carbon atoms arranged tetrahedrally around it. The hybridization in diamond is sp^3. The three-dimensional covalent bonding contributes to diamond's unusual hardness. Diamond is one of the hardest substances known; it is used in cutting tools and quality grindstones (Figure 9.15).

Hybridization is discussed in Section 7-4.

Graphite is planar, with the carbon atoms arranged in a hexagonal pattern. Each carbon atom is bonded to three others, two by single bonds, one by a double bond. The hybridization is sp^2. The forces between adjacent layers in graphite are of the dispersion type and are quite weak. A "lead" pencil really contains a graphite rod, thin layers of which rub off onto the paper as you write (Figure 9.16).

At 25°C and 1 atm, graphite is the stable form of carbon. Diamond, in principle, should slowly transform to graphite under ordinary conditions. Fortunately

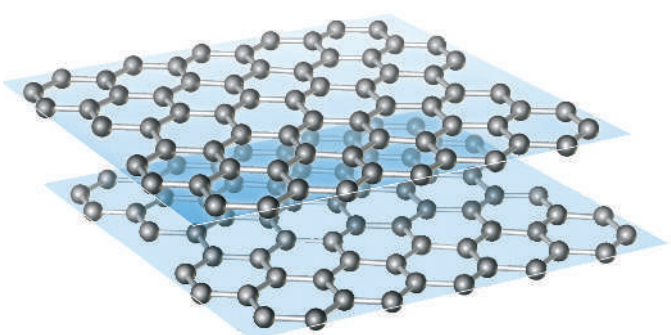


Figure 9.16 The structure of graphite. Graphite has a two-dimensional layer structure with weak dispersion forces between the layers.

for the owners of diamond rings, this transition occurs at zero rate unless the diamond is heated to about 1500°C, at which temperature the conversion occurs rapidly. For understandable reasons, no one has ever become very excited over the commercial possibilities of this process. The more difficult task of converting graphite to diamond has aroused much greater enthusiasm.

At high pressures, diamond is the stable form of carbon, since it has a higher density than graphite (3.51 vs 2.26 g/cm^3). The industrial synthesis of diamond from graphite or other forms of carbon is carried out at about 100,000 atm and 2000°C.

Compounds of Silicon

Perhaps the simplest compound with a network covalent structure is quartz, the most common form of SiO_2 and the major component of sand. In quartz, each silicon atom bonds tetrahedrally to four oxygen atoms. Each oxygen atom bonds to two silicons, thus linking adjacent tetrahedra to one another (Figure 9.17). Notice that the network of covalent bonds extends throughout the entire crystal. Unlike most pure solids, quartz does not melt sharply to a liquid. Instead, it turns to a viscous mass over a wide temperature range, first softening at about 1400°C. The viscous fluid probably contains long —Si—O—Si—O— chains, with enough bonds broken to allow flow.

More than 90% of the rocks and minerals found in the earth's crust are silicates, which are essentially ionic. Typically the anion has a network covalent structure in which SiO_4^{4-} tetrahedra are bonded to one another in one, two, or three dimensions. The structure shown at the left of Figure 9.18, where the anion is a one-dimensional infinite chain, is typical of fibrous minerals such as diopside, $CaSiO_3 \cdot MgSiO_3$. Asbestos has a related structure in which two chains are linked together to form a double strand.

The structure shown at the right of Figure 9.18 is typical of layer minerals such as talc, $Mg_3(OH)_2Si_4O_{10}$. Here SiO_4^{4-} tetrahedra are linked together to form an infinite sheet. The layers are held loosely together by weak dispersion forces, so they easily slide past one another. As a result, talcum powder, like graphite, has a slippery feeling.

Among the three-dimensional silicates are the *zeolites,* which contain cavities or tunnels in which Na^+ or Ca^{2+} ions may be trapped. Synthetic zeolites with made-to-order holes are used in home water softeners. When hard water containing Ca^{2+} ions flows through a zeolite column, an exchange reaction occurs. If we represent the formula of the zeolite as NaZ, where Z^- represents a complex, three-dimensional anion, the water-softening reaction can be represented by the equation

$$Ca^{2+}(aq) + 2NaZ(s) \longrightarrow CaZ_2(s) + 2Na^+(aq)$$

Sodium ions migrate out of the cavities; Ca^{2+} ions from the hard water move in to replace them.

This type of water softener shouldn't be used if you're trying to reduce sodium intake.

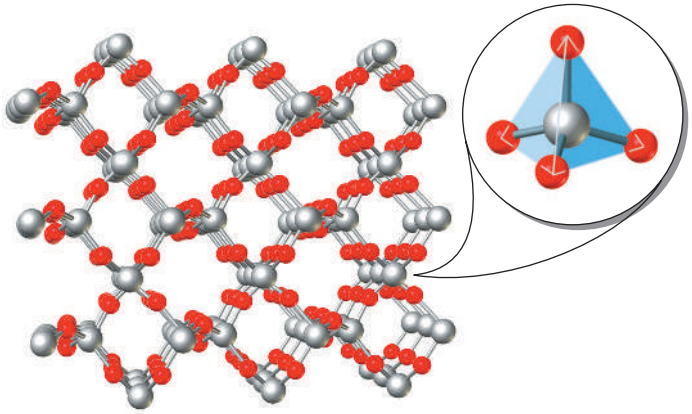


Figure 9.17 Crystal structure of quartz. The Si (gray) and O (red) atoms form six-membered rings. Each Si atom is bonded tetrahedrally to four O atoms.

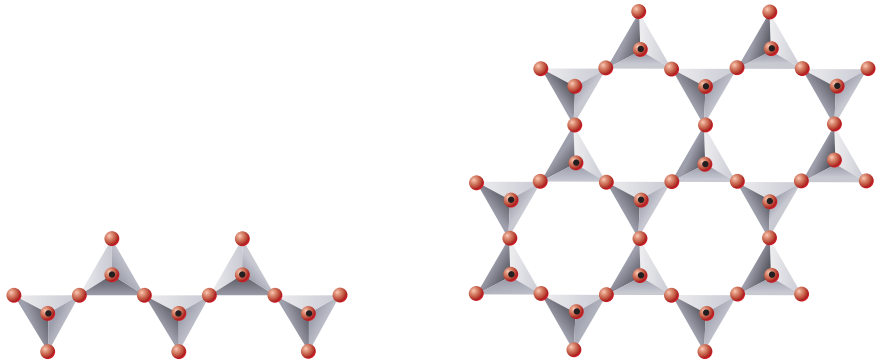


Figure 9.18 Silicate lattices. The red circles represent oxygen atoms. The black dot in the center of the red circle represents the Si atom, which is at the center of a tetrahedron. *(Left)* Diopside has a one-dimensional infinite chain. *(Right)* A portion of the talc structure, which is composed of infinite sheets.

Ionic Solids

An ionic solid consists of cations and anions (e.g., Na^+, Cl^-). No simple, discrete molecules are present in NaCl or other ionic compounds; rather, the ions are held in a regular, repeating arrangement by strong ionic bonds, electrostatic interactions between oppositely charged ions. Because of this structure, shown in Figure 9.14, ionic solids have the following properties:

1. ***Ionic solids are nonvolatile and have high-melting points*** (typically from 600°C to 2000°C). Ionic bonds must be broken to melt the solid, separating oppositely charged ions from each other. Only at high temperatures do the ions acquire enough kinetic energy for this to happen.
2. ***Ionic solids do not conduct electricity because the charged ions are fixed in position.*** They become good conductors, however, when melted or dissolved in water. In both cases, in the melt or solution, the ions (such as Na^+ and Cl^-) are free to move through the liquid and thus can conduct an electric current.
3. ***Many, but not all, ionic compounds*** (e.g., NaCl but not $CaCO_3$) ***are soluble in water, a polar solvent.*** In contrast, ionic compounds are insoluble in nonpolar solvents such as benzene (C_6H_6) or carbon tetrachloride (CCl_4).

Charged particles must move to carry a current.

The relative strengths of different ionic bonds can be estimated from Coulomb's law, which gives the electrical energy of interaction between a cation and anion in contact with one another:

$$E = \frac{k \times Q_1 \times Q_2}{d}$$

Here, Q_1 and Q_2 are the charges of anion and cation, and d, the distance between the centers of the two ions, is the sum of the ionic radii (Appendix 2):

$$d = r_{\text{cation}} + r_{\text{anion}}$$

The quantity k is a constant whose magnitude need not concern us. Because the cation and anion have opposite charges, E is a negative quantity. This makes sense; energy is evolved when two oppositely charged ions, originally far apart with $E = 0$, approach one another closely. Conversely, energy has to be absorbed to separate the ions from each other.

From Coulomb's law, the strength of the ionic bond should depend on two factors:

1. ***The charges of the ions.*** The bond in CaO (+2, −2 ions) is considerably stronger than that in NaCl (+1, −1 ions). This explains why the melting point of calcium oxide (2927°C) is so much higher than that of sodium chloride (801°C).
2. ***The size of the ions.*** The ionic bond in NaCl (mp = 801°C) is somewhat stronger than that in KBr (mp = 734°C) because the internuclear distance is smaller in NaCl:

$$d_{\text{NaCl}} = r_{\text{Na}^+} + r_{\text{Cl}^-} = 0.095 \text{ nm} + 0.181 \text{ nm} = 0.276 \text{ nm}$$
$$d_{\text{KBr}} = r_{\text{K}^+} + r_{\text{Br}^-} = 0.133 \text{ nm} + 0.195 \text{ nm} = 0.328 \text{ nm}$$

Metals

A more sophisticated model of metals is described in Appendix 4.

Figure 9.14d illustrates a simple model of bonding in metals known as the **electron-sea model.** The metallic crystal is pictured as an array of positive ions, for example, Na^+, Mg^{2+}. These are anchored in position, like buoys in a mobile "sea" of electrons. These electrons are not attached to any particular positive ion but rather can wander through the crystal. The electron-sea model explains many of the characteristic properties of metals:

1. *High electrical* conductivity. The presence of large numbers of relatively mobile electrons explains why metals have electrical conductivities several hundred times greater than those of typical nonmetals. Silver is the best electrical conductor but is too expensive for general use. Copper, with a conductivity close to that of silver, is the metal most commonly used for electrical wiring. Although a much poorer conductor than copper, mercury is used in many electrical devices, such as silent light switches, in which a liquid conductor is required.

2. *High* thermal conductivity. Heat is carried through metals by collisions between electrons, which occur frequently. Saucepans used for cooking commonly contain aluminum, copper, or stainless steel; their handles are made of a nonmetallic material that is a good thermal insulator.

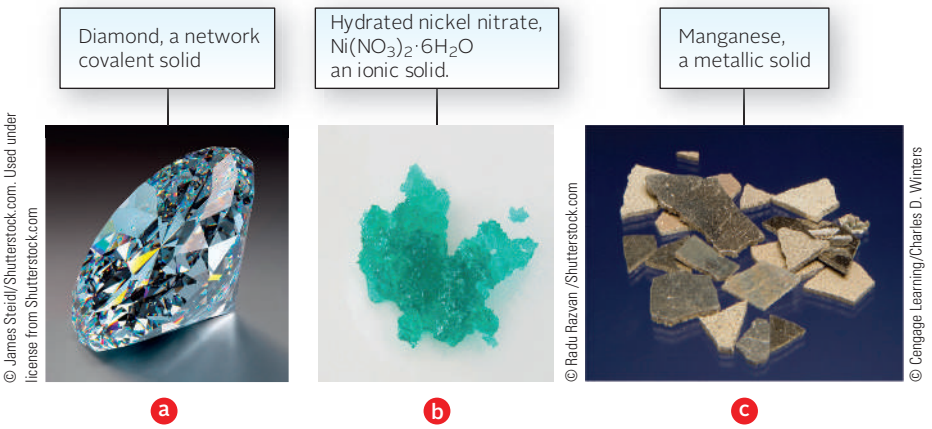
3. *Ductility and* malleability. Most metals are ductile (capable of being drawn out into a wire) and malleable (capable of being hammered into thin sheets). In a metal, the electrons act like a flexible glue holding the atomic nuclei together. As a result, metal crystals can be deformed without shattering.

4. Luster. Polished metal surfaces reflect light. Most metals have a silvery white metallic color because they reflect light of all wavelengths. Because electrons are not restricted to a particular bond, they can absorb and re-emit light over a wide wavelength range. Gold and copper absorb some light in the blue region of the visible spectrum and so appear yellow (gold) or red (copper).

5. *Insolubility in water and other common solvents.* No metals dissolve in water; electrons cannot go into solution, and cations cannot dissolve by themselves. The only liquid metal, mercury, dissolves many metals, forming solutions called *amalgams*. An Ag-Sn-Hg amalgam is still used in filling teeth.

In general, the melting points of metals cover a wide range, from −39°C for mercury to 3410°C for tungsten. This variation in melting point corresponds to a similar variation in the strength of the metallic bond. Generally speaking, the lowest melting metals are those that form +1 cations, like sodium (mp = 98°C) and potassium (mp = 64°C).

Much of what has been said about the four structural types of solids in Sections 9-4 and 9-5 is summarized in Table 9.6.



Solids with different structures.

EXAMPLE 9.7 CONCEPTUAL

For each species in column A, choose the description in column B that best applies.

A	B
CO_2	(a) ionic, high-melting
$CuSO_4$	(b) liquid metal, good conductor
SiO_2	(c) polar molecule, soluble in water
Hg	(d) ionic, insoluble in water
	(e) network covalent, high-melting
	(f) nonpolar molecule, gas at 25°C

STRATEGY

1. Characterize each species with respect to type, forces within and between particles, and if necessary, physical properties.
2. Find the appropriate matches.

SOLUTION

(a) CO_2	molecule, nonpolar
	Only match is (f) even if you did not know that CO_2 is a gas at 25°C.
(b) $CuSO_4$	ionic, water soluble
	Only match is (a) even if you did not know that $CuSO_4$ has a high melting point.
(c) SiO_2	network covalent
	Only match is (e).
(d) Hg	metal, liquid at room temperature
	Only match is (b).

Table 9.6 Structures and Properties of Types of Substances

Type	Structural Particles	Forces Within Particles	Forces Between Particles	Properties	Examples
Molecular	Molecules				
	(a) nonpolar	Covalent bond	Dispersion	Low mp, bp; often gas or liquid at 25°C; nonconductors; insoluble in water, soluble in organic solvents	H_2 CCl_4
	(b) polar	Covalent bond	Dispersion, dipole, H bond	Similar to nonpolar but generally higher mp and bp, more likely to be water-soluble	$HCl(g)$ NH_3
Network covalent	Atoms	—	Covalent bond	Hard solids with very high melting points; nonconductors; insoluble in common solvents	C SiO_2
Ionic	Ions	—	Ionic bond	High mp; conductors in molten state or water solution; often soluble in water, insoluble in organic solvents	NaCl MgO $CaCO_3$
Metallic	Cations, mobile electrons	—	Metallic bond	Variable mp; good conductors in solid; insoluble in common solvents	Na Fe

9-6 Crystal Structures

Solids tend to crystallize in definite geometric forms that often can be seen by the naked eye. In ordinary table salt, cubic crystals of NaCl are clearly visible. Large, beautifully formed crystals of such minerals as fluorite, CaF_2, are found in nature. It is possible to observe distinct crystal forms of many metals under a microscope.

Crystals have definite geometric forms because the atoms or ions present are arranged in a definite, three-dimensional pattern. The nature of this pattern can be deduced by a technique known as x-ray diffraction. The basic information that comes out of such studies has to do with the dimensions and geometric form of the **unit cell,** the smallest structural unit that, repeated over and over again in three dimensions, generates the crystal. In all, there are 14 different kinds of unit cells. Our discussion will be limited to a few of the simpler unit cells found in metals and ionic solids.

Metals

Three of the simpler unit cells found in metals, shown in Figure 9.19, are the following:

1. **Simple cubic cell (SC).** This is a cube that consists of eight atoms whose centers are located at the corners of the cell. Atoms at adjacent corners of the cube touch one another.
2. **Face-centered cubic cell (FCC).** Here, there is an atom at each corner of the cube and one in the center of each of the six faces of the cube. In this structure, atoms at the corners of the cube do not touch one another; they are forced slightly apart. Instead, contact occurs along a face diagonal. The atom at the center of each face touches atoms at opposite corners of the face.
3. **Body-centered cubic cell (BCC).** This is a cube with atoms at each corner and one in the center of the cube. Here again, corner atoms do not touch each

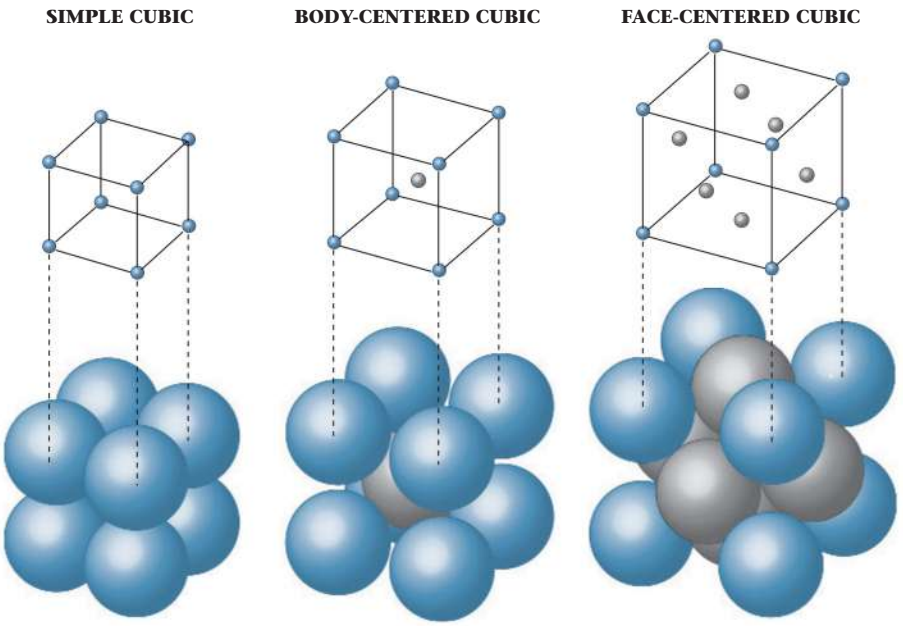


Figure 9.19 Three types of unit cells. In each case, there is an atom at each of the eight corners of the cube. In the body-centered cubic unit cell, there is an additional atom in the center of the cube. In the face-centered cubic unit cell, there is an atom in the center of each of the six faces.

Table 9.7 Properties of Cubic Unit Cells

	Simple	BCC	FCC
Number of atoms per unit cell	1	2	4
Relation between side of cell, s, and atomic radius, r	$2r = s$	$4r = s\sqrt{3}$	$4r = s\sqrt{2}$
% of empty space	47.6	32.0	26.0

other. Instead, contact occurs along the body diagonal; the atom at the center of the cube touches atoms at opposite corners.

Table 9.7 lists three other ways in which these types of cubic cells differ from one another.

1. ***Number of atoms per unit cell.*** Keep in mind that a huge number of unit cells are in contact with each other, interlocking to form a three-dimensional crystal. This means that several of the atoms in a unit cell do not belong exclusively to that cell. Specifically

- an atom at the corner of a cube forms a part of eight different cubes that touch at that point. (To convince yourself of this, look back at Figure 2.15 focus on the small sphere in the center.) In this sense, only $\frac{1}{8}$ of a corner atom belongs to a particular cell.
- an atom at the center of the face of a cube is shared by another cube that touches that face. In effect, only $\frac{1}{2}$ of that atom can be assigned to a given cell. This means, for example, that the number of atoms per FCC unit cell is

$$(8 \text{ corner atoms} \times \tfrac{1}{8}) + (6 \text{ face atoms} \times \tfrac{1}{2}) = 4 \text{ atoms per cube}$$

2. ***Relation between side of cell (s) and atomic radius (r).*** To see how these two quantities are related, consider an FCC cell in which atoms touch along a face diagonal. As you can see from Figure 9.20.

- the distance along the face diagonal, d, is equal to four atomic radii

$$d = 4r$$

- d can be related to the length of a side of the cell by the Pythagorean theorem, $d^2 = s^2 + s^2 = 2s^2$. Taking the square root of both sides,

$$d = s\sqrt{2}$$

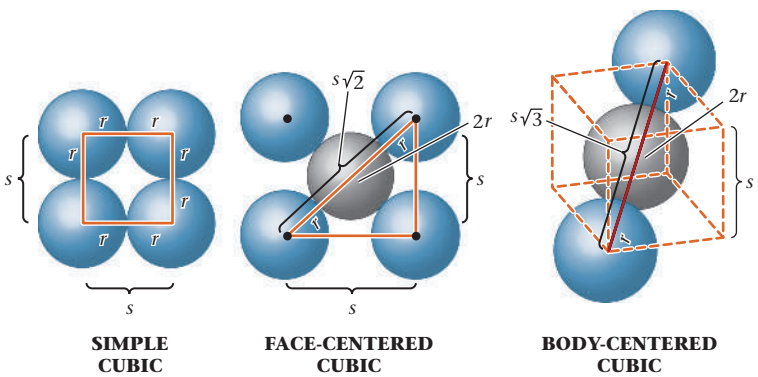


Figure 9.20 Relation between atomic radius (*r*) and length of edge (*s*) for cubic cells. In the simple cubic cell, $2r = s$. In the face-centered cubic cell, the face diagonal is equal to $s\sqrt{2}$ (hypotenuse of a right triangle) and to $4r$. Thus, $s\sqrt{2} = 4r$. In the body-centered cubic cell, the body diagonal is equal to $s\sqrt{3}$ (diagonal of a cube) and to $4r$. Thus, $s\sqrt{3} = 4r$.

Equating the two expressions for d, we have

$$4r = s\sqrt{2}$$

This relation offers an experimental way of determining the atomic radius of a metal, if the nature and dimensions of the unit cell are known.

EXAMPLE 9.8 GRADED

Silver is a metal commonly used in jewelry and photography. It crystallizes with a face-centered cubic (FCC) unit cell 0.407 nm on an edge.

a What is the atomic radius of silver in cm? (1 nm = 10^{-7} cm)

ANALYSIS

Information given:	type of cubic cell (face-centered) length of side, s(0.407 nm) nm to cm conversion (1 nm = 1×10^{-7} cm)
Information implied:	side and atomic radius relationship in a face-centered cubic cell
Asked for:	atomic radius of silver in cm

STRATEGY

1. Relate the atomic radius, r, to the side of the cube, s, in a face-centered cubic cell (FCC). See Table 9.7.
2. Substitute into the equation $4r = s\sqrt{2}$.
3. Convert nm to cm.

SOLUTION

$4r = s\sqrt{2}$

$$r = \frac{0.407 \text{ nm } (\sqrt{2})}{4} = 0.144 \text{ nm} \times \frac{1 \times 10^{-7} \text{ cm}}{1 \text{ nm}} = 1.44 \times 10^{-8} \text{ cm}$$

b What is the volume of a single silver atom? (The volume of a spherical ball of radius r is $V = \frac{4}{3}\pi r^3$.)

ANALYSIS

Information given:	from part (a); atomic radius, r (1.44×10^{-8} cm) formula for the volume of a sphere ($V = \frac{4}{3}\pi r^3$)
Asked for:	volume of a single Ag atom

STRATEGY

Assume that the atom is a perfect sphere and substitute into the formula for the volume of a sphere.

SOLUTION

V

$$V = \tfrac{4}{3}\pi r^3 = \tfrac{4}{3}\pi(1.44 \times 10^{-8} \text{ cm})^3 = 1.25 \times 10^{-23} \text{ cm}^3$$

c What is the density of a single silver atom?

ANALYSIS

Information given:	from part (b): atomic volume, V(1.25×10^{-23} cm^3) formula for the volume of a sphere ($V = \frac{4}{3}\pi r^3$)
Information implied:	molar mass of Ag Avogadro's number
Asked for:	density of a single Ag atom

STRATEGY

1. Find the mass of a single Ag atom. Recall that there are 6.022×10^{23} atoms of silver in one molar mass of silver (107.9 g/mol). Use that as a conversion factor.
2. Recall that density = mass/volume.

continued

SOLUTION

1. mass of 1 Ag atom

$$1 \text{ Ag atom} \times \frac{107.9 \text{ g}}{6.022 \times 10^{23} \text{ atoms}} = 1.792 \times 10^{-22} \text{ g}$$

2. density

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{1.792 \times 10^{-22} \text{ g}}{1.25 \times 10^{-23} \text{ cm}^3} = 14.3 \text{ g/cm}^3$$

END POINTS

1. In face-centered cubic cells, the fraction of empty space is 0.26.
2. The calculated density in part (c) assumes no empty space. If empty space is factored in, [(0.26)(14.3) = 3.7], then 3.7 g/cm^3 has to be subtracted from the density obtained in part (c). The calculated density is therefore [14.3 − 3.7] = 10.6 g/cm^3. The experimentally obtained value is 10.5 g/cm^3.

3. ***Percentage of empty space.*** Metal atoms in a crystal, like marbles in a box, tend to pack closely together. As you can see from Table 9.7, nearly half of a simple cubic unit cell is empty space. This makes the SC structure very unstable; only one metal (polonium, $Z = 84$) has this type of unit cell. The body-centered cubic structure has less waste space; about 20 metals, including all those in Group 1, have a BCC unit cell. A still more efficient way of packing spheres of the same size is the face-centered cubic structure, where the fraction of empty space is only 0.26. About 40 different metals have a structure based on a face-centered cubic cell or a close relative in which the packing is equally efficient (hexagonal closest packed structure).

Golf balls and oranges pack naturally in an FCC structure.

CHEMISTRY THE **HUMAN** SIDE

The crystal structures discussed in this section were determined by a powerful technique known as x-ray diffraction (Figure A, page 242). By studying the pattern produced when the scattered rays strike a target, it is possible to deduce the geometry of the unit cell. With molecular crystals, one can go a step further, identifying the geometry and composition of the molecule. A father and son team of two English physicists, William H. (1862–1942) and William L. Bragg (1890–1971), won the Nobel Prize in 1915 for pioneer work in this area.

The Braggs and their successors strongly sought out talented women scientists to develop the new field of x-ray crystallography. Foremost among these women was Dorothy Crowfoot Hodgkin, who spent almost all of her professional career at Oxford University in England. As the years passed she unraveled the structures of successively more complex natural products. These included penicillin, which she studied between 1942 and 1949, vitamin B-12 (1948–1957), and her greatest triumph, insulin, which she worked on for more than 30 years. Among her students at Oxford was Margaret Thatcher, the future prime minister. In 1964, Dorothy Hodgkin became the third woman to win the Nobel Prize in Chemistry. The first two women Nobel laureates in Chemistry were Marie Curie and Irène Joliot-Curie. Forty-five years later (in 2009), a fourth woman, Ada Yonath, an Israeli crystallographer, won the Nobel Prize in Chemistry.

Bettmann/Corbis

Dorothy Crowfoot Hodgkin
(1910–1994)

Hodgkin's accomplishments were all the more remarkable when you consider some of the obstacles she had to overcome. At the age of 24, she developed rheumatoid arthritis, a crippling disease of the immune system. Gradually she lost the use of her hands; ultimately she was confined to a wheelchair. Dorothy Hodgkin succeeded because she combined a first-rate intellect with an almost infinite capacity for hard work. Beyond that, she was one of those rare individuals who inspire loyalty by taking genuine pleasure in the successes of other people. A colleague referred to her as "the gentle genius."

Dorothy's husband, Thomas Hodgkin, was a scholar in his own right with an interest in the history of Africa. Apparently realizing that hers was the greater talent, he acted as a "house-husband" for their three children so she would have more time to devote to research. One wonders how Dorothy and Thomas Hodgkin reacted to the 1964 headline in a London tabloid, "British Wife Wins Nobel Prize."

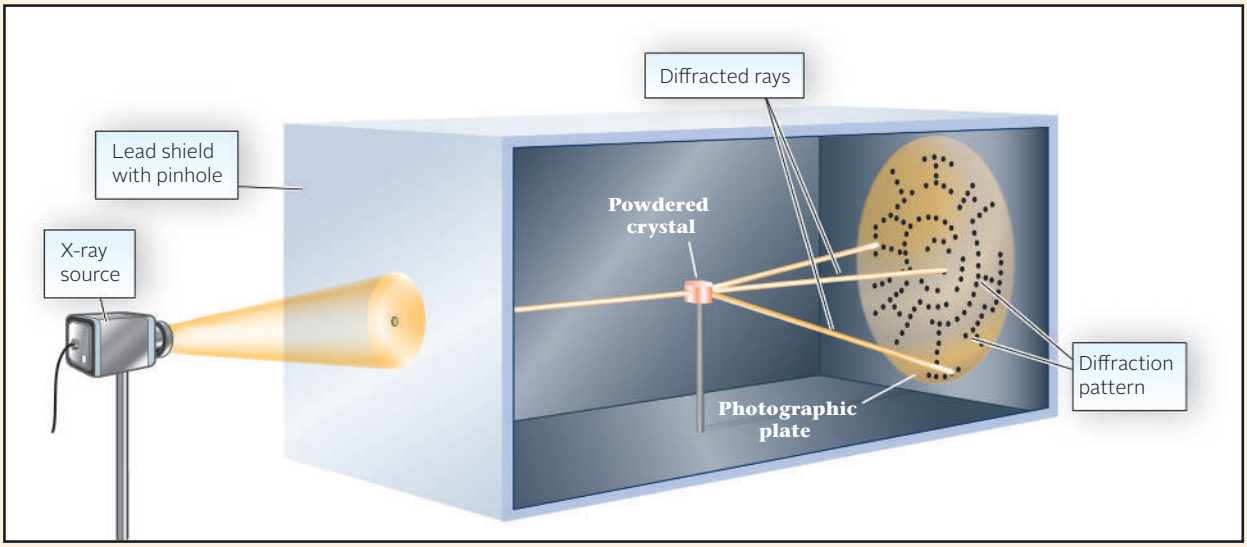
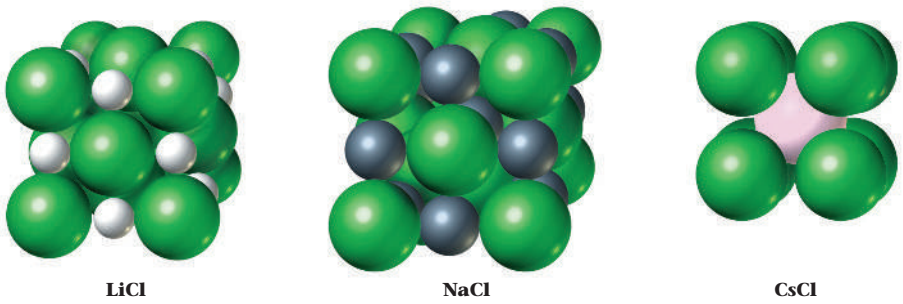


Figure A X-ray diffraction. Knowing the angles and intensities at which x-rays are diffracted by a crystal, it is possible to calculate the distances between layers of atoms.

Figure 9.21 Three types of lattices in ionic crystals. In LiCl, the Cl^- ions are in contact with each other, forming a face-centered cubic lattice. In NaCl, the Cl^- ions are forced slightly apart by the larger Na^+ ions. In CsCl, the large Cs^+ ion at the center touches the Cl^- ions at each corner of the cube.



Ionic Crystals

The geometry of ionic crystals, in which there are two different kinds of ions, is more difficult to describe than that of metals. However, in many cases the packing can be visualized in terms of the unit cells described in Figure 9.21. Lithium chloride, LiCl, is a case in point. Here, the larger Cl^- ions form a face-centered cubic lattice (Figure 9.21). The smaller Li^+ ions fit into "holes" between the Cl^- ions. This puts a Li^+ ion at the center of each edge of the cube.

In the sodium chloride crystal, the Na^+ ion is slightly too large to fit into holes in a face-centered lattice of Cl^- ions (Figure 9.21). As a result, the Cl^- ions are pushed slightly apart so that they are no longer touching, and only Na^+ ions are in contact with Cl^- ions. However, the relative positions of positive and negative ions remain the same as in LiCl:◂ Each anion is surrounded by six cations and each cation by six anions.

The structures of LiCl and NaCl are typical of all the alkali halides (Group 1 cation, Group 17 anion) except those of cesium. Because of the large size of the Cs^+ ion, CsCl crystallizes in a quite different structure. Here, each Cs^+ ion is located at the center of a simple cube outlined by Cl^- ions. The Cs^+ ion at the center touches all the Cl^- ions at the corners; the Cl^- ions do not touch each other. As you can see, each Cs^+ ion is surrounded by eight Cl^- ions, and each Cl^- ion is surrounded by eight Cs^+ ions.◂

◂ NaCl is FCC in both Na^+ and Cl^- ions; CsCl is BCC in both Cs^+ and Cl^- ions.

EXAMPLE 9.9

Consider Figure 9.21. The length of an edge of a cubic cell, s, is the distance between the center of an atom or ion at the "top" of the cell and the center of the atom or ion at the "bottom." Taking the ionic radii of Li^+, Na^+, and Cl^- to be 0.060 nm, 0.095 nm, and 0.181 nm, respectively, determine s for NaCl and LiCl.

STRATEGY

Use Figure 9.21 to determine along which lines the ions touch.

SOLUTION

NaCl	The atoms touch along a side. s = 1 r of Cl^- + 2 r of Na^+ + 1 r of Cl^- = 0.181 nm + 2(0.095 nm) + 0.181 nm = 0.552 nm
LiCl	The chloride atoms touch along a face diagonal. s = 1 r of Cl^- + 2 r of Cl^- + 1 r of Cl^- = 4 r of Cl^- = 4(0.181 nm) = 0.724 nm length of face diagonal = $s\sqrt{2}$ = (0.724 nm) ($\sqrt{2}$) = 0.512 nm

CHEMISTRY **BEYOND** THE CLASSROOM

Supercritical Carbon Dioxide

Carbon dioxide has been in the news recently because of its possible contribution to global climate change. However, supercritical carbon dioxide has found many practical applications. It is the supercritical fluid most extensively studied because it is cheap, nontoxic, and relatively easy to bring to supercritical status.

Carbon dioxide usually behaves as a gas in air or as a solid called dry ice when it is frozen. It behaves as a supercritical fluid above its critical temperature (31°C) and critical pressure (73 atm). As a supercritical fluid it expands to fill its container like a gas but it has a density like that of a liquid (Figure A).

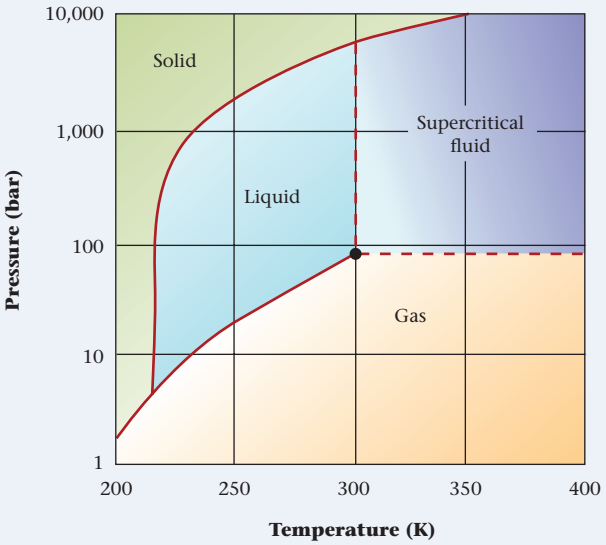


Figure A Phase diagram for carbon dioxide. Supercritical carbon dioxide is shown in the violet-shaded region.

Caffeine used to be extracted using the solvent dichloromethane (CH_2Cl_2). Unfortunately, dichloromethane was suspected to be a carcinogen so a different solvent had to be found. More than 20 years ago, supercritical CO_2 was tried as an alternative method for the extraction of caffeine from coffee beans. It was forced through the green coffee beans and the infused beans were then sprayed under high pressure with water to remove the dissolved caffeine. The caffeine was isolated by passing the water through activated charcoal filters, or by distillation (Chapter 1), crystallization, or reverse osmosis (Chapter 10). The recovered caffeine was then sold mostly to beverage manufacturers and pharmaceutical companies. This process was so effective that most of the coffee sold today is decaffeinated by this process (Figure B).

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Figure B Decaffeinated coffee is one product that employs supercritical carbon dioxide in the production process.

The dry cleaning industry now has several pilot plants using supercritical CO_2 as a solvent for removing oils, stains, and grime from clothes that cannot be washed in water. The industry is trying to replace the more commonly used solvent, perchloroethylene (PERC), which has been linked to liver and kidney damage in people working in dry cleaning plants and in people in urban areas who live near these plants. Supercritical CO_2 has one drawback, however. It does not dissolve many of the proteins in food stains, waxes, and salts because of its nonpolar nature. Research is now ongoing to find detergents that will enhance carbon dioxide's effectivity in stain removal. Several polymer detergents look promising.

A decade ago, a study by a team of researchers from the Massachusetts Institute of Technology reported the use of supercritical CO_2 to deactivate live bacteria. Medical research is now engaged in the study of supercritical CO_2 as an alternative option for tissue transplant sterilization. It is particularly attractive for sterilizing bone and tendon fragments used for torn ACLs (anterior cruciate ligaments) or spinal fusions. These fragments are typically sterilized by irradiation or by treatment with steam. These treatments are often found to compromise the strength of the fragments by degrading the collagen, making them unusable for grafts.

Other projects involving supercritical CO_2, to name a few, are the extraction of cholesterol from meat, fat from potato chips, and nicotine from tobacco. Supercritical CO_2 heat pumps are now marketed in Asia using CO_2 as a natural refrigerant.

Many scientists are very excited at the prospects of finding more uses for this novel compound. Ironically, its supercritical phase may redeem it from the bad press that gaseous CO_2 has received lately.

Key Concepts

1. Use the ideal gas law to determine whether a liquid will completely vaporize.
   (Example 9.1; Problems 1–6)
2. Use the Clausius-Clapeyron equation to relate vapor pressure to temperature.
   (Example 9.2; Problems 7–14)
3. Use a phase diagram to determine the phase(s) present at a given *T* and *P*.
   (Example 9.3; Problems 15–24)
4. Identify the type of intermolecular forces in different substances.
   (Examples 9.4–9.6; Problems 25–38)
5. Classify substances as molecular, network covalent, ionic, or metallic.
   (Example 9.7; Problems 39–48)
6. Relate unit cell dimensions to atomic or ionic radii.
   (Examples 9.8, 9.9; Problems 49–58)

Key Equations

Clausius-Clapeyron

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

Atomic radius (r) versus side (s) of unit cell: SC: $2r = s$ FCC: $4r = s\sqrt{2}$ BCC: $4r = s\sqrt{3}$

Key Terms

body-centered cubic cell (BCC)
boiling point
critical pressure
critical temperature
face-centered cubic cell (FCC)
deposition
dipole forces
dispersion force
electron-sea model
hydrogen bond
intermolecular forces
network covalent
normal boiling point
phase diagram
simple cubic cell (SC)
sublimation
triple point
unit cell
vapor pressure

Summary Problem

Consider propylamine, $C_3H_7NH_2$. It is used as a component of some herbicides, a regulating agent for plastics, and is used as an additive for the petroleum industry. Its structural formula is

$$H_3C—CH_2—CH_2—NH_2$$

Some of its physical properties are:
density: 0.719 g/mL
normal boiling point: 48.7°C
normal freezing point: −83°C
critical temperature: 234°C
heat of vaporization: 30.7 kJ/mol

(a) What intermolecular forces would you expect to find in propylamine?

(b) Compare the boiling point of propylamine to nitrogen, methylamine (CH_3NH_2), ammonium chloride, and silicon dioxide (SiO_2).

(c) Would you expect propylamine to conduct electricity?

(d) Compare its solubility in water to that of nitrogen gas and silicon dioxide.

(e) Give the symbol of a nonmetal that is a better conductor of electricity than propylamine.

(f) Give the formula of a solid compound that, unlike propylamine, has a network covalent structure.

(g) Draw a rough sketch of the phase diagram of propylamine. Assume that the solid phase is more dense than the liquid phase.

(h) If you want to purify propylamine by sublimation, at what approximate temperature would you operate?

(i) A sample of propylamine vapor at 250°C and 1 atm is cooled at constant pressure. At what temperature does the liquid first appear?

(j) Estimate the vapor pressure of propylamine at 25°C.

(k) Estimate the temperature at which the vapor pressure of propylamine is 0.500 atm.

(l) A sample of 1.00 mL of propylamine is placed in a one-liter flask at 22°C where the vapor pressure is 269 mm Hg. Show by calculation whether there is any liquid left in the flask when equilibrium is established.

Answers

(a) dispersion, dipole, H bonds
(b) higher than N_2 and methylamine; lower than NH_4Cl and SiO_2
(c) no
(d) more soluble than N_2 or SiO_2
(e) C (graphite) or Si
(f) SiO_2
(g) See Figure 9.9 for the general configuration. Put in the appropriate temperatures and pressures.
(h) below about −83°C
(i) 48.7°C
(j) 305 mm Hg
(k) 30.5°C
(l) no liquid left

Questions and Problems

Even-numbered questions and Challenge Problems have answers in Appendix 5 and fully worked solutions in the *Student Solutions Manual*.

9-2 Liquid-Vapor Equilibrium

1. Methyl alcohol can be used as a fuel instead of, or combined with, gasoline. A sample of methyl alcohol, CH_3OH, in a flask of constant volume exerts a pressure of 254 mm Hg at 57°C. The flask is slowly cooled.
(a) Assuming no condensation, use the ideal gas law to calculate the pressure of the vapor at 35°C; at 45°C.
(b) Compare your answers in (a) with the equilibrium vapor pressures of methyl alcohol: 203 mm Hg at 35°C; 325 mm Hg at 45°C.
(c) On the basis of your answers to (a) and (b), predict the pressure exerted by the methyl alcohol in the flask at 35°C; at 45°C.
(d) What physical states of methyl alcohol are present in the flask at 35°C? at 45°C?

2. Benzene, a known carcinogen, was once widely used as a solvent. A sample of benzene vapor in a flask of constant volume exerts a pressure of 325 mm Hg at 80°C. The flask is slowly cooled.
(a) Assuming no condensation, use the ideal gas law to calculate the pressure of the vapor at 50°C; at 60°C.
(b) Compare your answers in (a) to the equilibrium vapor pressures of benzene: 269 mm Hg at 50°C, 389 mm Hg at 60°C.
(c) On the basis of your answers to (a) and (b), predict the pressure exerted by the benzene at 50°C; at 60°C.

3. The vapor pressure of $I_2(s)$ at 30°C is 0.466 mm Hg.
(a) How many milligrams of iodine will sublime into an evacuated 750.0-mL flask?
(b) If 3.00 mg of I_2 are used, what will the final pressure in the flask be?
(c) If 7.85 mg of I_2 are used, what will the final pressure in the flask be?

4. Camphor, $C_{10}H_{16}O$, is the active ingredient in vapor-steam products like Vicks VapoRub®. Its vapor pressure at 20°C is 0.18 mm Hg.

(**a**) How many milligrams of camphor will sublime into an evacuated 0.500-L flask?

(**b**) A 125-mL flask contains 0.15 mg of camphor at 20°C. What is the pressure in the flask?

5. Trichloroethane, $C_2H_3Cl_3$ is used as a degreaser (solvent for waxes and oils). Its density is 1.435 g/mL and its vapor pressure at 20°C is 124 mm Hg.

(**a**) How many mL will vaporize in an evacuated 1.50-L flask at 20°C?

(**b**) A 3.00-mL sample is poured into an evacuated 1.5-L flask at 20°C. Will all the liquid vaporize? If not, what is the pressure in the flask?

(**c**) A similar 3.00-mL sample is poured into an evacuated 20.00-L flask at 20°C. What physical state(s) is/are in the flask?

6. *p*-Dichlorobenzene, $C_6H_4Cl_2$, can be one of the ingredients in mothballs. Its vapor pressure at 20°C is 0.40 mm Hg.

(**a**) How many milligrams of $C_6H_4Cl_2$ will sublime into an evacuated 750-mL flask at 20°C?

(**b**) If 5.0 mg of *p*-dichlorobenzene were put into an evacuated 750-mL flask, how many milligrams would remain in the solid phase?

(**c**) What is the final pressure in an evacuated 500-mL flask at 20°C that contains 2.00 mg of *p*-dichlorobenzene? Will there be any solid in the flask?

7. Chloroform, $CHCl_3$, was once used as an anesthetic. In spy movies it is the liquid put in handkerchiefs to render victims unconscious. Its vapor pressure is 197 mm Hg at 23°C and 448 mm Hg at 45°C. Estimate its

(**a**) heat of vaporization.

(**b**) normal boiling point.

8. Dichloromethane, CH_2Cl_2, is widely used as a "degreaser" and paint stripper. Its vapor pressure is 381.0 mm Hg at 21.9°C and 465.8 mm Hg at 26.9°C. Estimate

(**a**) its heat of vaporization (ΔH_{vap}).

(**b**) its normal boiling point.

9. Winter Park, a town in the Rocky Mountains of Colorado, has an altitude of 9100 (2 significant figures) feet. Water (ΔH_{vap} = 40.7 kJ/mol) boils at 91°C in Winter Park. What is the normal atmospheric pressure in Winter Park?

10. Glacier National Park in Montana is a favorite vacation spot for backpackers. It is about 4100 ft above sea level with an atmospheric pressure of 681 mm Hg. At what temperature does water (ΔH_{vap} = 40.7 kJ/mol) boil in Glacier National Park?

11. At a resort in Sante Fe, New Mexico, the barometric pressure is 625 mm Hg. Water boils in an open pot at 94.5°C. A pressure cooker is set for 1.75 atm.

(**a**) At what temperature will water boil in that pressure cooker? (For water, ΔH_{vap} = 40.7 kJ/mol.)

(**b**) What is the difference between the boiling point in the open pot and in the pressure cooker?

12. At sea level, the barometric pressure is 760 mm Hg. Calculate the difference in the normal boiling point for water boiled in an open pot and water boiled in a pressure cooker set for 1.75 atm. (ΔH_{vap} for water = 40.7 kJ/mol)

13. The data below give the vapor pressure of octane, a major component of gasoline.

vp (mm Hg)	10	40	100	400
t(°C)	19.2	45.1	65.7	104.0

Plot ln(vp) versus 1/T. Use your graph to estimate the heat of vaporization of octane. ($\ln P = A - \dfrac{\Delta H_{vap}}{R}\left(\dfrac{1}{T}\right)$, where A is the y-intercept and ΔH_{vap} is the slope.)

14. Consider the following data for the vapor pressure of diethyl ether, a widely used anesthetic in the early days of surgery.

vp (mm Hg)	146	231	355	531
t(°C)	−5	5	15	25

Follow the instructions in Question 13 to estimate the heat of vaporization of diethyl ether.

9-3 Phase Diagrams

15. Referring to Figure 9.7, state what phase(*s*) is/are present at

(**a**) 1 atm, 100°C.

(**b**) 0.5 atm, 100°C.

(**c**) 0.8 atm, 50°C.

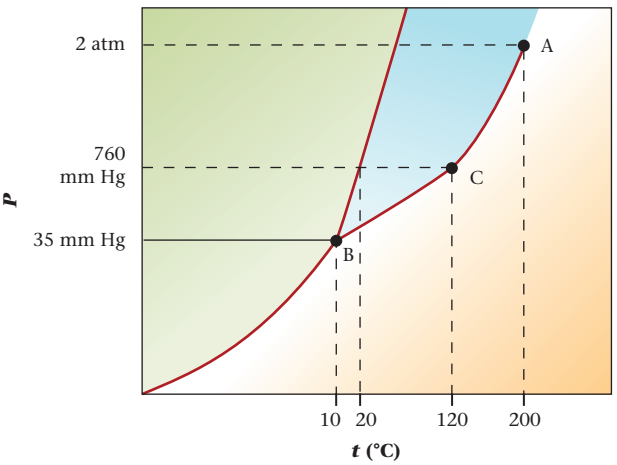
16. Referring to Figure 9.7, state what phase(s) is (are) present at

(**a**) 1 atm, 10°C.

(**b**) 3 mm Hg, 20°C.

(**c**) 1000 mm Hg, 75°C.

17. Consider the phase diagram of the compound X below. Use the phase diagram to answer the following questions.



_____ (**a**) What is the physical state of the compound at 35 mm Hg and −50°C?

_____ (**b**) What is the normal boiling point of the compound?

_____ (**c**) Where is the critical point?

_____ (**d**) Where is the triple point?

_____ (**e**) What change occurs when at a constant pressure of 30 mm Hg, the temperature is decreased from 120°C to 20°C?

_____ (**f**) Which phase is the densest phase?

18. Consider the phase diagram of the compound in Problem 17 to answer the following questions.

_____ (a) What is the physical state of the compound at 35 mm Hg and 120°C?
_____ (b) What is the normal freezing point of the compound?
_____ (c) What is the point *A* called?
_____ (d) What is the point *B* called?
_____ (e) What is the point *C* called?
_____ (f) What change occurs when at a constant pressure of 33 mm Hg, the temperature is decreased from 40°C to −20°C?
_____ (g) Will the solid float on the liquid?
_____ (h) Can the compound exist as a liquid at 180°C and 2 atm pressure?

19. Argon gas has its triple point at −189.3°C and 516 mm Hg. It has a critical point at −122°C and 48 atm. The density of the solid is 1.65 g/cm^3, whereas that of the liquid is 1.40 g/cm^3. Sketch the phase diagram for argon and use it to fill in the blanks below with the words "boils," "melts," "sublimes," or "condenses."

(a) Solid argon at 500 mm Hg _____ when the temperature is increased.
(b) Solid argon at 2 atm _____ when the temperature is increased.
(c) Argon gas at −150°C _____ when the pressure is increased.
(d) Argon gas at −165°C _____ when the pressure is increased.

20. Iodine has a triple point at 114°C, 90 mm Hg. Its critical temperature is 535°C. The density of the solid is 4.93 g/cm^3, and that of the liquid is 4.00 g/cm^3. Sketch the phase diagram for iodine and use it to fill in the blanks using either "liquid" or "solid."

(a) Iodine vapor at 80 mm Hg condenses to the _____ when cooled sufficiently.
(b) Iodine vapor at 125°C condenses to the _____ when enough pressure is applied.
(c) Iodine vapor at 700 mm Hg condenses to the _____ when cooled above the triple point temperature.

21. Given the following data about xenon,

normal boiling point = −108°C
normal melting point = −112°C
triple point = −121°C at 281 mm Hg
critical point = 16.6°C at 58 atm

(a) Construct an approximate phase diagram for xenon.
(b) Estimate the vapor pressure of xenon at −115°C.
(c) Is the density of solid Xe larger than that for liquid Xe?

22. Given the following data about CO_2:

- triple point: −57°C, 5.11 atm
- critical point: 31°C, 73 atm
- sublimes at −78.5°C, 1 atm
- The solid is the denser phase.

(a) Construct a simplified (not to scale) phase diagram for CO_2.
(b) Estimate the vapor pressure of CO_2 at 0°C.
(c) At 10 atm pressure and −50°C, is CO_2 a liquid?

23. A pure substance X has the following properties: mp = 90°C, increasing slightly as pressure increases; normal bp = 120°C; liquid vp = 65 mm Hg at 100°C, 20 mm Hg at the triple point.

(a) Draw a phase diagram for X.
(b) Label solid, liquid, and vapor regions of the diagram.
(c) What changes occur if, at a constant pressure of 100 mm Hg, the temperature is raised from 100°C to 150°C?

24. A pure substance A has a liquid vapor pressure of 6 atm at 550°C. Its triple point is at 5 atm, 350°C. The solid phase is denser than the liquid phase.

(a) Sketch the phase diagram for compound A.
(b) From the phase diagram, estimate the temperature at which the compound boils when 6.3 atm of pressure are applied.
(c) What changes occur when, at a constant pressure of 4 atm, the temperature drops from 400°C to 100°C?

9-4 Molecular Substances; Intermolecular Forces

25. Arrange the following in order of decreasing boiling point.
(a) I_2 (b) F_2 (c) Cl_2 (d) Br_2

26. Arrange the following compounds in order of increasing boiling point.
(a) Ar (b) He (c) Ne (d) Xe

27. Which of the following would you expect to show dispersion forces? dipole forces?
(a) $GeBr_4$ (b) C_2H_2 (c) HF (*g*) (d) $TeCl_2$

28. Which of the following compounds would you expect to show dispersion forces? Dipole forces?
(a) F_2 (b) CO (c) CO_2 (d) H_2CO

29. Which of the following would show hydrogen bonding?
(a) CH_3OH (b) $CH_3{-}\underset{\displaystyle H}{\underset{|}{N}}{-}CH_3$
(c) CH_3NH_2 (d) HF

30. Which of the following compounds show hydrogen bonding?
(a) CH_3F (b) HO—OH
(c) NH_3F (d) $H_3C{-}O{-}CH_3$

31. Explain in terms of forces between structural units why
(a) HI has a higher boiling point than HBr.
(b) GeH_4 has a higher boiling point than SiH_4.
(c) H_2O_2 has a higher melting point than C_3H_8.
(d) NaCl has a higher boiling point than CH_3OH.

32. Explain in terms of structural units why
(a) CO_2 has a lower boiling point than Na_2CO_3.
(b) N_2H_4 has a higher boiling point than C_2H_6.
(c) formic acid, $H{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}OH$, has a lower boiling point than benzoic acid, $C_6H_5{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}OH$.
(d) CO has a higher boiling point than N_2.

33. In which of the following processes is it necessary to break covalent bonds as opposed to simply overcoming intermolecular forces?
(a) melting mothballs made of naphthalene
(b) dissolving HBr gas in water to form hydrobromic acid
(c) vaporizing ethyl alcohol, C_2H_5OH
(d) changing ozone, O_3, to oxygen gas, O_2

34. In which of the following processes is it necessary to break covalent bonds as opposed to simply overcoming intermolecular forces?
(a) Decomposing HCl to H_2 and Cl_2
(b) Dissolving NaCl in water
(c) Freezing ethyl alcohol
(d) Subliming iodine

35. For each of the following pairs, choose the member with the lower boiling point. Explain your reason in each case.
(a) NaCl or PCl_3 (b) NH_3 or AsH_3
(c) C_3H_7OH or $C_2H_5OCH_3$ (d) HI(*g*) or HCl(*g*)

36. Follow the directions for Question 35 for the following substances.
(a) LiCl or CCl_4 (b) CH_3OH or CH_3F
(c) H_2O or SO_2 (d) N_2 or Cl_2

37. What are the strongest attractive forces that must be overcome to
(a) boil silicon hydride, SiH_4?
(b) vaporize calcium chloride?
(c) dissolve Cl_2 in carbon tetrachloride, CCl_4?
(d) melt iodine?

38. What are the strongest attractive forces that must be overcome to
(a) melt ice? (b) sublime bromine?
(c) boil chloroform ($CHCl_3$)? (d) vaporize benzene (C_6H_6)?

9-5 Network Covalent, Ionic, and Metallic Solids

39. Classify each of the following solids as metallic, network covalent, ionic, or molecular.
(a) It is insoluble in water, melts above 500°C, and does not conduct electricity either as a solid, dissolved in water, or molten.
(b) It dissolves in water but does not conduct electricity as an aqueous solution, as a solid, or when molten.
(c) It dissolves in water, melts above 100°C, and conducts electricity when present in an aqueous solution.

40. Classify each of the following solids as metallic, network covalent, ionic, or molecular.
(a) It melts below 100°C and is insoluble in water.
(b) It conducts electricity only when melted.
(c) Mostly insoluble in water and conducts electricity.

41. Of the four general types of solids, which one(s)
(a) are generally low-boiling?
(b) are ductile and malleable?
(c) are generally soluble in nonpolar solvents?

42. Of the four general types of solids, which one(s)
(a) are generally insoluble in water?
(b) have very high melting points?
(c) conduct electricity as solids?

43. Classify each of the following species as molecular, network covalent, ionic, or metallic.
(a) Na (b) Na_2SO_4 (c) C_6H_6
(d) C_{60} (e) HCl(*aq*)

44. Classify each of the following species as metallic, network covalent, ionic, or molecular.
(a) W (b) NO_2 (c) C (diamond)
(d) $FeCl_2$ (e) C_2H_2

45. Give the formula of a solid containing Si that is
(a) molecular
(b) ionic
(c) network covalent

46. Give the formula of a solid containing oxygen that is
(a) a polar molecule (b) ionic
(c) network covalent (d) a nonpolar molecule

47. Describe the structural units in
(a) NaI (b) N_2 (c) KO_2 (d) Au

48. Describe the structural units in
(a) C (graphite)
(b) SiC
(c) $FeCl_2$
(d) C_2H_2

9-6 Crystal Structures

49. Molybdenum has an atomic radius of 0.145 nm. The volume of its cubic unit cell is 0.0375 nm^3. What is the geometry of the molybdenum unit cell?

50. Nickel has an atomic radius of 0.162 nm. The edge of its cubic unit cell is 0.458 nm. What is the geometry of the nickel unit cell?

51. Lead (atomic radius = 0.181 nm) crystallizes with a face-centered cubic unit cell. What is the length of a side of the cell?

52. Iridium crystallizes in a face-centered unit cell. The side of the cell is 0.3833 nm. Calculate the volume of the cell and the radius of an iridium atom.

53. In the LiCl structure shown in Figure 9.21, the chloride ions form a face-centered cubic unit cell 0.513 nm on an edge. The ionic radius of Cl^- is 0.181 nm.
(a) Along a cell edge, how much space is between the Cl^- ions?
(b) Would an Na^+ ion (r = 0.095 nm) fit into this space? a K^+ ion (r = 0.133 nm)?

54. Potassium iodide has a unit cell similar to that of sodium chloride (Figure 9.21). The ionic radii of K^+ and I^- are 0.133 nm and 0.216 nm, respectively. How long is
(a) one side of the cube?
(b) the face diagonal of the cube?

55. For a cell of the CsCl type (Figure 9.21), how is the length of one side of the cell, s, related to the sum of the radii of the ions, $r_{cation} + r_{anion}$?

56. Consider the CsCl cell (Figure 9.21). The ionic radii of Cs^+ and Cl^- are 0.169 and 0.181 nm, respectively. What is the length of
(a) the body diagonal?
(b) the side of the cell?

57. Consider the sodium chloride unit cell shown in Figure 9.21. Looking only at the front face (five large Cl^- ions, four small Na^+ ions),
(a) how many cubes share each of the Na^+ ions in this face?
(b) how many cubes share each of the Cl^- ions in this face?

58. Consider the CsCl unit shown in Figure 9.21. How many Cs^+ ions are there per unit cell? How many Cl^- ions? (Note that each Cl^- ion is shared by eight cubes.)

Unclassified

59. A 1.25-L clean and dry flask is sealed. The air in the flask is at 27°C and 38% relative humidity. The flask is put in a cooler at 5°C. How many grams of water will condense in the flask? (Use the table in Appendix 1 for the vapor pressure of water at various temperatures.)

60. Aluminum metal crystallizes with a face-centered cubic unit cell. The volume of the cell is 0.0662 nm^3.

(**a**) What is the atomic radius of aluminum in cm?

(**b**) What is the volume of a single aluminum atom?

(**c**) What is the density of a single aluminum atom?

(**d**) In face-centered cubic cell packing, the fraction of empty space is 26.0%. When this is factored in, what is the calculated density of aluminum?

61. Consider a sealed flask with a movable piston that contains 5.25 L of O_2 saturated with water vapor at 25°C. The piston is depressed at constant temperature so that the gas is compressed to a volume of 2.00 L. (Use the table in Appendix 1 for the vapor pressure of water at various temperatures.)

(**a**) What is the vapor pressure of water in the compressed gas mixture?

(**b**) How many grams of water condense when the gas mixture is compressed?

62. Packing efficiency is defined as the percent of the total volume of a solid occupied by (spherical) atoms. The formula is

$$\text{packing efficiency} = \frac{\text{volume of the atom(s) in the cell}}{\text{volume of the cell}} \times 100$$

The volume of one atom is $\frac{4}{3}\pi r^3$ and the volume of the cell is s^3. Calculate the packing efficiency of

(**a**) a simple cubic cell (1 atom/cell).

(**b**) a face-centered cubic cell (4 atoms/cell).

(**c**) a body-centered cubic cell (2 atoms/cell).

Use Table 9.6 to relate r to s.

63. Mercury is an extremely toxic substance. Inhalation of the vapor is just as dangerous as swallowing the liquid. How many milliliters of mercury will saturate a room that is $15 \times 12 \times 8.0$ ft with mercury vapor at 25°C? The vapor pressure of Hg at 25°C is 0.00163 mm Hg and its density is 13 g/mL.

64. An experiment is performed to determine the vapor pressure of formic acid. A 30.0-L volume of helium gas at 20.0°C is passed through 10.00 g of liquid formic acid (HCOOH) at 20.0°C. After the experiment, 7.50 g of liquid formic acid remains. Assume that the helium gas becomes saturated with formic acid vapor and the total gas volume and temperature remain constant. What is the vapor pressure of formic acid at 20.0°C?

65. Chloroform, $CHCl_3$, has a normal boiling point of 61°C. Its vapor pressure at 43°C is 0.526 atm. What is the concentration (in g/L) of $CHCl_3$ when it saturates the air at 27°C?

Conceptual Problems

66. Which of the following statements are true?

(**a**) The critical temperature must be reached to change liquid to gas.

(**b**) To melt a solid at constant pressure, the temperature must be above the triple point.

(**c**) CHF_3 can be expected to have a higher boiling point than $CHCl_3$ because CHF_3 has hydrogen bonding.

(**d**) One metal crystallizes in a body-centered cubic cell and another in a face-centered cubic cell of the same volume. The two atomic radii are related by the factor $\sqrt{1.5}$.

67. Write the letter(s) corresponding to the bond(s) and/or force(s) associated with each species below.

A – dispersion forces
B – dipole-dipole interaction
C – ionic bond
D – metallic bond
E – covalent bond within a network covalent solid
F – hydrogen bond.

(**a**) C (diamond) (**b**) CH_3 (**c**) Au
(**d**) SO_3 (**e**) NH_3 (**f**) KCl

68. In the blanks provided, answer the questions below, using **LT** (for *is less than*), **GT** (for *is greater than*), **EQ** (for *is equal to*), or **MI** (for *more information required*).

(**a**) The boiling point of C_3H_7OH (MM = 60.0 g/mol) _____ the boiling point of $C_2H_6C{=}O$ (MM = 58.0 g/mol).

(**b**) The vapor pressure of X is 250 mm Hg at 57°C. Given a sealed flask at 57°C that contains only gas, the pressure in the flask _____ 245 mm Hg.

(**c**) The melting-point curve for Y tilts to the right of a straight line. The density of Y(*l*) _____ the density of Y(*s*).

(**d**) The normal boiling point of A is 85°C, while the normal boiling point of B is 45°C. The vapor pressure of A at 85°C _____ the vapor pressure of B at 45°C.

(**e**) The triple point of A is 25 mm Hg and 5°C. The melting point of A _____ 5°C.

69. Answer the questions below, by filling in the blanks with **LT** for *is less than*, **GT** for *is greater than*, **EQ** for *is equal to*, or **MI** for *more information required*.

(**a**) At 50°C, benzene has a vapor pressure of 269 mm Hg. A flask that contains both benzene liquid and vapor at 50°C has a pressure _____ 269 mm Hg.

(**b**) Ether has a vapor pressure of 537 mm Hg at 25°C. A flask that contains only ether vapor at 37°C has a pressure _____ 537 mm Hg.

(**c**) The boiling point of H_2O _____ the boiling point of C_3H_8.

(**d**) The energy required to vaporize liquid bromine _____ the energy required to decompose Br_2 into Br atoms.

(**e**) The dispersion forces present in naphthalene, $C_{10}H_8$, _____ the dispersion forces present in butane, C_4H_{10}.

70. A liquid has a vapor pressure of 159 mm Hg at 20°C and 165 mm Hg at 30°C. Different amounts of the liquid are added to three identical evacuated steel tanks kept at 20°C. The tanks are all fitted with pressure gauges. For each part, write

L/G if both liquid and gas are present.
G if only gas is present.
I if the situation is impossible.

(**a**) The pressure gauge in Flask I registers a pressure of 256 mm Hg.

(**b**) The pressure gauge in Flask II registers a pressure of 135 mm Hg.

(**c**) The pressure gauge in Flask III registers a pressure of 165 mm Hg at 30°C. The temperature is lowered to 20°C, and the gauge registers a pressure of 159 mm Hg.

71. Indicate whether the following statements are true or false.

(**a**) The triple point in the phase diagram of a pure substance is the temperature and pressure at which the substance can boil, freeze, and sublime at the same time.

(**b**) CHF_3 can be expected to have a higher boiling point than $CHCl_3$ because $CHCl_3$ has hydrogen bonds.

(**c**) The strength of covalent bonds within a molecule has no effect on the melting or boiling points of the compound made up of that molecule.

(**d**) As the gas from a condensable gas (e.g., propane) in a tank is used up, the pressure gradually decreases.

(**e**) The critical temperature is the temperature above which only the gaseous phase can exist.

72. What is the difference between

(**a**) a covalent bond and an ionic bond?

(**b**) boiling point and critical point?

(**c**) deposition and sublimation?

(**d**) freezing point and triple point?

73. Four shiny solids are labeled A, B, C, and D. Given the following information about the solids, deduce the identity of A, B, C, and D.

(**1**) The solids are a graphite rod, a silver bar, a lump of "fool's gold" (iron sulfide), and iodine crystals.

(**2**) B, C, and D are insoluble in water. A is slightly soluble.

(**3**) Only C can be hammered into a sheet.

(**4**) C and D conduct electricity as solids; B conducts when melted; A does not conduct as a solid, melted, or dissolved in water.

74. Consider the vapor pressure curves of molecules A, B, and C shown below.

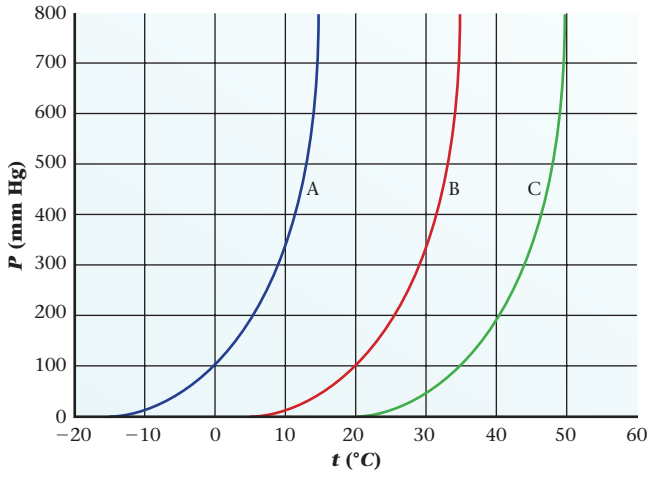
(**a**) Which compound (A, B, or C) has the weakest forces between molecules?

(**b**) Which compound (A, B, or C) has a normal boiling point at about 15°C?

(**c**) At what temperature will B boil if the atmospheric pressure is 500 mm Hg?

(**d**) At 25°C and 400 mm Hg, what is the physical state of A?

(**e**) At what pressure will C boil at 40°C?



Challenge Problems

75. The following data are given for CCl_4:

normal melting point = −23°C
normal boiling point = 77°C
density of liquid = 1.59 g/mL
vapor pressure at 25°C = 110 mm Hg

How much heat is required to vaporize 20.0 L of CCl_4 at its normal boiling point?

76. Iron crystallizes in a body-centered unit cell. Its atomic radius is 0.124 nm. Its density is 7.86 g/cm^3. Using this information, estimate Avogadro's number.

77. A flask with a volume of 10.0 L contains 0.400 g of hydrogen gas and 3.20 g of oxygen gas. The mixture is ignited and the reaction

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O$$

goes to completion. The mixture is cooled to 27°C. Assuming 100% yield,

(**a**) What physical state(s) of water is (are) present in the flask?

(**b**) What is the final pressure in the flask?

(**c**) What is the pressure in the flask if 3.2 g of each gas is used?

78. Trichloroethane, $C_2H_3Cl_3$, is the active ingredient in aerosols that claim to stain-proof men's ties. Trichloroethane has a vapor pressure of 100.0 mm Hg at 20.0°C and boils at 74.1°C. An uncovered cup ($\frac{1}{2}$ pint) of trichloroethane (d = 1.325 g/mL) is kept in an 18-ft^3 refrigerator at 39°F. What percentage (by mass) of the trichloroethane is left as a liquid when equilibrium is established?

79. It has been suggested that the pressure exerted on a skate blade is sufficient to melt the ice beneath it and form a thin film of water, which makes it easier for the blade to slide over the ice. Assume that a skater weighs 120 lb and the blade has an area of 0.10 in^2. Calculate the pressure exerted on the blade (1 atm = 15 lb/in^2). From information in the text, calculate the decrease in melting point at this pressure. Comment on the plausibility of this explanation and suggest another mechanism by which the water film might be formed.

80. As shown in Figure 9.20, Li^+ ions fit into a closely packed array of Cl^- ions, but Na^+ ions do not. What is the value of the r_{cation}/r_{anion} ratio at which a cation just fits into a structure of this type?

81. When the temperature drops from 20°C to 10°C, the pressure of a cylinder of compressed N_2 drops by 3.4%. The same temperature change decreases the pressure of a propane (C_3H_8) cylinder by 42%. Explain the difference in behavior.