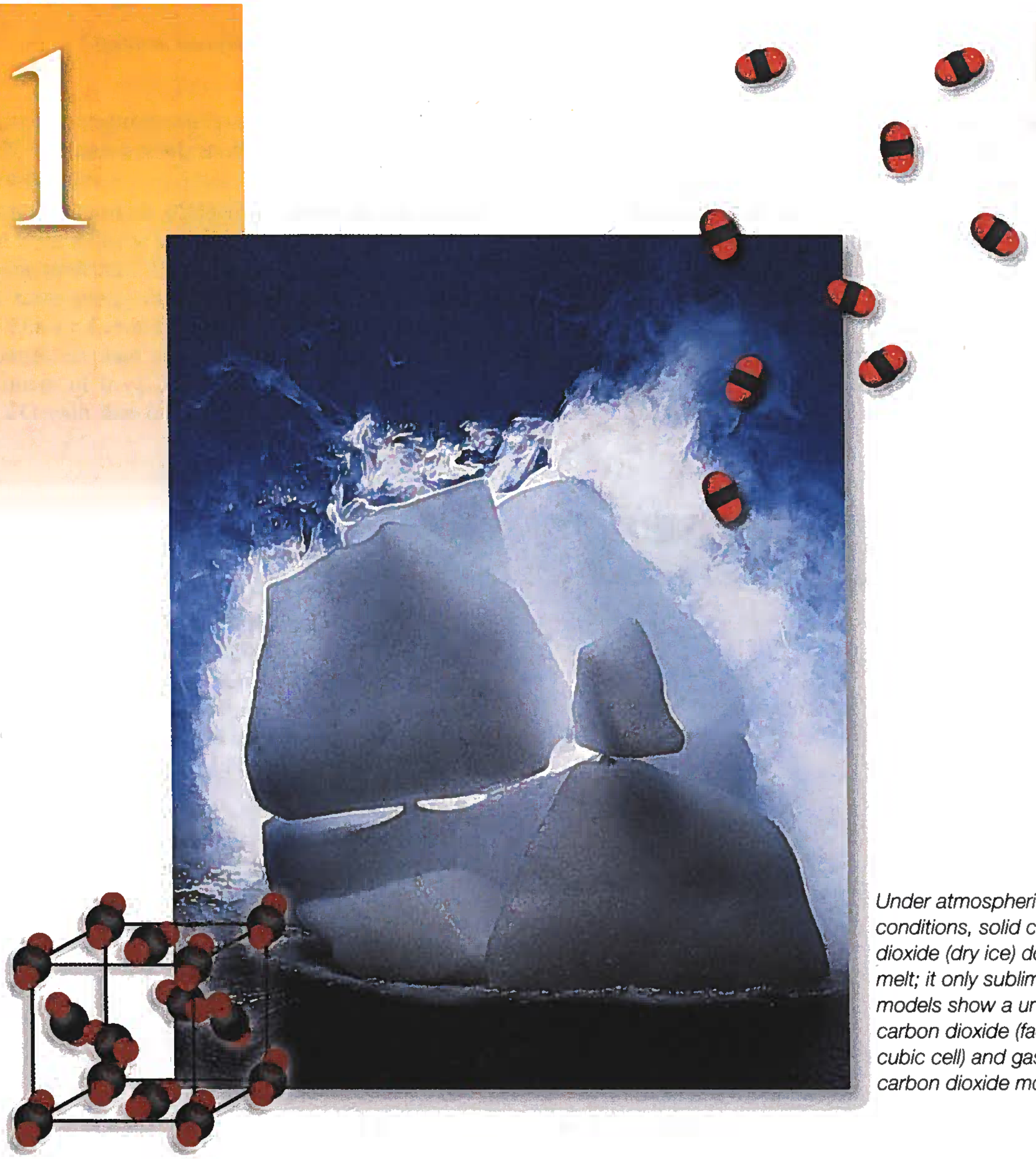
11



Under atmospheric conditions, solid carbon dioxide (dry ice) does not melt; it only sublimes. The models show a unit cell of carbon dioxide (face-centered cubic cell) and gaseous carbon dioxide molecules.

Intermolecular Forces and Liquids and Solids

A LOOK AHEAD

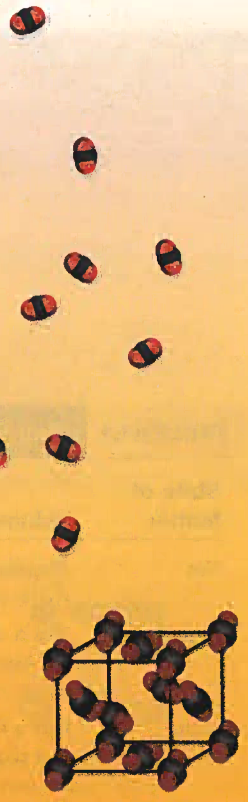
- We begin by applying the kinetic molecular theory to liquids and solids and compare their properties with those of gases. (11.1)
- Next, we examine the different types of intermolecular forces between molecules and between ions and molecules. We also study a special type of intermolecular interaction called hydrogen bonding that involves hydrogen and electronegative elements nitrogen, oxygen, and fluorine. (11.2)
- We see that two important properties of liquids—surface tension and viscosity—can be understood in terms of intermolecular forces. (11.3)
- We then move on to the world of solids and learn about the nature of crystals and ways of packing spheres to form different unit cells. (11.4)
- We see that the best way to determine the dimensions of a crystal structure is by X-ray diffraction, which is based on the scattering of X rays by the atoms or molecules in a crystal. (11.5)
- The major types of crystals are ionic, covalent, molecular, and metallic. Intermolecular forces help us understand their structure and physical properties such as density, melting point, and electrical conductivity. (11.6)
- We learn that solids can also exist in the amorphous form, which lacks orderly three-dimensional arrangement. A well-known example of a amorphous solid is glass. (11.7)
- We next study phase changes, or transitions among gas, liquids, and solids. We see that the dynamic equilibrium between liquid and vapor gives rise to equilibrium vapor pressure. The energy required for vaporization depends on the strength of intermolecular forces. We also learn that every substance has a critical temperature above which its vapor form cannot be liquefied. We then examine liquid-solid and solid-vapor transitions. (11.8)
- The various types of phase transitions are summarized in a phase diagram, which helps us understand conditions under which a phase is stable and changes in pressure and/or temperature needed to bring about a phase transition. (11.9)

Interactive Activity Summary

1. Animation: Packing Spheres (11.4)
2. Animation: Equilibrium Vapor Pressure (11.8)

Although we live immersed in a mixture of gases that make up Earth's atmosphere, we are more familiar with the behavior of liquids and solids because they are more visible. Every day we use water and other liquids for drinking, bathing, cleaning, and cooking, and we handle, sit upon, and wear solids.

Molecular motion is more restricted in liquids than in gases; and in solids, the atoms and molecules are packed even more tightly together. In fact, in a solid they are held in well-defined positions and are capable of little free motion relative to one another. In this chapter we will examine the structure of liquids and solids and discuss some of the fundamental properties of these two states of matter.



11.1 The Kinetic Molecular Theory of Liquids and Solids

In Chapter 5 we used the kinetic molecular theory to explain the behavior of gases in terms of the constant, random motion of gas molecules. In gases, the distances between molecules are so great (compared with their diameters) that at ordinary temperatures and pressures (say, 25°C and 1 atm), there is no appreciable interaction between the molecules. Because there is a great deal of empty space in a gas—that is, space that is not occupied by molecules—gases can be readily compressed. The lack of strong forces between molecules also allows a gas to expand to fill the volume of its container. Furthermore, the large amount of empty space explains why gases have very low densities under normal conditions.

Liquids and solids are quite a different story. The principal difference between the condensed states (liquids and solids) and the gaseous state is the distance between molecules. In a liquid, the molecules are so close together that there is very little empty space. Thus, liquids are much more difficult to compress than gases, and they are also much denser under normal conditions. Molecules in a liquid are held together by one or more types of attractive forces, which will be discussed in Section 11.2. A liquid also has a definite volume, because molecules in a liquid do not break away from the attractive forces. The molecules can, however, move past one another freely, and so a liquid can flow, can be poured, and assumes the shape of its container.

In a solid, molecules are held rigidly in position with virtually no freedom of motion. Many solids are characterized by long-range order; that is, the molecules are arranged in regular configurations in three dimensions. There is even less empty space in a solid than in a liquid. Thus, solids are almost incompressible and possess definite shape and volume. With very few exceptions (water being the most important), the density of the solid form is higher than that of the liquid form for a given substance. It is not uncommon for two states of a substance to coexist. An ice cube (solid) floating in a glass of water (liquid) is a familiar example. Chemists refer to the different states of a substance that are present in a system as phases. A ***phase*** is *a homogeneous part of the system in contact with other parts of the system but separated from them by a well-defined boundary.* Thus, our glass of ice water contains both the solid phase and the liquid phase of water. In this chapter we will use the term "phase" when talking about changes of state involving one substance, as well as systems containing more than one phase of a substance. Table 11.1 summarizes some of the characteristic properties of the three phases of matter.

TABLE 11.1 Characteristic Properties of Gases, Liquids, and Solids

State of Matter	Volume/Shape	Density	Compressibility	Motion of Molecules
Gas	Assumes the volume and shape of its container	Low	Very compressible	Very free motion
Liquid	Has a definite volume but assumes the shape of its container	High	Only slightly compressible	Slide past one another freely
Solid	Has a definite volume and shape	High	Virtually incompressible	Vibrate about fixed positions

11.2 Intermolecular Forces

Intermolecular forces are *attractive forces between molecules.* Intermolecular forces are responsible for the nonideal behavior of gases described in Chapter 5. They exert even more influence in the condensed phases of matter—liquids and solids. As the temperature of a gas drops, the average kinetic energy of its molecules decreases. Eventually, at a sufficiently low temperature, the molecules no longer have enough energy to break away from the attraction of neighboring molecules. At this point, the molecules aggregate to form small drops of liquid. This transition from the gaseous to the liquid phase is known as *condensation.*

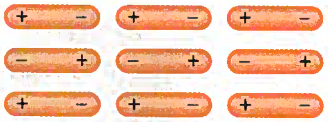


Figure 11.1 *Molecules that have a permanent dipole moment tend to align with opposite polarities in the solid phase for maximum attractive interaction.*

In contrast to intermolecular forces, ***intramolecular forces*** *hold atoms together in a molecule.* (Chemical bonding, discussed in Chapters 9 and 10, involves intramolecular forces.) Intramolecular forces stabilize individual molecules, whereas intermolecular forces are primarily responsible for the bulk properties of matter (for example, melting point and boiling point).

Generally, intermolecular forces are much weaker than intramolecular forces. It usually requires much less energy to evaporate a liquid than to break the bonds in the molecules of the liquid. For example, it takes about 41 kJ of energy to vaporize 1 mole of water at its boiling point; but about 930 kJ of energy are necessary to break the two O—H bonds in 1 mole of water molecules. The boiling points of substances often reflect the strength of the intermolecular forces operating among the molecules. At the boiling point, enough energy must be supplied to overcome the attractive forces among molecules before they can enter the vapor phase. If it takes more energy to separate molecules of substance A than of substance B because A molecules are held together by stronger intermolecular forces, then the boiling point of A is higher than that of B. The same principle applies also to the melting points of the substances. In general, the melting points of substances increase with the strength of the intermolecular forces.

To discuss the properties of condensed matter, we must understand the different types of intermolecular forces. *Dipole-dipole, dipole-induced dipole,* and *dispersion forces* make up what chemists commonly refer to as ***van der Waals forces,*** after the Dutch physicist Johannes van der Waals (see Section 5.8). Ions and dipoles are attracted to one another by electrostatic forces called *ion-dipole forces,* which are *not* van der Waals forces. *Hydrogen bonding* is a particularly strong type of dipole-dipole interaction. Because only a few elements can participate in hydrogen bond formation, it is treated as a separate category. Depending on the phase of a substance, the nature of chemical bonds, and the types of elements present, more than one type of interaction may contribute to the total attraction between molecules, as we will see below.

Dipole-Dipole Forces

Dipole-dipole forces are *attractive forces between polar molecules,* that is, between molecules that possess dipole moments (see Section 10.2). Their origin is electrostatic, and they can be understood in terms of Coulomb's law. The larger the dipole moment, the greater the force. Figure 11.1 shows the orientation of polar molecules in a solid. In liquids, polar molecules are not held as rigidly as in a solid, but they tend to align in a way that, on average, maximizes the attractive interaction.

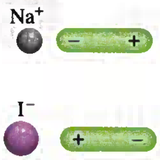


Figure 11.2 *Two types of ion-dipole interaction.*

Ion-Dipole Forces

Coulomb's law also explains ***ion-dipole forces,*** which *attract an ion (either a cation or an anion) and a polar molecule to each other* (Figure 11.2). The strength of this

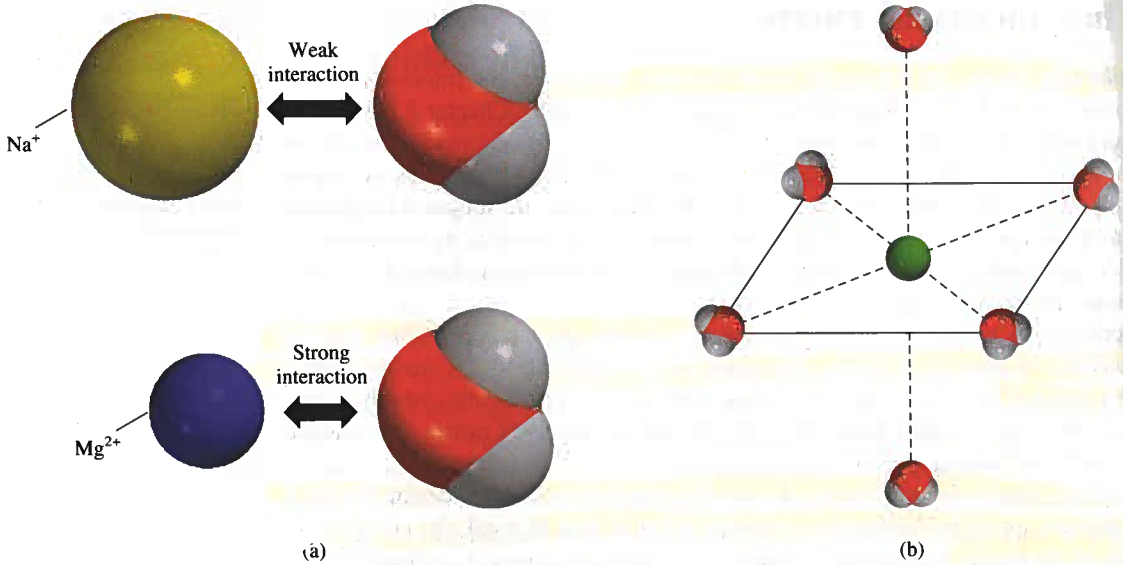


Figure 11.3 *(a) Interaction of a water molecule with a Na^+ ion and a Mg^{2+} ion. (b) In aqueous solutions, metal ions are usually surrounded by six water molecules in an octahedral arrangement.*

interaction depends on the charge and size of the ion and on the magnitude of the di moment and size of the molecule. The charges on cations are generally more con trated, because cations are usually smaller than anions. Therefore, a cation interacts mo strongly with dipoles than does an anion having a charge of the same magnitude.

Hydration, discussed in Section 4.1, is one example of ion-dipole intera Heat of hydration (see p. 252) is the result of the favorable interaction between cations and anions of an ionic compound with water. Figure 11.3 shows the ion-dip interaction between the Na^+ and Mg^{2+} ions with a water molecule, which has a la dipole moment (1.87 D). Because the Mg^{2+} ion has a higher charge and a sma ionic radius (78 pm) than that of the Na^+ ion (98 pm), it interacts more strongly w water molecules. (In reality, each ion is surrounded by a number of water molecu in solution.) Consequently, the heats of hydration for the Na^+ and Mg^{2+} ions a −405 kJ/mol and −1926 kJ/mol, respectively.[†] Similar differences exist for anio different charges and sizes.

Dispersion Forces

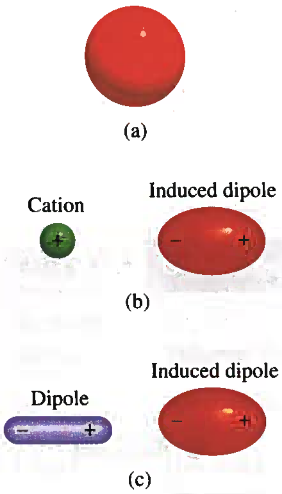


Figure 11.4 *(a) Spherical charge distribution in a helium atom. (b) Distortion caused by the approach of a cation. (c) Distortion caused by the approach of a dipole.*

What attractive interaction occurs in nonpolar substances? To learn the answer to th question, consider the arrangement shown in Figure 11.4. If we place an ion or a pol molecule near an atom (or a nonpolar molecule), the electron distribution of the ato (or molecule) is distorted by the force exerted by the ion or the polar molecule, resul ing in a kind of dipole. The dipole in the atom (or nonpolar molecule) is said to an ***induced dipole*** because *the separation of positive and negative charges in the at (or nonpolar molecule) is due to the proximity of an ion or a polar molecule.* T attractive interaction between an ion and the induced dipole is called *ion-indu dipole interaction,* and the attractive interaction between a polar molecule and th induced dipole is called *dipole-induced dipole interaction.*

The likelihood of a dipole moment being induced depends not only on the cha on the ion or the strength of the dipole but also on the *polarizability* of the atom molecule—that is, the ease with which the electron distribution in the atom (or mo ecule) can be distorted. Generally, the larger the number of electrons and the mo

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[†] Heats of hydration of individual ions cannot be measured directly, but they can be reliably estimated

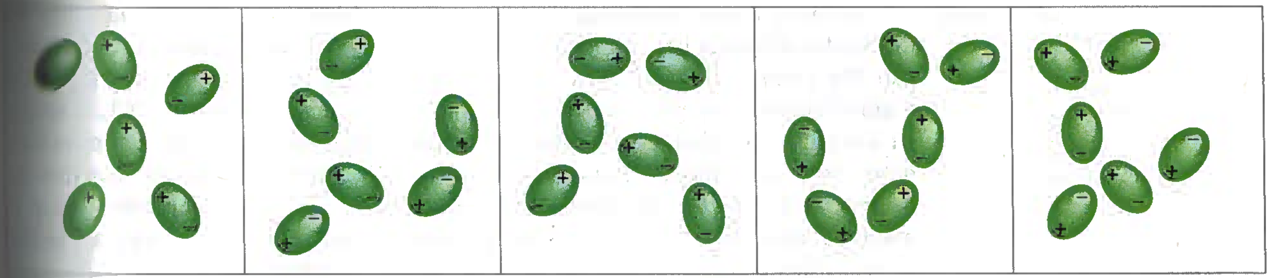


Figure 11.5 *Induced dipoles interacting with each other. Such patterns exist only momentarily; new arrangements are formed in the next instant. This type of interaction is responsible for the condensation of nonpolar gases.*

diffuse the electron cloud in the atom or molecule, the greater its polarizability. By *diffuse cloud* we mean an electron cloud that is spread over an appreciable volume, so that the electrons are not held tightly by the nucleus.

Polarizability allows gases containing atoms or nonpolar molecules (for example, He and N_2) to condense. In a helium atom the electrons are moving at some distance from the nucleus. At any instant it is likely that the atom has a dipole moment created by the specific positions of the electrons. This dipole moment is called an *instantaneous dipole* because it lasts for just a tiny fraction of a second. In the next instant the electrons are in different locations and the atom has a new instantaneous dipole, and so on. Averaged over time (that is, the time it takes to make a dipole moment measurement), however, the atom has no dipole moment because the instantaneous dipoles all cancel one another. In a collection of He atoms, an instantaneous dipole of one He atom can induce a dipole in each of its nearest neighbors (Figure 11.5). At the next moment, a different instantaneous dipole can create temporary dipoles in the surrounding He atoms. The important point is that this kind of interaction produces *dispersion forces, attractive forces that arise as a result of temporary dipoles induced in atoms or molecules.* At very low temperatures (and reduced atomic speeds), dispersion forces are strong enough to hold He atoms together, causing the gas to condense. The attraction between nonpolar molecules can be explained similarly.

A quantum mechanical interpretation of temporary dipoles was provided by Fritz London† in 1930. London showed that the magnitude of this attractive interaction is directly proportional to the polarizability of the atom or molecule. As we might expect, dispersion forces may be quite weak. This is certainly true for helium, which has a boiling point of only 4.2 K, or −269°C. (Note that helium has only two electrons, which are tightly held in the 1*s* orbital. Therefore, the helium atom has a low polarizability.)

For simplicity we use the term "intermolecular forces" for both atoms and molecules.

Dispersion forces, which are also called London forces, usually increase with molar mass because molecules with larger molar mass tend to have more electrons, and dispersion forces increase in strength with the number of electrons. Furthermore, larger molar mass often means a bigger atom whose electron distribution is more easily disturbed because the outer electrons are less tightly held by the nuclei. Table 11.2 compares the melting points of similar substances that consist of nonpolar molecules. As expected, the melting point increases as the number of electrons in the molecule increases. Because these are all nonpolar molecules, the only attractive intermolecular forces present are the dispersion forces.

TABLE 11.2

Melting Points of Similar Nonpolar Compounds

Compound	Melting Point (°C)
CH_4	−182.5
CF_4	−150.0
CCl_4	−23.0
CBr_4	90.0
CI_4	171.0

---

† Fritz London (1900–1954). German physicist. London was a theoretical physicist whose major work was on superconductivity in liquid helium.

In many cases, dispersion forces are comparable to or even greater than the dipole-dipole forces between polar molecules. For a dramatic illustration, let us compare the boiling points of CH_3F (−78.4°C) and CCl_4 (76.5°C). Although CH_3F has a dipole moment of 1.8 D, it boils at a much lower temperature than CCl_4, a nonpolar molecule. CCl_4 boils at a higher temperature simply because it contains more electrons. As a result, the dispersion forces between CCl_4 molecules are stronger than the dispersion forces plus the dipole-dipole forces between CH_3F molecules. (Keep in mind that dispersion forces exist among species of all types, whether they are neutral or bear a net charge and whether they are polar or nonpolar.)

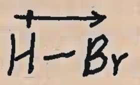
Example 11.1 shows that if we know the kind of species present, we can readily determine the types of intermolecular forces that exist between the species.

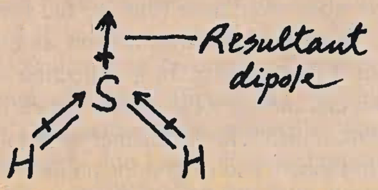
Example 11.1

What type(s) of intermolecular forces exist between the following pairs: (a) HBr and H_2S, (b) Cl_2 and CBr_4, (c) I_2 and NO_3^-, (d) NH_3 and C_6H_6?

Strategy Classify the species into three categories: ionic, polar (possessing a dipole moment), and nonpolar. Keep in mind that dispersion forces exist between *all* species.

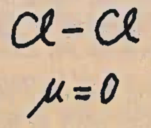
Solution (a) Both HBr and H_2S are polar molecules

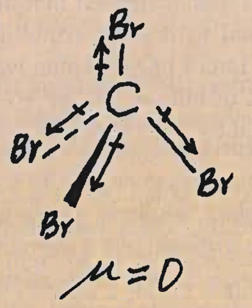




Therefore, the intermolecular forces present are dipole-dipole forces, as well as dispersion forces.

(b) Both Cl_2 and CBr_4 are nonpolar, so there are only dispersion forces between these molecules.





(c) I_2 is a homonuclear diatomic molecule and therefore nonpolar, so the forces between it and the ion NO_3^- are ion-induced dipole forces and dispersion forces.

(d) NH_3 is polar, and C_6H_6 is nonpolar. The forces are dipole-induced dipole forces and dispersion forces.

Similar problem: 11.10.

Practice Exercise Name the type(s) of intermolecular forces that exists between molecules (or basic units) in each of the following species: (a) LiF, (b) CH_4, (c) SO_2.

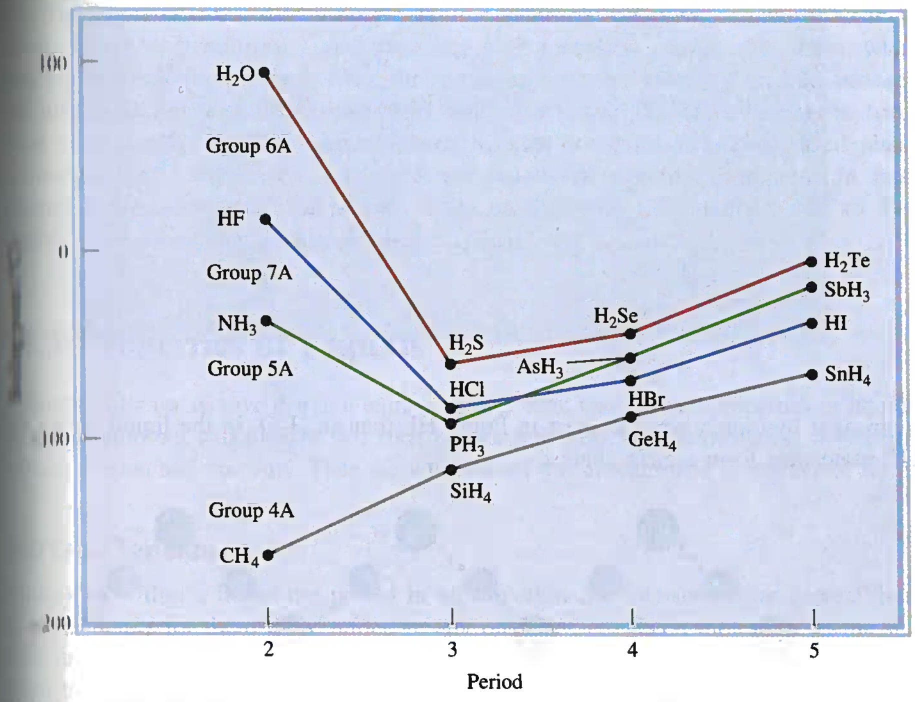


Figure 11.6 *Boiling points of the hydrogen compounds of Groups 4A, 5A, 6A, and 7A elements. Although normally we expect the boiling point to increase as we move down a group, we see that three compounds (NH_3, H_2O, and HF) behave differently. The anomaly can be explained in terms of intermolecular hydrogen bonding.*

The Hydrogen Bond

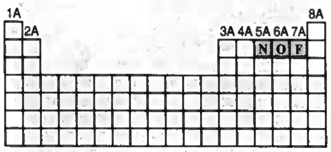
Normally, the boiling points of a series of similar compounds containing elements in the same periodic group increase with increasing molar mass. This increase in boiling point is due to the increase in dispersion forces for molecules with more electrons. Hydrogen compounds of Group 4A follow this trend, as Figure 11.6 shows. The lightest compound, CH_4, has the lowest boiling point, and the heaviest compound, SnH_4, has the highest boiling point. However, hydrogen compounds of the elements in Groups 5A, 6A, and 7A do not follow this trend. In each of these series, the lightest compound (NH_3, H_2O, and HF) has the highest boiling point, contrary to our expectations based on molar mass. This observation must mean that there are stronger intermolecular attractions in NH_3, H_2O, and HF, compared to other molecules in the same groups. In fact, this particularly strong type of intermolecular attraction is called the ***hydrogen bond,*** which is *a special type of dipole-dipole interaction between the hydrogen atom in a polar bond, such as N—H, O—H, or F—H, and an electronegative O, N, or F atom.* The interaction is written

$$\text{A—H} \cdots \text{B} \quad \text{or} \quad \text{A—H} \cdots \text{A}$$

A and B represent O, N, or F; A—H is one molecule or part of a molecule and B is a part of another molecule; and the dotted line represents the hydrogen bond. The three atoms usually lie in a straight line, but the angle AHB (or AHA) can deviate as much as 30° from linearity. Note that the O, N, and F atoms all possess at least one lone pair that can interact with the hydrogen atom in hydrogen bonding.

The average strength of a hydrogen bond is quite large for a dipole-dipole interaction (up to 40 kJ/mol). Thus, hydrogen bonds have a powerful effect on the structures and properties of many compounds. Figure 11.7 shows several examples of hydrogen bonding.

The strength of a hydrogen bond is determined by the coulombic interaction between the lone-pair electrons of the electronegative atom and the hydrogen nucleus. For example, fluorine is more electronegative than oxygen, and so we would expect



The three most electronegative elements that take part in hydrogen bonding.

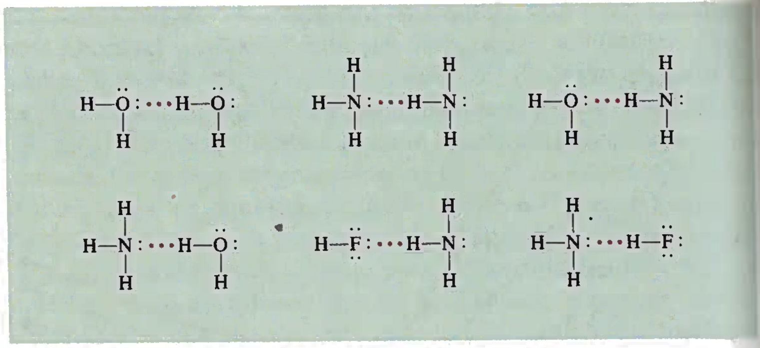
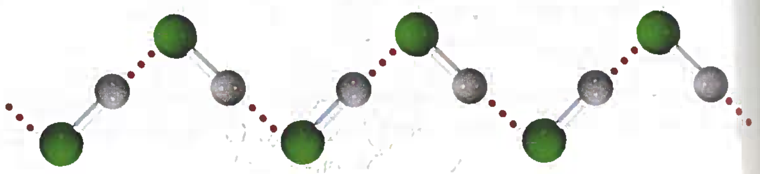
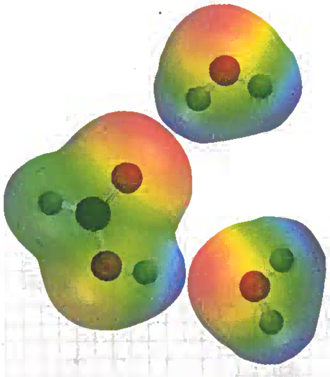


Figure 11.7 *Hydrogen bonding in water, ammonia, and hydrogen fluoride. Solid lines represent covalent bonds, and dotted lines represent hydrogen bonds.*

a stronger hydrogen bond to exist in liquid HF than in H_2O. In the liquid HF molecules form zigzag chains:



The boiling point of HF is lower than that of water because each H_2O takes *four* intermolecular hydrogen bonds. Therefore, the forces holding the mole together are stronger in H_2O than in HF. We will return to this very important erty of water in Section 11.3. Example 11.2 shows the type of species that can hydrogen bonds with water.



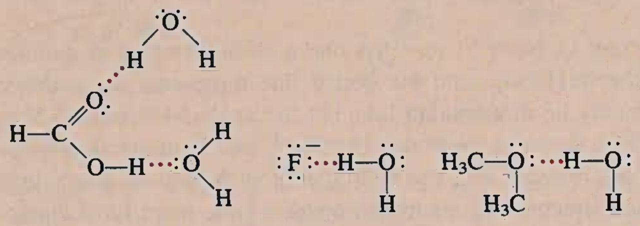
HCOOH forms hydrogen bonds with two H_2O molecules.

Example 11.2

Which of the following can form hydrogen bonds with water? CH_3OCH_3, CH_4, F^-, HCOOH, Na^+.

Strategy A species can form hydrogen bonds with water if it contains one of the three electronegative elements (F, O, or N) or it has an H atom bonded to one of these three elements.

Solution There are no electronegative elements (F, O, or N) in either CH_4 or Na^+. Therefore, only CH_3OCH_3, F^-, and HCOOH can form hydrogen bonds with water.



Check Note that HCOOH (formic acid) can form hydrogen bonds with water in two different ways.

Similar problem: 11.12.

Practice Exercise Which of the following species are capable of hydrogen bonding among themselves? (a) H_2S, (b) C_6H_6, (c) CH_3OH.

The intermolecular forces discussed so far are all attractive in nature. Keep in mind, though, that molecules also exert repulsive forces on one another. Thus, when two molecules approach each other, the repulsion between the electrons and between the nuclei in the molecules comes into play. The magnitude of the repulsive force rises very steeply as the distance separating the molecules in a condensed phase decreases. This is the reason that liquids and solids are so hard to compress. In these phases, the molecules are already in close contact with one another, and so they greatly resist being compressed further.

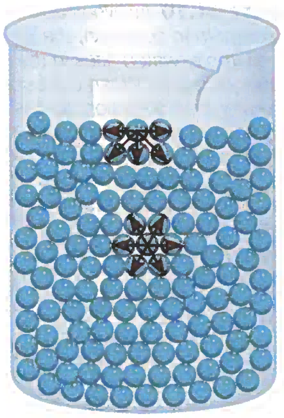


Figure 11.8 *Intermolecular forces acting on a molecule in the surface layer of a liquid and in the interior region of the liquid.*

11.3 Properties of Liquids

Intermolecular forces give rise to a number of structural features and properties of liquids. In this section we will look at two such phenomena associated with liquids in general: surface tension and viscosity. Then we will discuss the structure and properties of water.

Surface Tension

Molecules within a liquid are pulled in all directions by intermolecular forces; there is no tendency for them to be pulled in any one way. However, molecules at the surface are pulled downward and sideways by other molecules, but not upward away from the surface (Figure 11.8). These intermolecular attractions thus tend to pull the molecules into the liquid and cause the surface to tighten like an elastic film. Because there is little or no attraction between polar water molecules and, say, the nonpolar wax molecules on a freshly waxed car, a drop of water assumes the shape of a small round bead, because a sphere minimizes the surface area of a liquid. The waxy surface of a wet apple also produces this effect (Figure 11.9).

A measure of the elastic force in the surface of a liquid is surface tension. The ***surface tension*** is *the amount of energy required to stretch or increase the surface of a liquid by a unit area* (for example, by 1 cm^2). Liquids that have strong intermolecular forces also have high surface tensions. Thus, because of hydrogen bonding, water has a considerably greater surface tension than most other liquids.

Surface tension enables the water strider to "walk" on water.

Another example of surface tension is *capillary action.* Figure 11.10(a) shows water rising spontaneously in a capillary tube. A thin film of water adheres to the wall of the glass tube. The surface tension of water causes this film to contract, and as it does, it pulls the water up the tube. Two types of forces bring about capillary action. One is ***cohesion,*** which is *the intermolecular attraction between like molecules* (in this case, the water molecules). The second force, called ***adhesion,*** is *an attraction between unlike molecules,* such as those in water and in the sides of a glass tube. If adhesion is stronger than cohesion, as it is in Figure 11.10(a), the contents of the tube will be pulled upward. This process continues until the adhesive force is balanced by the weight of the water in the tube. This action is by no means universal among liquids, as Figure 11.10(b) shows. In mercury, cohesion is greater than the adhesion between mercury and glass, so that when a capillary tube is dipped in mercury, the result is a depression or lowering, at the mercury level—that is, the height of the liquid in the capillary tube is below the surface of the mercury.

Figure 11.9 *Water beads on an apple which has a waxy surface.*

Viscosity

The expression "slow as molasses in January" owes its truth to another physical property of liquids called viscosity. ***Viscosity*** is *a measure of a fluid's resistance to flow.* The greater the viscosity, the more slowly the liquid flows. The viscosity of a liquid

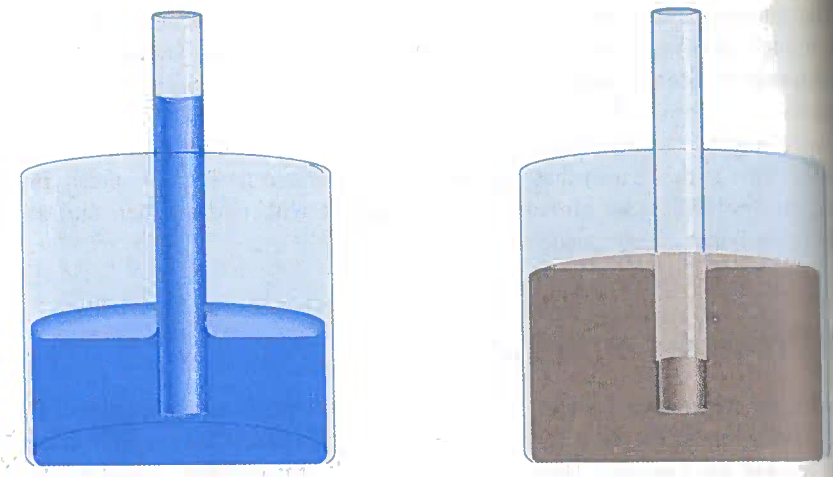
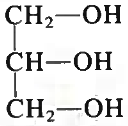

(a) (b)

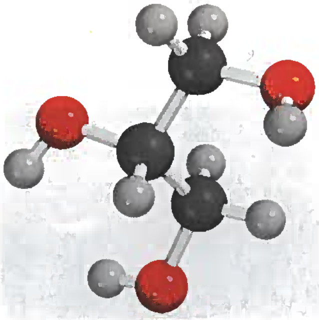
Figure 11.10 *(a) When adhesion is greater than cohesion, the liquid (for example, water) rises in the capillary tube. (b) When cohesion is greater than adhesion, as it is for mercury, a depression of the liquid in the capillary tube results. Note that the meniscus in the tube of water is concave, or rounded downward, whereas that in the tube of mercury is convex, or rounded upward.*

usually decreases as temperature increases; thus, hot molasses flows much faster th cold molasses.

Liquids that have strong intermolecular forces have higher viscosities than th that have weak intermolecular forces (Table 11.3). Water has a higher viscosity th many other liquids because of its ability to form hydrogen bonds. Interestingly, th viscosity of glycerol is significantly higher than that of all the other liquids listed i Table 11.3. Glycerol has the structure



$$\begin{array}{l} CH_2\text{—}OH \\ | \\ CH\text{—}OH \\ | \\ CH_2\text{—}OH \end{array}$$



Glycerol is a clear, odorless, syrupy liquid used to make explosives, ink, and lubricants.

Like water, glycerol can form hydrogen bonds. Each glycerol molecule has th —OH groups that can participate in hydrogen bonding with other glycerol molecul

TABLE 11.3 Viscosity of Some Common Liquids at 20°C

Liquid	Viscosity (N s/m^2)*
Acetone (C_3H_6O)	3.16×10^{-4}
Benzene (C_6H_6)	6.25×10^{-4}
Blood	4×10^{-3}
Carbon tetrachloride (CCl_4)	9.69×10^{-4}
Ethanol (C_2H_5OH)	1.20×10^{-3}
Diethyl ether ($C_2H_5OC_2H_5$)	2.33×10^{-4}
Glycerol ($C_3H_8O_3$)	1.49
Mercury (Hg)	1.55×10^{-3}
Water (H_2O)	1.01×10^{-3}

*The SI units of viscosity are newton-second per meter squared.

Furthermore, because of their shape, the molecules have a great tendency to become entangled rather than to slip past one another as the molecules of less viscous liquids do. These interactions contribute to its high viscosity.

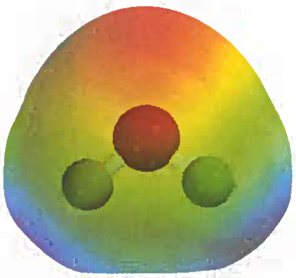
The Structure and Properties of Water

If water did not have the ability to form hydrogen bonds, it would be a gas at room temperature.

Water is so common a substance on Earth that we often overlook its unique nature. All life processes involve water. Water is an excellent solvent for many ionic compounds, as well as for other substances capable of forming hydrogen bonds with water.

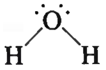
As Table 6.2 shows, water has a high specific heat. The reason is that to raise the temperature of water (that is, to increase the average kinetic energy of water molecules), we must first break the many intermolecular hydrogen bonds. Thus, water can absorb a substantial amount of heat while its temperature rises only slightly. The converse is also true: Water can give off much heat with only a slight decrease in its temperature. For this reason, the huge quantities of water that are present in our lakes and oceans can effectively moderate the climate of adjacent land areas by absorbing heat in the summer and giving off heat in the winter, with only small changes in the temperature of the body of water.

The most striking property of water is that its solid form is less dense than its liquid form: ice floats at the surface of liquid water. The density of almost all other substances is greater in the solid state than in the liquid state (Figure 11.11).



Electrostatic potential map of water.

To understand why water is different, we have to examine the electronic structure of the H_2O molecule. As we saw in Chapter 9, there are two pairs of nonbonding electrons, or two lone pairs, on the oxygen atom:



Although many compounds can form intermolecular hydrogen bonds, the difference between H_2O and other polar molecules, such as NH_3 and HF, is that each oxygen atom can form *two* hydrogen bonds, the same as the number of lone electron pairs on the oxygen atom. Thus, water molecules are joined together in an extensive three-dimensional network in which each oxygen atom is approximately tetrahedrally bonded to four hydrogen atoms, two by covalent bonds and two by hydrogen bonds. This equality in the number of hydrogen atoms and lone pairs is not characteristic of NH_3 or HF or, for that matter, of any other molecule capable of forming hydrogen

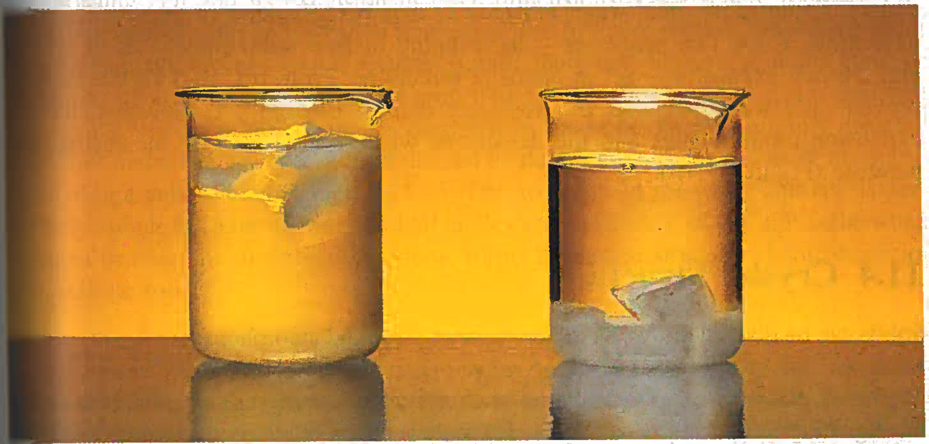


Figure 11.11 *Left: Ice cubes float on water. Right: Solid benzene sinks to the bottom of liquid benzene.*

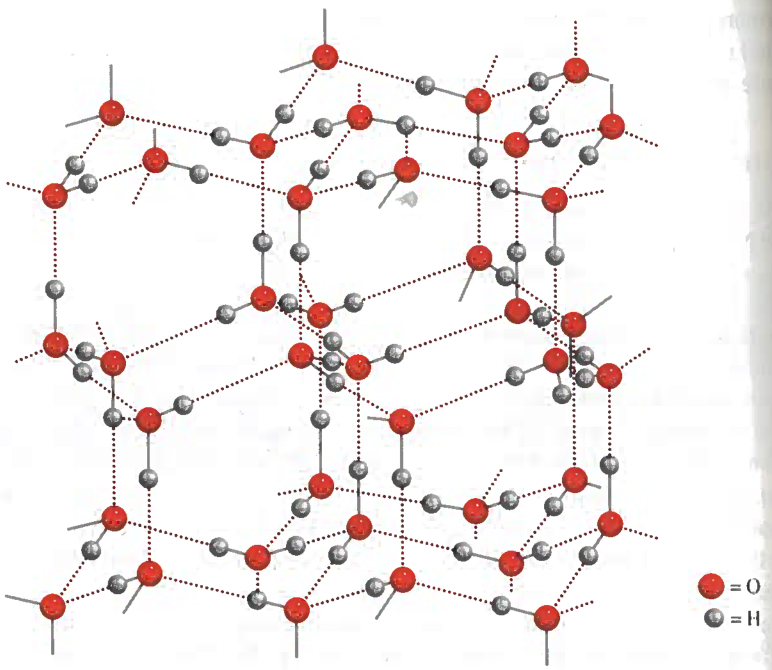


Figure 11.12 *The three-dimensional structure of ice. Each O atom is bonded to four H atom covalent bonds are shown by short solid lines and the weaker hydrogen bonds by long dotted li between O and H. The empty space in the structure accounts for the low density of ice.*

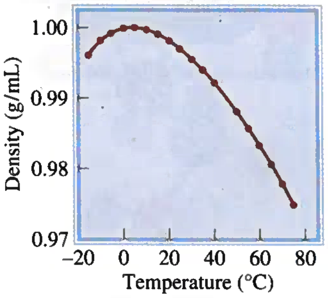


Figure 11.13 *Plot of density versus temperature for liquid water. The maximum density of water is reached at 4°C. The density of ice at 0°C is about 0.92 g/cm³.*

bonds. Consequently, these other molecules can form rings or chains, but not th dimensional structures.

The highly ordered three-dimensional structure of ice (Figure 11.12) preve the molecules from getting too close to one another. But consider what happ when ice melts. At the melting point, a number of water molecules have enou kinetic energy to break free of the intermolecular hydrogen bonds. These mo cules become trapped in the cavities of the three-dimensional structure, which broken down into smaller clusters. As a result, there are more molecules per volume in liquid water than in ice. Thus, because density = mass/volume, the d sity of water is greater than that of ice. With further heating, more water mo cules are released from intermolecular hydrogen bonding, so that the density water tends to increase with rising temperature just above the melting point. course, at the same time, water expands as it is being heated so that its density decreased. These two processes—the trapping of free water molecules in cavit and thermal expansion—act in opposite directions. From 0°C to 4°C, the trappi prevails and water becomes progressively denser. Beyond 4°C, however, therm expansion predominates and the density of water decreases with increasing te perature (Figure 11.13).

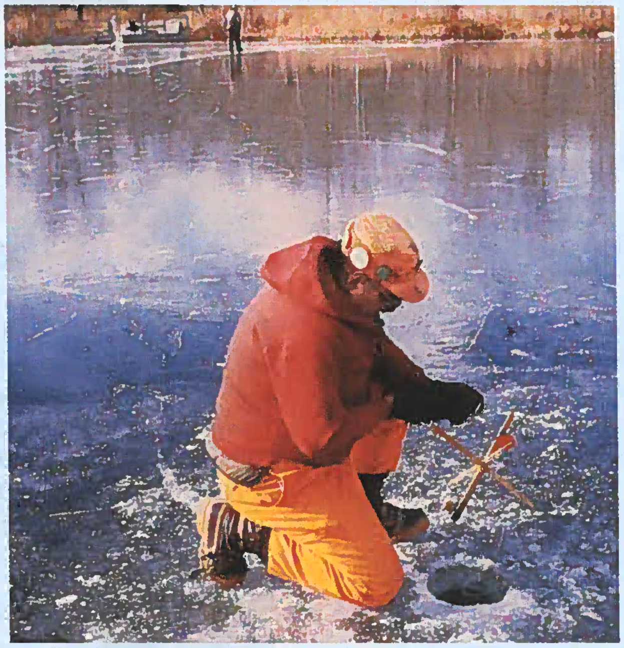
11.4 Crystal Structure

Solids can be divided into two categories: crystalline and amorphous. Ice is a ***crystalli solid,*** which *possesses rigid and long-range order; its atoms, molecules, or ions occu specific positions.* The arrangement of such particles in a crystalline solid is such th the net attractive intermolecular forces are at their maximum. The forces responsible

CHEMISTRY in Action

Why Do Lakes Freeze from the Top Down?

The fact that ice is less dense than water has a profound ecological significance. Consider, for example, the temperature changes in the fresh water of a lake in a cold climate. As the temperature of the water near the surface drops, the density of this water increases. The colder water then sinks toward the bottom, while warmer water, which is less dense, rises to the top. This normal convection motion continues until the temperature throughout the water reaches 4°C. Below this temperature, the density of water begins to decrease with decreasing temperature (see Figure 11.13), so that it no longer sinks. On further cooling, the water begins to freeze at the surface. The ice layer formed does not sink because it is less dense than the liquid; it even acts as a thermal insulator for the water below it. Were ice heavier, it would sink to the bottom of the lake and eventually the water would freeze upward. Most living organisms in the body of water could not survive being frozen in ice. Fortunately, lake water does not freeze upward from the bottom. This unusual property of water makes the sport of ice fishing possible.



Ice fishing. The ice layer that forms on the surface of a lake insulates the water beneath and maintains a high enough temperature to sustain aquatic life.

the stability of a crystal can be ionic forces, covalent bonds, van der Waals forces, hydrogen bonds, or a combination of these forces. *Amorphous solids* such as glass lack a well-defined arrangement and long-range molecular order. We will discuss them in Section 11.7. In this section we will concentrate on the structure of crystalline solids.

A ***unit cell*** is *the basic repeating structural unit of a crystalline solid.* Figure 11.14 shows a unit cell and its extension in three dimensions. Each sphere represents an atom, ion, or molecule and is called a *lattice point.* In many crystals, the lattice point does not actually contain such a particle. Rather, there may be several atoms, ions, or molecules identically arranged about each lattice point. For simplicity, however, we will assume that each lattice point is occupied by an atom. This is certainly the case with most metals. Every crystalline solid can be described in terms of one of the seven types of unit cells shown in Figure 11.15. The geometry of the cubic unit cell is particularly simple because all sides and all angles are equal. Any of the unit cells, when repeated in space in all three dimensions, forms the lattice structure characteristic of a crystalline solid.

Animation:
Packing Spheres
ARIS

Packing Spheres

We can understand the general geometric requirements for crystal formation by considering the different ways of packing a number of identical spheres (Ping-Pong balls,

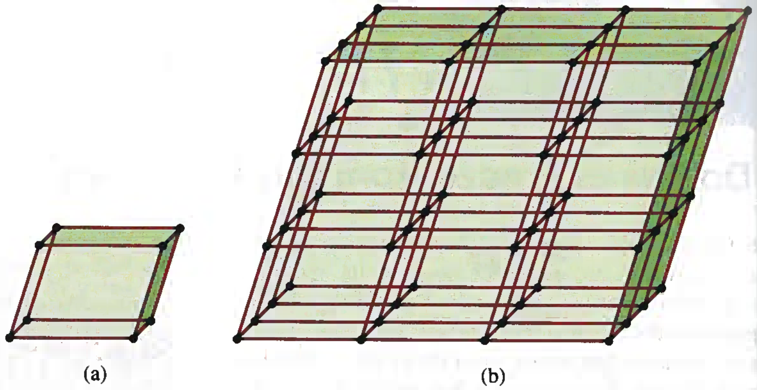
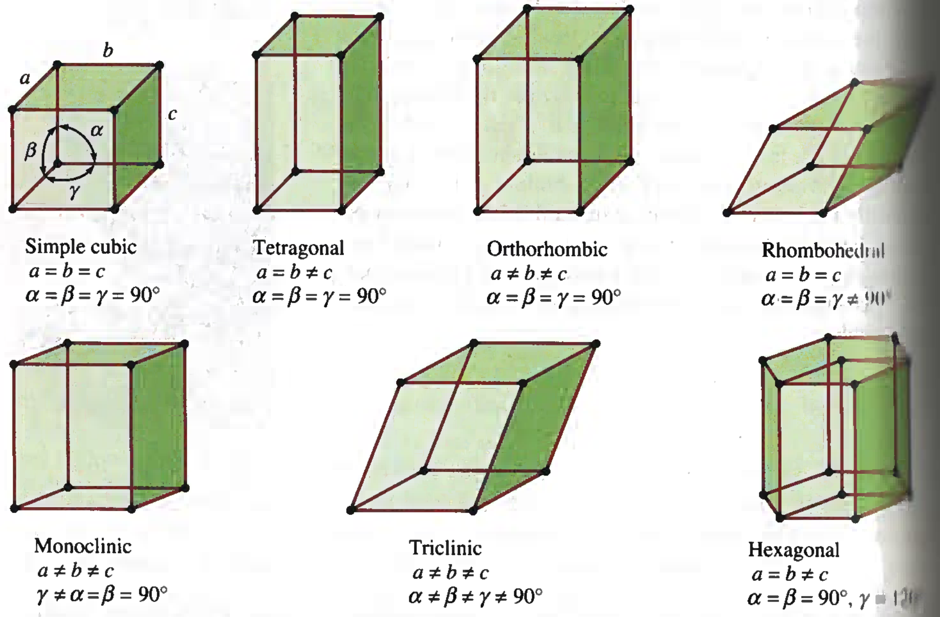


Figure 11.14 *(a) A unit cell and (b) its extension in three dimensions. The black spheres represent either atoms or molecules.*



Simple cubic
$a = b = c$
$\alpha = \beta = \gamma = 90°$

Tetragonal
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$

Orthorhombic
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$

Rhombohedral
$a = b = c$
$\alpha = \beta = \gamma \neq 90$

Monoclinic
$a \neq b \neq c$
$\gamma \neq \alpha = \beta = 90°$

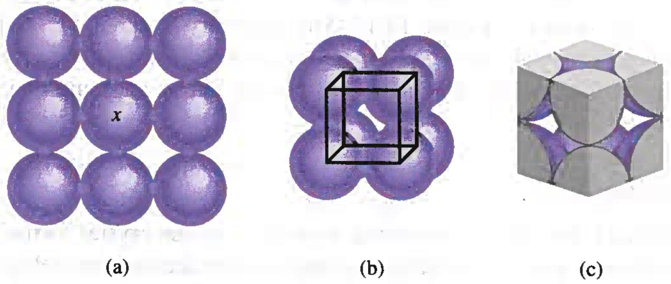
Triclinic
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$

Hexagonal
$a = b \neq c$
$\alpha = \beta = 90°, \gamma$

Figure 11.15 *The seven types of unit cells. Angle α is defined by edges b and c, angle β by edges a and c, and angle γ by edges a and b.*

for example) to form an ordered three-dimensional structure. The way the spheres arranged in layers determines what type of unit cell we have.

In the simplest case, a layer of spheres can be arranged as shown in Figure 11.16 The three-dimensional structure can be generated by placing a layer above and bel this layer in such a way that spheres in one layer are directly over the spheres in layer below it. This procedure can be extended to generate many, many layers, the case of a crystal. Focusing on the sphere labeled with an "x," we see that it



(a) (b) (c)

Figure 11.16 *Arrangement of identical spheres in a simple cubic cell. (a) Top view of one layer of spheres. (b) Definition of a simple cubic cell. (c) Since each sphere is shared by eight unit cells and there are eight corners in a cube, there is the equivalent of one complete sphere inside a simple cubic unit cell.*

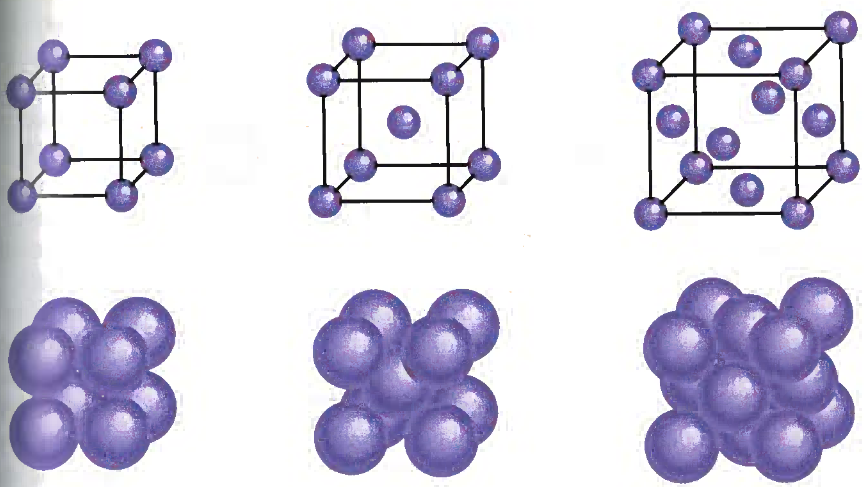

Simple cubic
Body-centered cubic
Face-centered cubic

Figure 11.17 *Three types of cubic cells. In reality, the spheres representing atoms, molecules, or ions are in contact with one another in these cubic cells.*

contact with four spheres in its own layer, one sphere in the layer above, and one sphere in the layer below. Each sphere in this arrangement is said to have a *coordination number* of 6 because it has six immediate neighbors. The ***coordination number*** is defined as *the number of atoms (or ions) surrounding an atom (or ion) in a crystal lattice.* Its value gives us a measure of how tightly the spheres are packed together—the larger the coordination number, the closer the spheres are to each other. The basic, repeating unit in the array of spheres is called a *simple cubic cell* (scc) [Figure 11.16(b)].

The other types of cubic cells are the *body-centered cubic cell* (bcc) and the *face-centered cubic cell* (fcc) (Figure 11.17). A body-centered cubic arrangement differs from a simple cube in that the second layer of spheres fits into the depressions of the first layer and the third layer into the depressions of the second layer (Figure 11.18). The coordination number of each sphere in this structure is 8 (each sphere is in contact with four spheres in the layer above and four spheres in the layer below). In the face-centered cubic cell, there are spheres at the center of each of the six faces of the cube, in addition to the eight corner spheres.

Because every unit cell in a crystalline solid is adjacent to other unit cells, most of a cell's atoms are shared by neighboring cells. For example, in all types of cubic cells, each corner atom belongs to eight unit cells [Figure 11.19(a)]; an edge atom is shared by four unit cells [Figure 11.19(b)], and a face-centered atom is shared by two unit cells [Figure 11.19(c)]. Because each corner sphere is shared by eight unit cells and there are eight corners in a cube, there will be the equivalent of only one complete sphere inside a simple cubic unit cell (see Figure 11.17). A body-centered cubic cell contains the equivalent of two complete spheres, one in the center and eight shared corner spheres. A face-centered cubic cell contains four

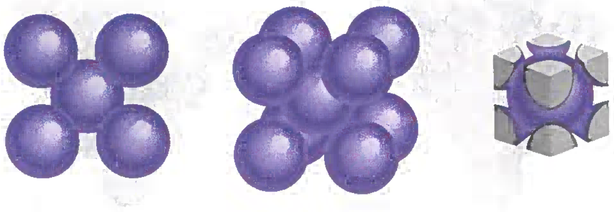
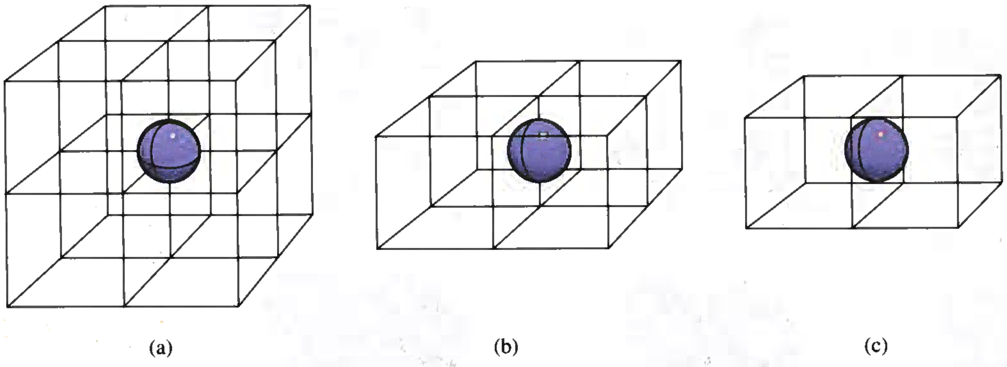

(a)
(b)
(c)

Figure 11.18 *Arrangement of identical spheres in a body-centered cube. (a) Top view. (b) Definition of a body-centered cubic unit cell. (c) There is the equivalent of two complete spheres inside a body-centered cubic unit cell.*



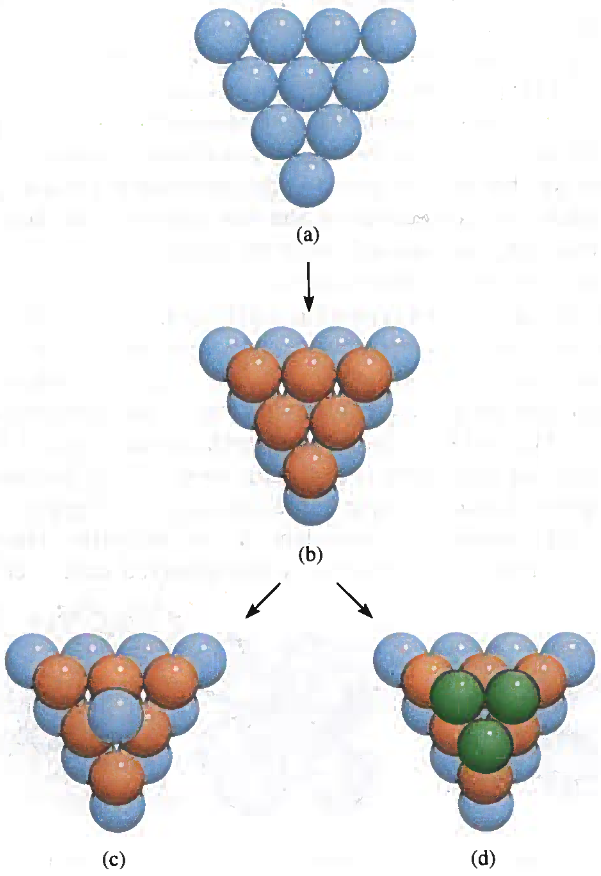
(a) (b) (c)

Figure 11.19 *(a) A corner atom in any cell is shared by eight unit cells. (b) An edge atom is shared by four unit cells. (c) A face-centered atom in a cubic cell is shared by two unit cells.*

complete spheres—three from the six face-centered atoms and one from the eight shared corner spheres.

Closest Packing

Clearly there is more empty space in the simple cubic and body-centered cubic cells than in the face-centered cubic cell. ***Closest packing,** the most efficient arrangement of spheres,* starts with the structure shown in Figure 11.20(a), which we call layer A.



(a) (b) (c) (d)

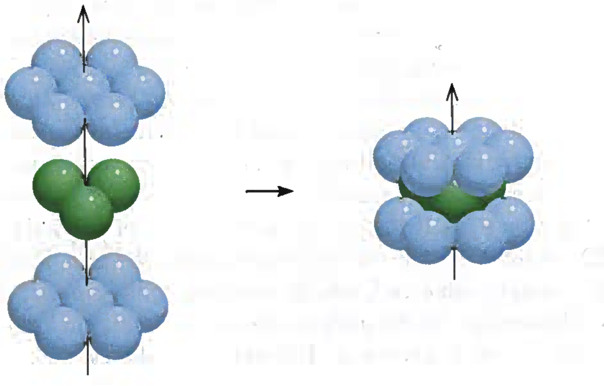
Figure 11.20 *(a) In a close-packed layer, each sphere is in contact with six others. (b) Spheres in the second layer fit into the depressions between the first-layer spheres. (c) In the hexagonal close-packed structure, each third-layer sphere is directly over a first-layer sphere. (d) In the cubic close-packed structure, each third-layer sphere fits into a depression that is directly over a depression in the first layer.*

Focusing on the only enclosed sphere, we see that it has six immediate neighbors in that layer. In the second layer (which we call layer B), spheres are packed into the depressions between the spheres in the first layer so that all the spheres are as close together as possible [Figure 11.20(b)].

There are two ways that a third-layer sphere may cover the second layer to achieve closest packing. The spheres may fit into the depressions so that each third-layer sphere is directly over a first-layer sphere [Figure 11.20(c)]. Because there is no difference between the arrangement of the first and third layers, we also call the third layer layer A. Alternatively, the third-layer spheres may fit into the depressions that lie directly over the depressions in the first layer [Figure 11.20(d)]. In this case, we call the third layer layer C. Figure 11.21 shows the "exploded views" and the structures resulting from these two arrangements. The ABA arrangement is known as the *hexagonal close-packed (hcp) structure,* and the ABC arrangement is the *cubic close-packed (ccp) structure,* which corresponds to the face-centered cube already described. Note that in the hcp structure, the spheres in every other layer occupy the same vertical position (ABABAB. . .), while in the ccp structure, the spheres in every fourth layer occupy the same vertical position (ABCABCA. . .). In both structures, each sphere has a coordination number of 12 (each sphere is in contact with six spheres in its own layer, three spheres in the layer above, and three spheres in the layer below). Both the hcp and ccp structures represent the most efficient way of packing identical spheres in a unit cell, and there is no way to increase the coordination number to beyond 12.

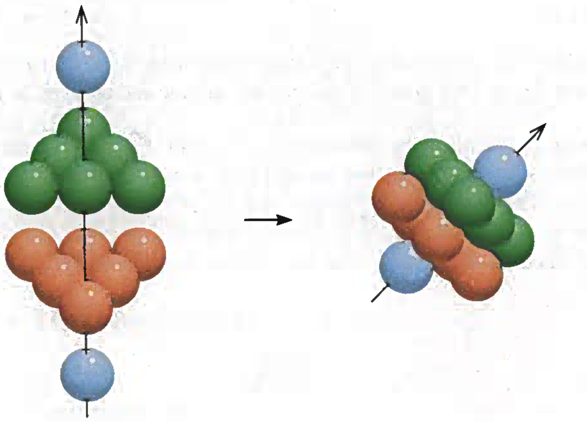
These oranges are in a closest packed arrangement, as shown in Figure 11.20(a).

Figure 11.21 *Exploded views of (a) a hexagonal close-packed structure and (b) a cubic close-packed structure. The arrow is tilted to show the face-centered cubic unit cell more clearly. Note that this arrangement is the same as the face-centered unit cell.*



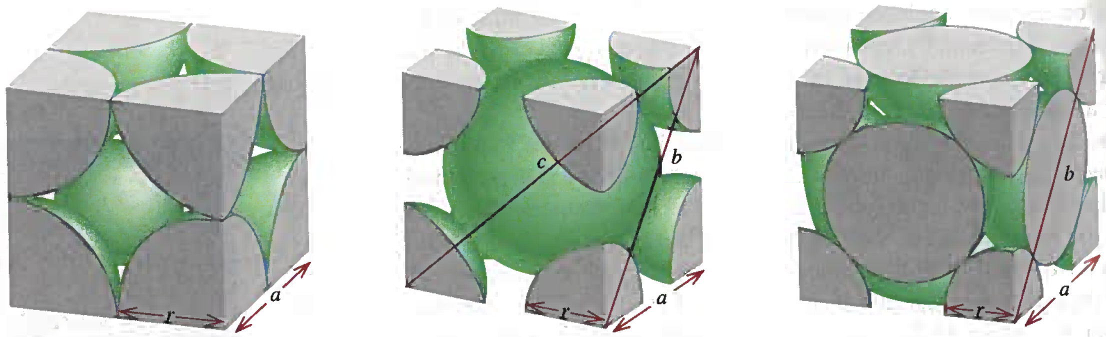
Exploded view Hexagonal close-packed structure

(a)



Exploded view Cubic close-packed structure

(b)



scc

$a = 2r$

bcc

$$b^2 = a^2 + a^2$$
$$c^2 = a^2 + b^2$$
$$= 3a^2$$
$$c = \sqrt{3}a = 4r$$
$$a = \frac{4r}{\sqrt{3}}$$

fcc

$$b = 4r$$
$$b^2 = a^2 + a^2$$
$$16r^2 = 2a^2$$
$$a = \sqrt{8}r$$

Figure 11.22 *The relationship between the edge length (a) and radius (r) of atoms in the simple cubic cell, body-centered cubic cell, and face-centered cubic cell.*

Many metals and noble gases, which are monatomic, form crystals with hcp or ccp structures. For example, magnesium, titanium, and zinc crystallize with their atoms in a hcp array, while aluminum, nickel, and silver crystallize in the ccp arrangement. All solid noble gases have the ccp structure except helium, which crystallizes in the hcp structure. It is natural to ask why a series of related substances, such as the transition metals or the noble gases, would form different crystal structures. The answer lies in the relative stability of a particular crystal structure, which is governed by intermolecular forces. Thus, magnesium metal has the hcp structure because this arrangement of Mg atoms results in the greatest stability of the solid.

Figure 11.22 summarizes the relationship between the atomic radius r and the edge length a of a simple cubic cell, a body-centered cubic cell, and a face-centered cubic cell. This relationship can be used to determine the atomic radius of a sphere if the density of the crystal is known, as Example 11.3 shows.

Example 11.3

Gold (Au) crystallizes in a cubic close-packed structure (the face-centered cubic unit cell) and has a density of 19.3 g/cm^3. Calculate the atomic radius of gold in picometers.

Strategy We want to calculate the radius of a gold atom. For a face-centered cubic unit cell, the relationship between radius (r) and edge length (a), according to Figure 11.22, is $a = \sqrt{8}r$. Therefore, to determine r of a Au atom, we need to find a. The volume of a cube is $V = a^3$ or $a = \sqrt[3]{V}$. Thus, if we can determine the volume of the unit cell, we can calculate a. We are given the density in the problem.

$$\overset{\text{given}}{\text{density}} = \frac{\overset{\text{need to find}}{\text{mass}}}{\underset{\text{want to calculate}}{\text{volume}}}$$

(Continued)

The sequence of steps is summarized as follows:

$$\begin{matrix}\text{density of} \\ \text{unit cell}\end{matrix} \longrightarrow \begin{matrix}\text{volume of} \\ \text{unit cell}\end{matrix} \longrightarrow \begin{matrix}\text{edge length} \\ \text{of unit cell}\end{matrix} \longrightarrow \begin{matrix}\text{radius of} \\ \text{Au atom}\end{matrix}$$

Solution

Step 1: We know the density, so in order to determine the volume, we find the mass of the unit cell. Each unit cell has eight corners and six faces. The total number of atoms within such a cell, according to Figure 11.19, is

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

The mass of a unit cell in grams is

$$\begin{aligned} m &= \frac{4\ \cancel{\text{atoms}}}{1\ \text{unit cell}} \times \frac{1\ \cancel{\text{mol}}}{6.022 \times 10^{23}\ \cancel{\text{atoms}}} \times \frac{197.0\ \text{g Au}}{1\ \cancel{\text{mol Au}}} \\ &= 1.31 \times 10^{-21}\ \text{g/unit cell} \end{aligned}$$

From the definition of density ($d = m/V$), we calculate the volume of the unit cell as follows:

Remember that density is an intensive property, so that it is the same for one unit cell and 1 cm^3 of the substance.

$$V = \frac{m}{d} = \frac{1.31 \times 10^{-21}\ \text{g}}{19.3\ \text{g/cm}^3} = 6.79 \times 10^{-23}\ \text{cm}^3$$

Step 2: Because volume is length cubed, we take the cubic root of the volume of the unit cell to obtain the edge length (a) of the cell

$$\begin{aligned} a &= \sqrt[3]{V} \\ &= \sqrt[3]{6.79 \times 10^{-23}\ \text{cm}^3} \\ &= 4.08 \times 10^{-8}\ \text{cm} \end{aligned}$$

Step 3: From Figure 11.22 we see that the radius of an Au sphere (r) is related to the edge length by

$$a = \sqrt{8}\, r$$

Therefore,

$$\begin{aligned} r &= \frac{a}{\sqrt{8}} = \frac{4.08 \times 10^{-8}\ \text{cm}}{\sqrt{8}} \\ &= 1.44 \times 10^{-8}\ \text{cm} \\ &= 1.44 \times 10^{-8}\ \cancel{\text{cm}} \times \frac{1 \times 10^{-2}\ \cancel{\text{m}}}{1\ \cancel{\text{cm}}} \times \frac{1\ \text{pm}}{1 \times 10^{-12}\ \cancel{\text{m}}} \\ &= 144\ \text{pm} \end{aligned}$$

Similar problem: 11.39.

Practice Exercise When silver crystallizes, it forms face-centered cubic cells. The unit cell edge length is 408.7 pm. Calculate the density of silver.

11.5 X-Ray Diffraction by Crystals

Virtually all we know about crystal structure has been learned from X-ray diffraction studies. ***X-ray diffraction*** refers to *the scattering of X rays by the units of a crystalline solid.* The scattering, or diffraction, patterns produced are used to deduce the arrangement of particles in the solid lattice.

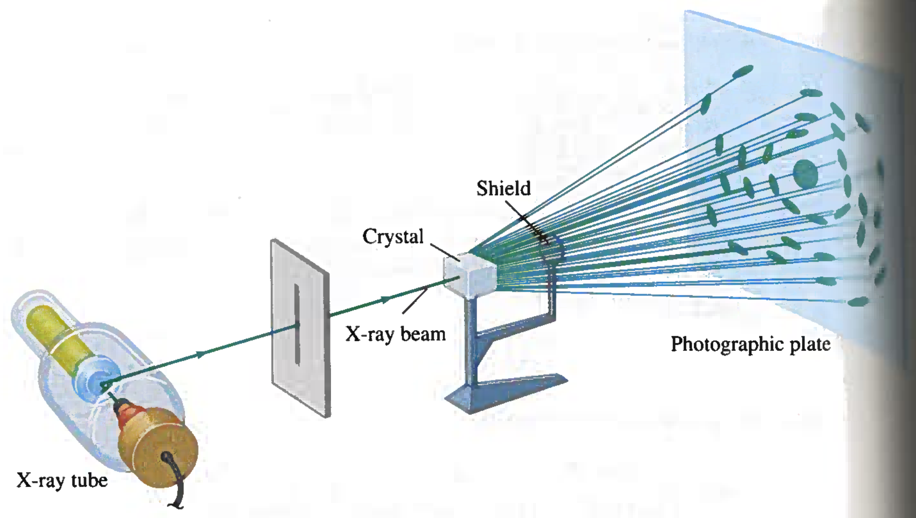


Figure 11.23 *An arrangement for obtaining the X-ray diffraction pattern of a crystal. The shield prevents the strong undiffracted X rays from damaging the photographic plate.*

In Section 10.6 we discussed the interference phenomenon associated with waves (see Figure 10.21). Because X rays are one form of electromagnetic radiation, and therefore waves, we would expect them to exhibit such behavior under suitable conditions. In 1912 the German physicist Max von Laue[†] correctly suggested that, because the wavelength of X rays is comparable in magnitude to the distances between lattice points in a crystal, the lattice should be able to *diffract* X rays. An X-ray diffraction pattern is the result of interference in the waves associated with X rays.

Figure 11.23 shows a typical X-ray diffraction setup. A beam of X rays is directed at a mounted crystal. Atoms in the crystal absorb some of the incoming radiation and then reemit it; the process is called the *scattering of X rays.*

To understand how a diffraction pattern may be generated, consider the scattering of X rays by atoms in two parallel planes (Figure 11.24). Initially, the two incident rays are *in phase* with each other (their maxima and minima occur at the same positions). The upper wave is scattered, or reflected, by an atom in the first layer, while the lower wave is scattered by an atom in the second layer. In order for these

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[†] Max Theodor Felix von Laue (1879–1960). German physicist. Von Laue received the Nobel Prize in Physics in 1914 for his discovery of X-ray diffraction.

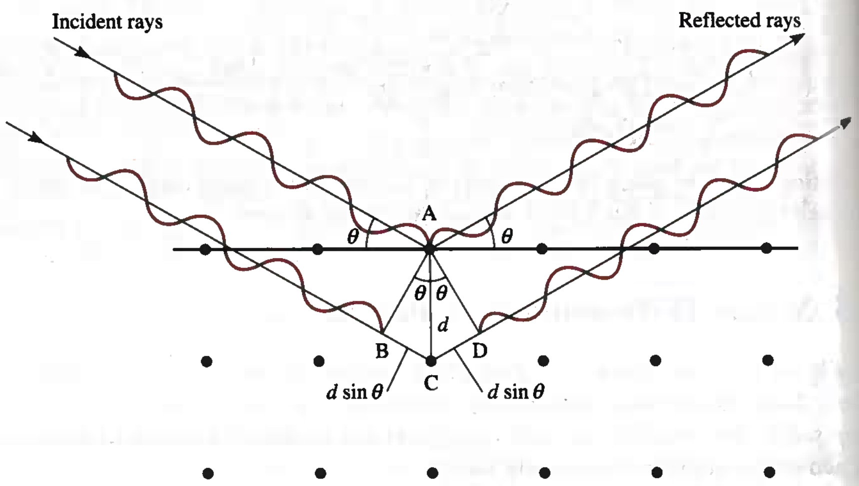


Figure 11.24 *Reflection of X rays from two layers of atoms. The lower wave travels a distance 2d sin θ longer than the upper wave does. For the two waves to be in phase again after reflection, it must be true that 2d sin θ = nλ, where λ is the wavelength of the X ray and n = 1, 2, 3, . . . The sharply defined spots in Figure 11.23 are observed only if the crystal is large enough to consist of hundreds of parallel layers.*

two scattered waves to be in phase again, the extra distance traveled by the lower wave must be an integral multiple of the wavelength (λ) of the X ray; that is,

$$BC + CD = 2d\sin\theta = n\lambda \qquad n = 1, 2, 3, \ldots$$

or

$$2d\sin\theta = n\lambda \tag{11.1}$$

where θ is the angle between the X rays and the plane of the crystal and d is the distance between adjacent planes. Equation (11.1) is known as the Bragg equation after William H. Bragg[‡] and Sir William L. Bragg.[§] The reinforced waves produce a dark spot on a photographic film for each value of θ that satisfies the Bragg equation.

Reinforced waves are waves that have interacted constructively (see Figure 10.21).

Example 11.4 illustrates the use of Equation (11.1).

Example 11.4

X rays of wavelength 0.154 nm strike an aluminum crystal; the rays are reflected at an angle of 19.3°. Assuming that $n = 1$, calculate the spacing between the planes of aluminum atoms (in pm) that is responsible for this angle of reflection. The conversion factor is obtained from 1 nm = 1000 pm.

Strategy This is an application of Equation (11.1).

Solution Converting the wavelength to picometers and using the angle of reflection (19.3°), we write

$$d = \frac{n\lambda}{2\sin\theta} = \frac{\lambda}{2\sin\theta}$$

$$= \frac{0.154\text{ nm} \times \dfrac{1000\text{ pm}}{1\text{ nm}}}{2\sin 19.3°}$$

$$= 233\text{ pm}$$

Similar problems: 11.47, 11.48.

Practice Exercise X rays of wavelength 0.154 nm are diffracted from a crystal at an angle of 14.17°. Assuming that $n = 1$, calculate the distance (in pm) between layers in the crystal.

The X-ray diffraction technique offers the most accurate method for determining bond lengths and bond angles in molecules in the solid state. Because X rays are scattered by electrons, chemists can construct an electron-density contour map from the diffraction patterns by using a complex mathematical procedure. Basically, an *electron-density contour map* tells us the relative electron densities at various locations in a molecule. The densities reach a maximum near the center of each atom. In this manner, we can determine the positions of the nuclei and hence the geometric parameters of the molecule.

11.6 Types of Crystals

The structures and properties of crystals, such as melting point, density, and hardness, are determined by the kinds of forces that hold the particles together. We can classify any crystal as one of four types: ionic, covalent, molecular, or metallic.

[‡] William Henry Bragg (1862–1942). English physicist. Bragg's work was mainly in X-ray crystallography. He shared the Nobel Prize in Physics with his son Sir William Bragg in 1915.

[§] Sir William Lawrence Bragg (1890–1972). English physicist. Bragg formulated the fundamental equation for X-ray diffraction and shared the Nobel Prize in Physics with his father in 1915.

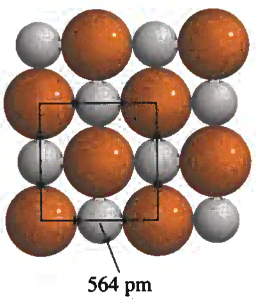


Figure 11.25 *Relation between the radii of Na^+ and Cl^- ions and the unit cell dimensions. Here the cell edge length is equal to twice the sum of the two ionic radii.*

These giant potassium dihydrogen phosphate crystals were grown in the laboratory. The largest one weighs 701 lb!

Ionic Crystals

Ionic crystals have two important characteristics: (1) They are composed of charged species and (2) anions and cations are generally quite different in size. Knowing the radii of the ions is helpful in understanding the structure and stability of these compounds. There is no way to measure the radius of an individual ion, but sometimes it is possible to come up with a reasonable estimate. For example, if we know the radius of I^- in KI is about 216 pm, we can determine the radius of K^+ ion in KI, and then that, the radius of Cl^- in KCl, and so on. The ionic radii in Figure 8.9 are average values derived from many different compounds. Let us consider the NaCl crystal, which has a face-centered cubic lattice (see Figure 2.13). Figure 11.25 shows that the edge length of the unit cell of NaCl is twice the sum of the ionic radii of Na^+ and Cl^-. Using the values given in Figure 8.9, we calculate the edge length to be 2(95 + 181) pm, or 552 pm. But the edge length shown in Figure 11.25 was determined by X-ray diffraction to be 564 pm. The discrepancy between these two values tells us that the radius of an ion actually varies slightly from one compound to another.

Figure 11.26 shows the crystal structures of three ionic compounds: CsCl, ZnS, and CaF_2. Because Cs^+ is considerably larger than Na^+, CsCl has the simple cubic lattice. ZnS has the *zincblende* structure, which is based on the face-centered cubic lattice. If the S^{2-} ions occupy the lattice points, the Zn^{2+} ions are located one-fourth of the distance along each body diagonal. Other ionic compounds that have the zincblende structure include CuCl, BeS, CdS, and HgS. CaF_2 has the *fluorite* structure. The Ca^{2+} ions occupy the lattice points, and each F^- ion is tetrahedrally surrounded by four Ca^{2+} ions. The compounds SrF_2, BaF_2, $BaCl_2$, and PbF_2 also have the fluorite structure.

Examples 11.5 and 11.6 show how to calculate the number of ions in and the density of a unit cell.

Example 11.5

How many Na^+ and Cl^- ions are in each NaCl unit cell?

Solution NaCl has a structure based on a face-centered cubic lattice. As Figure 2.13 shows, one whole Na^+ ion is at the center of the unit cell, and there are twelve Na^+ ions at the edges. Because each edge Na^+ ion is shared by four unit cells [see Figure 11.19(b)],

(Continued)

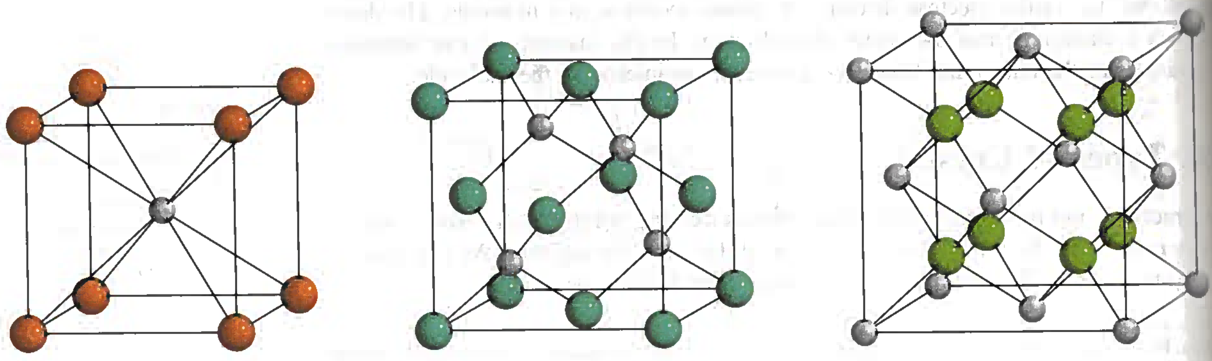

(a) (b) (c)

Figure 11.26 *Crystal structures of (a) CsCl, (b) ZnS, and (c) CaF_2. In each case, the cation is the smaller sphere.*

The total number of Na^+ ions is $1 + (12 \times \frac{1}{4}) = 4$. Similarly, there are six Cl^- ions at the face centers and eight Cl^- ions at the corners. Each face-centered ion is shared by two unit cells, and each corner ion is shared by eight unit cells [see Figures 11.19(a) and (c)], so the total number of Cl^- ions is $(6 \times \frac{1}{2}) + (8 \times \frac{1}{8}) = 4$. Thus, there are four Na^+ ions and four Cl^- ions in each NaCl unit cell. Figure 11.27 shows the portions of the Na^+ and Cl^- ions *within* a unit cell.

Check This result agrees with sodium chloride's empirical formula.

Practice Exercise How many atoms are in a body-centered cube, assuming that all atoms occupy lattice points?

Similar problem: 11.41.

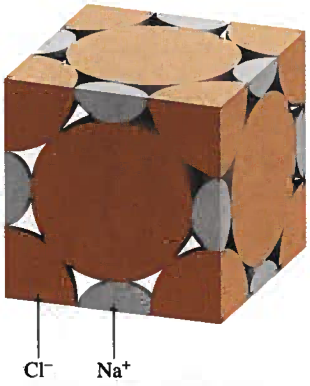


Figure 11.27 *Portions of Na^+ and Cl^- ions within a face-centered cubic unit cell.*

Example 11.6

The edge length of the NaCl unit cell is 564 pm. What is the density of NaCl in g/cm^3?

Strategy To calculate the density, we need to know the mass of the unit cell. The volume can be calculated from the given edge length because $V = a^3$. How many Na^+ and Cl^- ions are in a unit cell? What is the total mass in amu? What are the conversion factors between amu and g and between pm and cm?

Solution From Example 11.5 we see that there are four Na^+ ions and four Cl^- ions in each unit cell. So the total mass (in amu) of a unit cell is

$$\text{mass} = 4(22.99 \text{ amu} + 35.45 \text{ amu}) = 233.8 \text{ amu}$$

Converting amu to grams, we write

$$233.8 \text{ amu} \times \frac{1 \text{ g}}{6.022 \times 10^{23} \text{ amu}} = 3.882 \times 10^{-22} \text{ g}$$

The volume of the unit cell is $V = a^3 = (564 \text{ pm})^3$. Converting pm^3 to cm^3, the volume is given by

$$V = (564 \text{ pm})^3 \times \left(\frac{1 \times 10^{-12} \text{ m}}{1 \text{ pm}}\right)^3 \times \left(\frac{1 \text{ cm}}{1 \times 10^{-2} \text{ m}}\right)^3 = 1.794 \times 10^{-22} \text{ cm}^3$$

Finally, from the definition of density

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{3.882 \times 10^{-22} \text{ g}}{1.794 \times 10^{-22} \text{ cm}^3}$$
$$= \boxed{2.16 \text{ g/cm}^3}$$

Similar problem: 11.42.

Practice Exercise Copper crystallizes in a face-centered cubic lattice (the Cu atoms are at the lattice points only). If the density of the metal is 8.96 g/cm^3, what is the unit cell edge length in pm?

Most ionic crystals have high melting points, an indication of the strong cohesive forces holding the ions together. A measure of the stability of ionic crystals is the lattice energy (see Section 9.3); the higher the lattice energy, the more stable the compound. These solids do not conduct electricity because the ions are fixed in position. However, in the molten state (that is, when melted) or dissolved in water, the ions are free to move and the resulting liquid is electrically conducting.

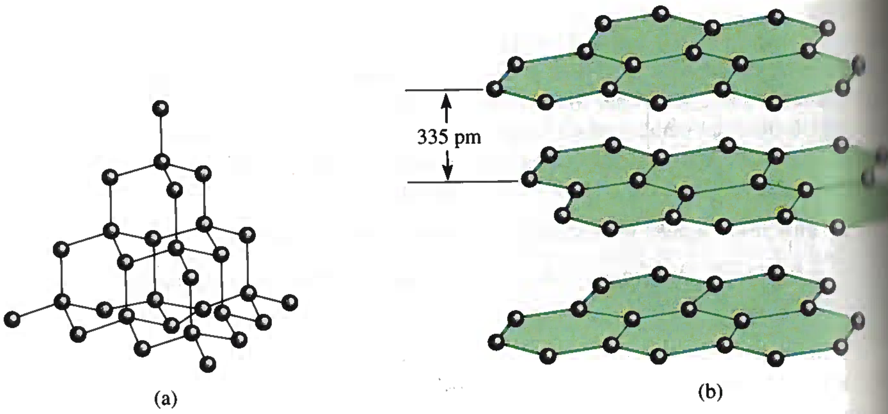


Figure 11.28 *(a) The structure of diamond. Each carbon is tetrahedrally bonded to four other carbon atoms. (b) The structure of graphite. The distance between successive layers is 335 pm.*

Covalent Crystals

In covalent crystals, atoms are held together in an extensive three-dimensional network entirely by covalent bonds. Well-known examples are the two allotropes of carbon: diamond and graphite (see Figure 8.17). In diamond, each carbon atom is sp^3-hybridized; it is bonded to four other atoms (Figure 11.28). The strong covalent bonds in three dimensions contribute to diamond's unusual hardness (it is the hardest material known) and very high melting point (3550°C). In graphite, carbon atoms are arranged in six-membered rings. The atoms are all sp^2-hybridized; each atom is covalently bonded to three other atoms. The remaining unhybridized 2*p* orbital is used in pi bonding. In fact, each layer of graphite has the kind of delocalized molecular orbital that is present in benzene (see Section 10 Because electrons are free to move around in this extensively delocalized molecular orbital, graphite is a good conductor of electricity in directions along the planes of carbon atoms. The layers are held together by weak van der Waals forces. The covalent bonds in graphite account for its hardness; however, because the layers can slide over one another, graphite is slippery to the touch and is effective as a lubricant. It is also used in pencils and in ribbons made for computer printers and typewriters.

The central electrode in flashlight batteries is made of graphite.

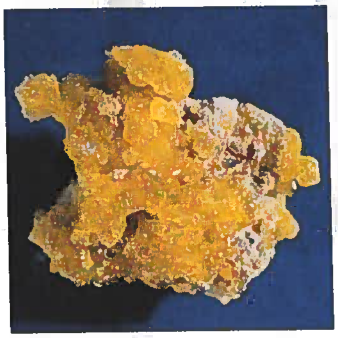
Another covalent crystal is quartz (SiO_2). The arrangement of silicon atoms in quartz is similar to that of carbon in diamond, but in quartz there is an oxygen atom between each pair of Si atoms. Because Si and O have different electronegativities, the Si—O bond is polar. Nevertheless, SiO_2 is similar to diamond in many respects, such as hardness and high melting point (1610°C).

Quartz.

Molecular Crystals

In a molecular crystal, the lattice points are occupied by molecules, and the attractive forces between them are van der Waals forces and/or hydrogen bonding. An example of a molecular crystal is solid sulfur dioxide (SO_2), in which the predominant attractive force is a dipole-dipole interaction. Intermolecular hydrogen bonding is mainly responsible for maintaining the three-dimensional lattice of ice (see Figure 11.1 Other examples of molecular crystals are I_2, P_4, and S_8.

In general, except in ice, molecules in molecular crystals are packed together as closely as their size and shape allow. Because van der Waals forces and hydrogen bonding are generally quite weak compared with covalent and ionic bonds, molecular crystals are more easily broken apart than ionic and covalent crystals. Indeed, most molecular crystals melt at temperatures below 100°C.



Sulfur.

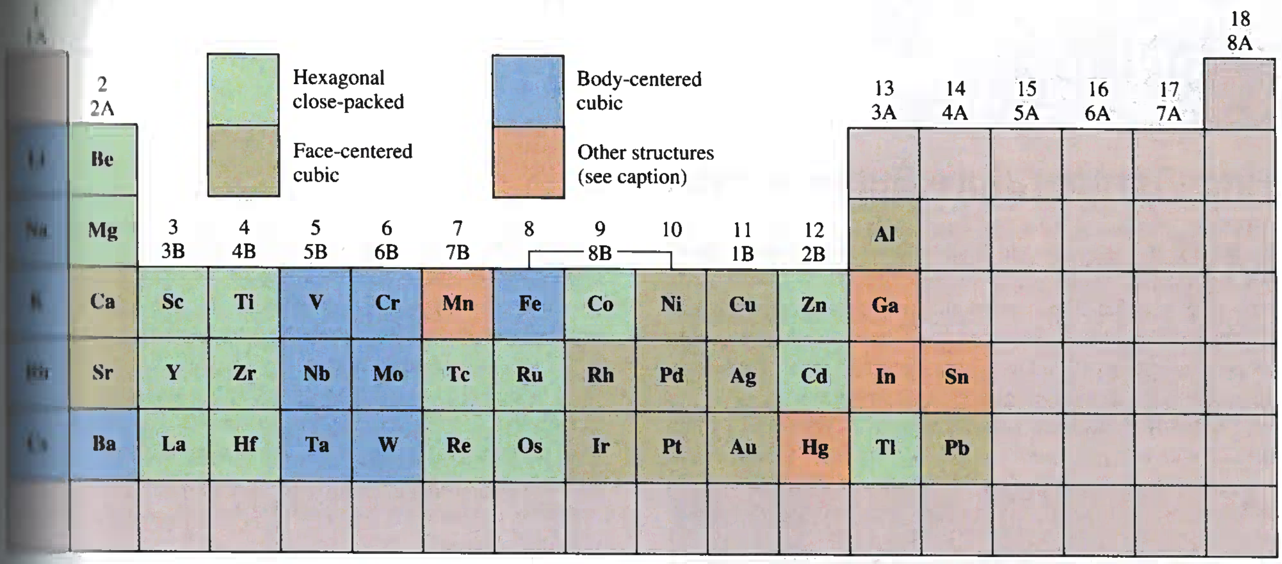


Figure 11.29 *Crystal structures of metals. The metals are shown in their positions in the periodic table. Mn has a cubic structure, Ga an orthorhombic structure, In and Sn a tetragonal structure, and Hg a rhombohedral structure (see Figure 11.15).*

Metallic Crystals

In a sense, the structure of metallic crystals is the simplest because every lattice point in a crystal is occupied by an atom of the same metal. Metallic crystals are generally body-centered cubic, face-centered cubic, or hexagonal close-packed (Figure 11.29). Consequently, metallic elements are usually very dense.

The bonding in metals is quite different from that in other types of crystals. In a metal, the bonding electrons are delocalized over the entire crystal. In fact, metal atoms in a crystal can be imagined as an array of positive ions immersed in a sea of delocalized valence electrons (Figure 11.30). The great cohesive force resulting from delocalization is responsible for a metal's strength. The mobility of the delocalized electrons makes metals good conductors of heat and electricity.

Table 11.4 summarizes the properties of the four different types of crystals discussed.

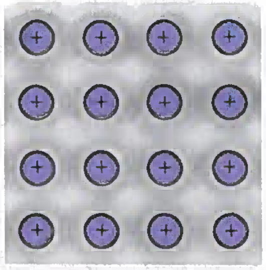
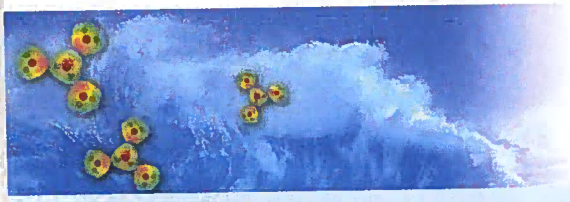


Figure 11.30 *A cross section of a metallic crystal. Each circled positive charge represents the nucleus and inner electrons of a metal atom. The gray area surrounding the positive metal ions indicates the mobile sea of electrons.*

TABLE 11.4 Types of Crystals and General Properties

Type of Crystal	Force(s) Holding the Units Together	General Properties	Examples
Ionic	Electrostatic attraction	Hard, brittle, high melting point, poor conductor of heat and electricity	NaCl, LiF, MgO, $CaCO_3$
Covalent	Covalent bond	Hard, high melting point, poor conductor of heat and electricity	C (diamond),† SiO_2 (quartz)
Molecular*	Dispersion forces, dipole-dipole forces, hydrogen bonds	Soft, low melting point, poor conductor of heat and electricity	Ar, CO_2, I_2, H_2O, $C_{12}H_{22}O_{11}$ (sucrose)
Metallic	Metallic bond	Soft to hard, low to high melting point, good conductor of heat and electricity	All metallic elements; for example, Na, Mg, Fe, Cu

*Included in this category are crystals made up of individual atoms.
†Diamond is a good thermal conductor.



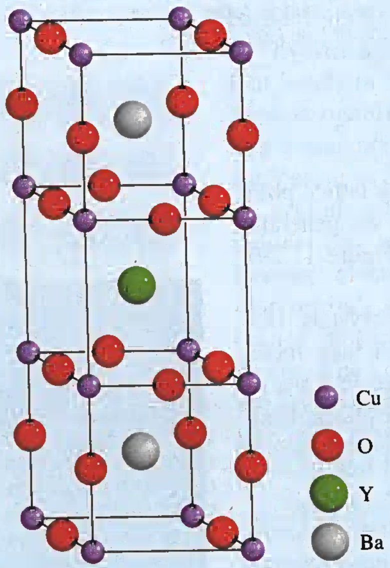
CHEMISTRY *in Action*

High-Temperature Superconductors

Metals such as copper and aluminum are good conductors of electricity, but they do possess some electrical resistance. In fact, up to about 20 percent of electrical energy may be lost in the form of heat when cables made of these metals are used to transmit electricity. Wouldn't it be marvelous if we could produce cables that possessed no electrical resistance?

Actually it has been known for over 90 years that certain metals and alloys, when cooled to very low temperatures (around the boiling point of liquid helium, or 4 K), lose their resistance totally. However, it is not practical to use these substances, called superconductors, for transmission of
power because the cost of maintaining electrical cables
low temperatures is prohibitive and would far exceed
ings from more efficient electricity transmission.

In 1986 two physicists in Switzerland discovered
class of materials that are superconducting at around 30
though 30 K is still a very low temperature, the improvem
the 4 K range was so dramatic that their work generated
interest and triggered a flurry of research activity. Within
scientists synthesized compounds that are supercond



Crystal structure of $YBa_2Cu_3O_x$ (x = 6 or 7). Because some of the O atom sites are vacant, the formula is not constant.

The levitation of a magnet above a high-temperature superconductor immersed in liquid nitrogen.

11.7 Amorphous Solids

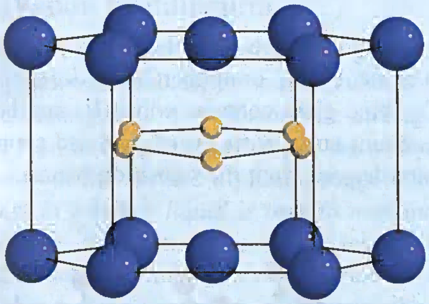
Solids are most stable in crystalline form. However, if a solid is formed rapidly
example, when a liquid is cooled quickly), its atoms or molecules do not have
to align themselves and may become locked in positions other than those of a
lar crystal. The resulting solid is said to be *amorphous*. ***Amorphous solids,*** such
glass, *lack a regular three-dimensional arrangement of atoms.* In this section, we
discuss briefly the properties of glass.

Glass is one of civilization's most valuable and versatile materials. It is also
of the oldest—glass articles date back as far as 1000 B.C. ***Glass*** commonly refe

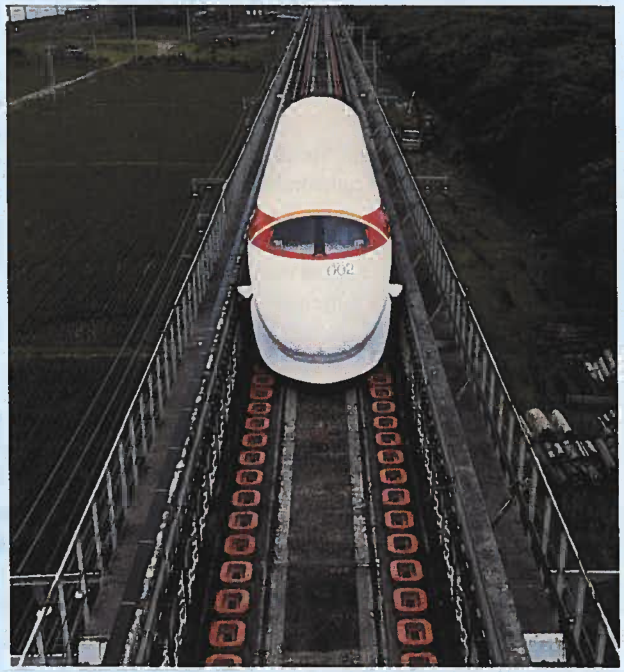
around 95 K, which is well above the boiling point of liquid nitrogen (77 K). The figure on p. 476 shows the crystal structure of one of these compounds, a mixed oxide of yttrium, barium, and copper with the formula $YBa_2Cu_3O_x$ (where $x = 6$ or 7). The accompanying figure shows a magnet being levitated above such a superconductor, which is immersed in liquid nitrogen.

Despite the initial excitement, this class of high-temperature superconductors has not fully lived up to its promise. After almost 20 years of intense research and development, scientists still puzzle over how and why these compounds superconduct. It has also proved difficult to make wires of these compounds, and other technical problems have limited their large-scale commercial applications thus far.

In another encouraging development, in 2001 scientists in Japan discovered that magnesium diboride (MgB_2) becomes superconducting at about 40 K. Although liquid neon (b.p. 27 K) must be used as coolant instead of liquid nitrogen, it is still much cheaper than using liquid helium. Magnesium diboride has several advantages as a high-temperature superconductor. First, it is an inexpensive compound (about $2 per gram) so large quantities are available for testing. Second, the mechanism of superconductivity in MgB_2 is similar to the well-understood metal alloy superconductors at 4 K. Third, it is much easier to fabricate this compound; that is, to make it into wires or thin films. With further research effort, it is hoped that someday soon different types of high-temperature superconductors will be used to build supercomputers, whose speeds are limited by how fast electric current flows, more powerful particle accelerators, efficient devices for nuclear fusion, and more accurate magnetic resonance imaging (MRI) machines for medical use. The progress in high-temperature superconductors is just warming up!



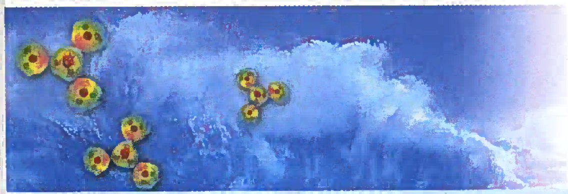
Crystal structure of MgB_2. The Mg atoms (blue) form a hexagonal layer, while the B atoms (gold) form a graphitelike honeycomb layer.



An experimental levitation train that operates on superconducting material at temperature of liquid helium.

an ***optically transparent fusion product of inorganic materials that has cooled to a rigid state without crystallizing.*** By fusion product we mean that the glass is formed by mixing molten silicon dioxide (SiO_2), its chief component, with compounds such as sodium oxide (Na_2O), boron oxide (B_2O_3), and certain transition metal oxides for color and other properties. In some respects glass behaves more like a liquid than a solid. X-ray diffraction studies show that glass lacks long-range periodic order.

There are about 800 different types of glass in common use today. Figure 11.31 shows two-dimensional schematic representations of crystalline quartz and amorphous quartz glass. Table 11.5 shows the composition and properties of quartz, Pyrex, and soda-lime glass.



CHEMISTRY in Action

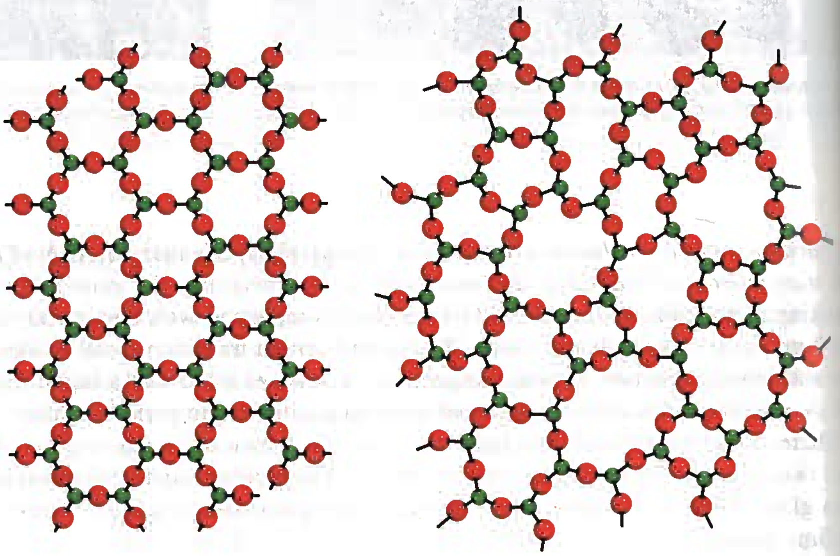
And All for the Want of a Button

In June 1812, Napoleon's mighty army, some 600,000 strong, marched into Russia. By early December, however, his forces were reduced to fewer than 10,000 men. An intriguing theory for Napoleon's defeat has to do with the tin buttons on his soldiers' coats! Tin has two allotropic forms called α (gray tin) and β (white tin). White tin, which has a cubic structure and a shiny metallic appearance, is stable at room temperature and above. Below 13°C, it slowly changes into gray tin. The random growth of the microcrystals of gray tin, which has a tetragonal structure, weakens the metal and makes it crumble. Thus, in the severe Russian winter, the soldiers were probably more busy holding their coats together with their hands than carrying weapons.

Actually, the so-called "tin disease" has been known for centuries. In the unheated cathedrals of medieval Europe, organ pipes made of tin were found to crumble as a result of the allotropic transition from white tin to gray tin. It is puzzling, therefore, that Napoleon, a great believer in keeping his troops fit for battle, would permit the use of tin for buttons. The tin story, if true, could be paraphrased in the old English N Rhyme: "And all for the want of a button."

Is Napoleon trying to instruct his soldiers how to keep their coats tig

The color of glass is due largely to the presence of metal ions (as oxides) example, green glass contains iron(III) oxide, Fe_2O_3, or copper(II) oxide, CuO; yell glass contains uranium(IV) oxide, UO_2; blue glass contains cobalt(II) and copp oxides, CoO and CuO; and red glass contains small particles of gold and copper. N that most of the ions mentioned here are derived from the transition metals.



(a) (b)

Figure 11.31 *Two-dimensional representation of (a) crystalline quartz and (b) noncrystalline quartz glass. The small spheres represent silicon. In reality, the structure of quartz is three-dimensional. Each Si atom is tetrahedrally bonded to four O atoms.*

TABLE 11.5 Composition and Properties of Three Types of Glass

Name	Composition	Properties and Uses
Pure quartz glass	100% SiO_2	Low thermal expansion, transparent to wide range of wavelengths. Used in optical research.
Pyrex glass	SiO_2, 60–80% B_2O_3, 10–25% Al_2O_3, small amount	Low thermal expansion; transparent to visible and infrared, but not to UV, radiation. Used mainly in laboratory and household cooking glassware.
Soda-lime glass	SiO_2, 75% Na_2O, 15% CaO, 10%	Easily attacked by chemicals and sensitive to thermal shocks. Transmits visible light, but absorbs UV radiation. Used mainly in windows and bottles.

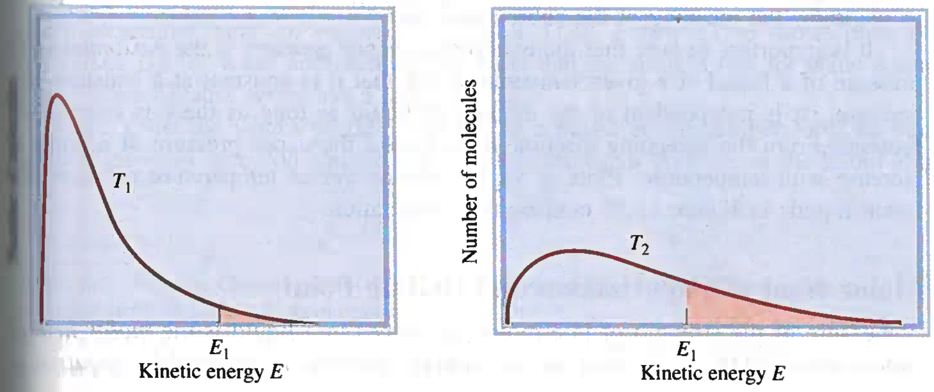
11.8 Phase Changes

The discussions in Chapter 5 and in this chapter have given us an overview of the properties of the three phases of matter: gas, liquid, and solid. ***Phase changes,*** *transformations from one phase to another,* occur when energy (usually in the form of heat) is added or removed. Phase changes are physical changes characterized by changes in molecular order; molecules in the solid phase have the greatest order, and those in the gas phase have the greatest randomness. Keeping in mind the relationship between energy change and the increase or decrease in molecular order will help us understand the nature of these physical changes.

Liquid-Vapor Equilibrium

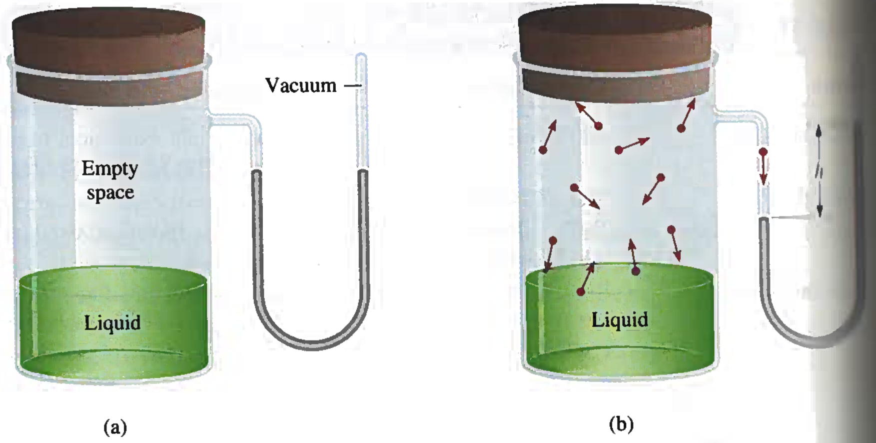
Molecules in a liquid are not fixed in a rigid lattice. Although they lack the total freedom of gaseous molecules, these molecules are in constant motion. Because liquids are denser than gases, the collision rate among molecules is much higher in the liquid phase than in the gas phase. When the molecules in a liquid have sufficient energy to escape from the surface a phase change occurs. ***Evaporation,*** or ***vaporization,*** is *the process in which a liquid is transformed into a gas.*

How does evaporation depend on temperature? Figure 11.32 shows the kinetic energy distribution of molecules in a liquid at two different temperatures. As we can see, the higher the temperature, the greater the kinetic energy, and hence more molecules are leaving the liquid.



(a) (b)

Figure 11.32 *Kinetic energy distribution curves for molecules in a liquid (a) at a temperature T_1 and (b) at a higher temperature T_2. Note that at the higher temperature, the curve flattens out. The shaded areas represent the number of molecules possessing kinetic energy equal to or greater than a certain kinetic energy E_1. The higher the temperature, the greater the number of molecules with high kinetic energy.*



(a) (b)

Figure 11.33 *Apparatus for measuring the vapor pressure of a liquid (a) before the evaporation begins and (b) at equilibrium, when no further change is evident. In (b) the number of molecules leaving the liquid is equal to the number of molecules returning to the liquid. The difference in the mercury levels (h) gives the equilibrium vapor pressure of the liquid at the specified temperature.*

Vapor Pressure

The difference between a gas and a vapor is explained on p. 171.

Animation:
Equilibrium Vapor Pressure
ARIS

When a liquid evaporates, its gaseous molecules exert a vapor pressure. Consider the apparatus shown in Figure 11.33. Before the evaporation process starts, the mercury levels in the U-shaped manometer tube are equal. As soon as some molecules leave the liquid, a vapor phase is established. The vapor pressure is measurable only when a fair amount of vapor is present. The process of evaporation does not continue indefinitely, however. Eventually, the mercury levels stabilize and no further changes are seen.

What happens at the molecular level during evaporation? In the beginning, the traffic is only one way: Molecules are moving from the liquid to the empty space. Soon the molecules in the space above the liquid establish a vapor phase. As the concentration of molecules in the vapor phase increases, some molecules *condense*, that is, they return to the liquid phase. ***Condensation,*** *the change from the gas phase to the liquid phase,* occurs because a molecule strikes the liquid surface and becomes trapped by intermolecular forces in the liquid.

The rate of evaporation is constant at any given temperature, and the rate of condensation increases with the increasing concentration of molecules in the vapor phase. A state of ***dynamic equilibrium,*** in which *the rate of a forward process is exactly balanced by the rate of the reverse process,* is reached when the rates of condensation and evaporation become equal (Figure 11.34). The ***equilibrium vapor pressure*** is *the vapor pressure measured when a dynamic equilibrium exists between condensation and evaporation.* We often use the simpler term "vapor pressure" when we talk about the equilibrium vapor pressure of a liquid. This practice is acceptable as long as we know the meaning of the abbreviated term.

Equilibrium vapor pressure is independent of the amount of liquid as long as there is some liquid present.

It is important to note that the equilibrium vapor pressure is the *maximum* vapor pressure of a liquid at a given temperature and that it is constant at a constant temperature. (It is independent of the amount of liquid as long as there is some liquid present.) From the foregoing discussion we expect the vapor pressure of a liquid to increase with temperature. Plots of vapor pressure versus temperature for three different liquids in Figure 11.35 confirm this expectation.

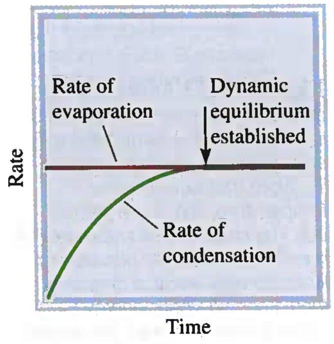


Figure 11.34 *Comparison of the rates of evaporation and condensation at constant temperature.*

Molar Heat of Vaporization and Boiling Point

A measure of the strength of intermolecular forces in a liquid is the ***molar heat of vaporization (ΔH_{vap}),*** defined as *the energy* (usually in kilojoules) *required to*

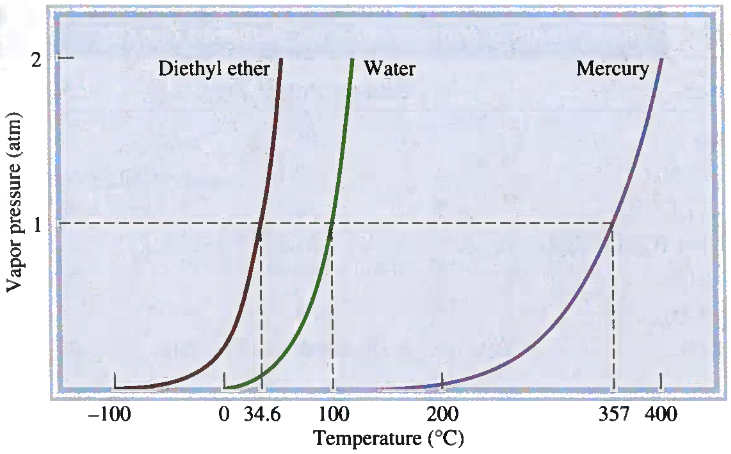


Figure 11.35 *The increase in vapor pressure with temperature for three liquids. The normal boiling points of the liquids (at 1 atm) are shown on the horizontal axis. The strong metallic bonding in mercury results in a much lower vapor pressure of the liquid at room temperature.*

vaporize 1 mole of a liquid. The molar heat of vaporization is directly related to the strength of intermolecular forces that exist in the liquid. If the intermolecular attraction is strong, it takes a lot of energy to free the molecules from the liquid phase. Consequently, the liquid has a relatively low vapor pressure and a high molar heat of vaporization.

The quantitative relationship between the vapor pressure P of a liquid and the absolute temperature T is given by the Clausius[†]-Clapeyron[‡] equation

$$\ln P = -\frac{\Delta H_{\text{vap}}}{RT} + C \qquad (11.2)$$

where ln is the natural logarithm, R is the gas constant (8.314 J/K · mol), and C is a constant. The Clausius-Clapeyron equation has the form of the linear equation $y = mx + b$:

$$\begin{array}{ccccc} \ln P = & \left(-\dfrac{\Delta H_{\text{vap}}}{R}\right) & \left(\dfrac{1}{T}\right) & + C \\ \updownarrow & \updownarrow & \updownarrow & \updownarrow \\ y = & m & x & + b \end{array}$$

By measuring the vapor pressure of a liquid at different temperatures (see Figure 11.35) and plotting ln P versus $1/T$, we determine the slope, which is equal to $-\Delta H_{\text{vap}}/R$. (ΔH_{vap} is assumed to be independent of temperature.) This is the method used to determine heats of vaporization (Table 11.6). Figure 11.36 shows plots of ln P versus $1/T$ for water and diethylether. Note that the straight line for water has a steeper slope because water has a larger ΔH_{vap}.

If we know the values of ΔH_{vap} and P of a liquid at one temperature, we can use the Clausius-Clapeyron equation to calculate the vapor pressure of the liquid at a

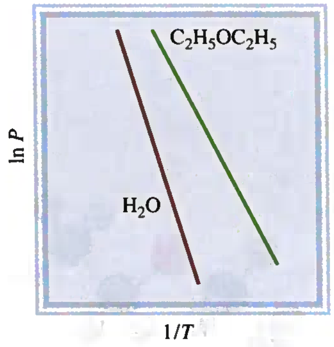


Figure 11.36 *Plots of ln P versus 1/T for water and diethyl ether. The slope in each case is equal to $-\Delta H_{vap}/R$.*

[†] Rudolf Julius Emanuel Clausius (1822–1888). German physicist. Clausius's work was mainly in electricity, kinetic theory of gases, and thermodynamics.

[‡] Benoit Paul Emile Clapeyron (1799–1864). French engineer. Clapeyron made contributions to the thermodynamic aspects of steam engines.

TABLE 11.6 Molar Heats of Vaporization for Selected Liquids

Substance	Boiling Point* (°C)	ΔH_{vap} (kJ/m
Argon (Ar)	−186	6.3
Benzene (C_6H_6)	80.1	31.0
Ethanol (C_2H_5OH)	78.3	39.3
Diethyl ether ($C_2H_5OC_2H_5$)	34.6	26.0
Mercury (Hg)	357	59.0
Methane (CH_4)	−164	9.2
Water (H_2O)	100	40.79

* Measured at 1 atm.

different temperature. At temperatures T_1 and T_2, the vapor pressures are P_1 and P_2. From Equation (11.2) we can write

$$\ln P_1 = -\frac{\Delta H_{vap}}{RT_1} + C \tag{11.3}$$

$$\ln P_2 = -\frac{\Delta H_{vap}}{RT_2} + C \tag{11.4}$$

Subtracting Equation (11.4) from Equation (11.3) we obtain

$$\begin{aligned}\ln P_1 - \ln P_2 &= -\frac{\Delta H_{vap}}{RT_1} - \left(-\frac{\Delta H_{vap}}{RT_2}\right)\\ &= \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\end{aligned}$$

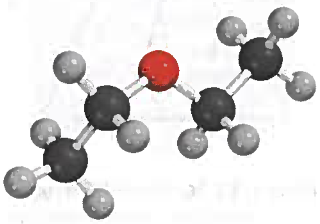
Hence

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

or

$$\ln \frac{P_1}{P_2} = \frac{\Delta H_{vap}}{R}\left(\frac{T_1 - T_2}{T_1T_2}\right) \tag{11.5}$$

Example 11.7 illustrates the use of Equation (11.5).



$C_2H_5OC_2H_5$

Example 11.7

Diethyl ether is a volatile, highly flammable organic liquid that is used mainly as a solvent. The vapor pressure of diethyl ether is 401 mmHg at 18°C. Calculate its vapor pressure at 32°C.

Strategy We are given the vapor pressure of diethyl ether at one temperature and asked to find the pressure at another temperature. Therefore, we need Equation (11.5).

(Continue

Solution Table 11.6 tells us that $\Delta H_{\text{vap}} = 26.0$ kJ/mol. The data are

$$P_1 = 401\ \text{mmHg} \qquad P_2 = ?$$
$$T_1 = 18°\text{C} = 291\ \text{K} \qquad T_2 = 32°\text{C} = 305\ \text{K}$$

From Equation (11.5) we have

$$\begin{aligned}\ln \frac{401}{P_2} &= \frac{26{,}000\ \text{J/mol}}{8.314\ \text{J/K}\cdot\text{mol}}\left[\frac{291\ \text{K} - 305\ \text{K}}{(291\ \text{K})(305\ \text{K})}\right]\\ &= -0.493\end{aligned}$$

Taking the antilog of both sides (see Appendix 4), we obtain

$$\frac{401}{P_2} = e^{-0.493} = 0.611$$

Hence

$$P_2 = 656\ \text{mmHg}$$

Check We expect the vapor pressure to be greater at the higher temperature. Therefore, the answer is reasonable.

Similar problem: 11.86.

Practice Exercise The vapor pressure of ethanol is 100 mmHg at 34.9°C. What is its vapor pressure at 63.5°C? (ΔH_{vap} for ethanol is 39.3 kJ/mol.)

A practical way to demonstrate the molar heat of vaporization is by rubbing an alcohol such as ethanol (C_2H_5OH) or isopropanol (C_3H_7OH), or rubbing alcohol, on your hands. These alcohols have a lower ΔH_{vap} than water, so that the heat from your hands is enough to increase the kinetic energy of the alcohol molecules and evaporate them. As a result of the loss of heat, your hands feel cool. This process is similar to perspiration, which is one of the means by which the human body maintains a constant temperature. Because of the strong intermolecular hydrogen bonding that exists in water, a considerable amount of energy is needed to vaporize the water in perspiration from the body's surface. This energy is supplied by the heat generated in various metabolic processes.

You have already seen that the vapor pressure of a liquid increases with temperature. Every liquid has a temperature at which it begins to boil. The ***boiling point*** is *the temperature at which the vapor pressure of a liquid is equal to the external pressure.* The *normal* boiling point of a liquid is the temperature at which it boils when the external pressure is 1 atm.

At the boiling point, bubbles form within the liquid. When a bubble forms, the liquid originally occupying that space is pushed aside, and the level of the liquid in the container is forced to rise. The pressure exerted *on* the bubble is largely atmospheric pressure, plus some *hydrostatic pressure* (that is, pressure due to the presence of liquid). The pressure *inside* the bubble is due solely to the vapor pressure of the liquid. When the vapor pressure becomes equal to the external pressure, the bubble rises to the surface of the liquid and bursts. If the vapor pressure in the bubble were lower than the external pressure, the bubble would collapse before it could rise. We can thus conclude that the boiling point of a liquid depends on the external pressure. (We usually ignore the small contribution due to the hydrostatic pressure.) For example, at 1 atm, water boils at 100°C, but if the pressure is reduced to 0.5 atm, water boils at only 82°C.

Because the boiling point is defined in terms of the vapor pressure of the liquid, we expect the boiling point to be related to the molar heat of vaporization. The higher ΔH_{vap}, the higher the boiling point. The data in Table 11.6 roughly confirm our prediction. Ultimately, both the boiling point and ΔH_{vap} are determined by the strength of intermolecular forces. For example, argon (Ar) and methane (CH_4), which have weak dispersion forces, have low boiling points and small molar heats of vaporization. Diethyl ether ($C_2H_5OC_2H_5$) has a dipole moment, and the dipole-dipole forces account for its moderately high boiling point and ΔH_{vap}. Both ethanol (C_2H_5OH) and water have strong hydrogen bonding, which accounts for their high boiling points and large ΔH_{vap} values. Strong metallic bonding causes mercury to have the highest boiling point and ΔH_{vap} of this group of liquids. Interestingly, the boiling point of benzene, which is nonpolar, is comparable to that of ethanol. Benzene has a high polarizability due to the distribution of its electrons in the delocalized pi molecular orbitals, and the dispersion forces among benzene molecules can be as strong as or even stronger than dipole-dipole forces and hydrogen bonds.

Critical Temperature and Pressure

The opposite of evaporation is condensation. In principle, a gas can be made to liquefy by either one of two techniques. By cooling a sample of gas we decrease the kinetic energy of its molecules, so that eventually molecules aggregate to form small drops of liquid. Alternatively, we can apply pressure to the gas. Compression reduces the average distance between molecules so that they are held together by mutual attraction. Industrial liquefaction processes combine these two methods.

Every substance has a ***critical temperature*** **(*T*$_c$)**, *above which its gas phase cannot be made to liquefy, no matter how great the applied pressure.* This is also *the highest temperature at which a substance can exist as a liquid.* Putting it another way, above the critical temperature there is no fundamental distinction between a liquid and a gas—we simply have a fluid. ***Critical pressure*** **(*P*$_c$)** is *the minimum pressure that must be applied to bring about liquefaction at the critical temperature.* The existence of the critical temperature can be qualitatively explained as follows. Intermolecular attraction is a finite quantity for any given substance and it is independent of temperature. Below T_c, this force is sufficiently strong to hold the molecules together (under some appropriate pressure) in a liquid. Above T_c, molecular motion becomes so energetic that the molecules can break away from this attraction. Figure 11.37 shows what happens when sulfur hexafluoride is heated above its critical temperature (45.5°C) and then cooled down to below 45.5°C.

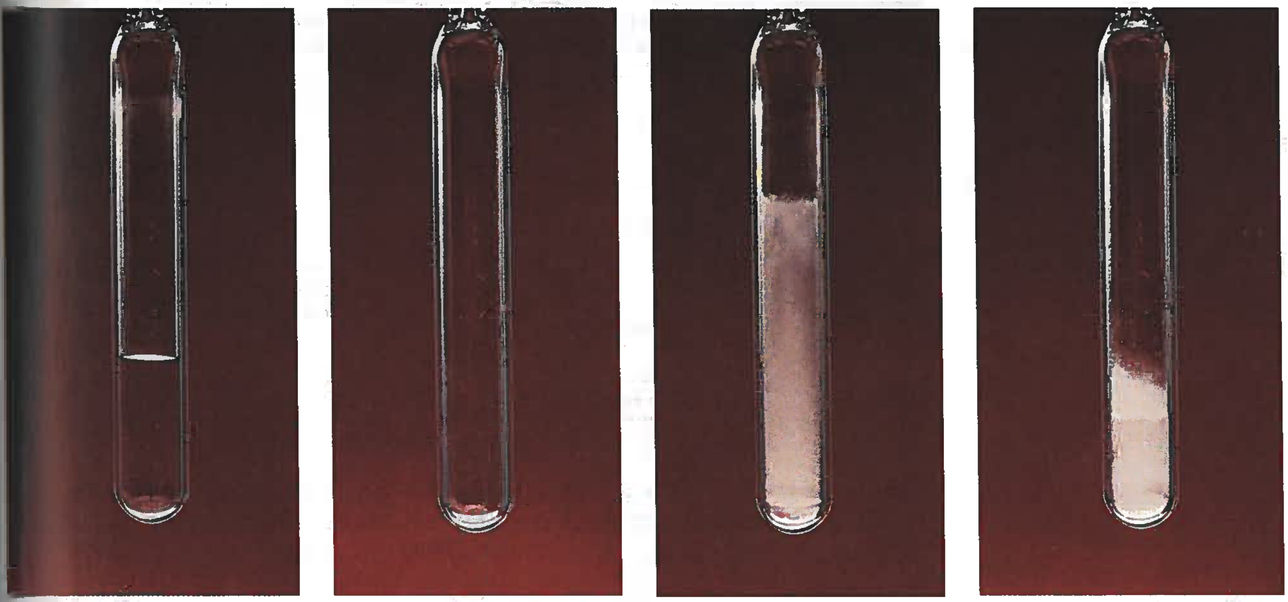
Intermolecular forces are independent of temperature; the kinetic energy of molecules increases with temperature.

Table 11.7 lists the critical temperatures and critical pressures of a number of common substances. The critical temperature of a substance reflects the strength of its intermolecular forces. Benzene, ethanol, mercury, and water, which have strong intermolecular forces, also have high critical temperatures compared with the other substances listed in the table.

Liquid-Solid Equilibrium

The transformation of liquid to solid is called *freezing*, and the reverse process is called *melting*, or *fusion*. The ***melting point*** *of a solid or the* ***freezing point*** *of a liquid* is *the temperature at which solid and liquid phases coexist in equilibrium.* The *normal* melting (or freezing) point of a substance is the temperature at which a substance melts (or freezes) at 1 atm pressure. We generally omit the word "normal" when the pressure is at 1 atm.

"Fusion" refers to the process of melting. Thus, a "fuse" breaks an electrical circuit when a metallic strip melts due to the heat generated by excessively high electrical current.



(a) (b) (c) (d)

Figure 11.37 *The critical phenomenon of sulfur hexafluoride. (a) Below the critical temperature the clear liquid phase is visible. (b) Above the critical temperature the liquid phase has disappeared. (c) The substance is cooled just below its critical temperature. The fog represents the condensation of vapor. (d) Finally, the liquid phase reappears.*

The most familiar liquid-solid equilibrium is that of water and ice. At 0°C and 1 atm, the dynamic equilibrium is represented by

$$\text{ice} \rightleftharpoons \text{water}$$

A practical illustration of this dynamic equilibrium is provided by a glass of ice water. As the ice cubes melt to form water, some of the water between ice cubes

TABLE 11.7 Critical Temperatures and Critical Pressures of Selected Substances

Substance	T_c (°C)	P_c (atm)
Ammonia (NH_3)	132.4	111.5
Argon (Ar)	−186	6.3
Benzene (C_6H_6)	288.9	47.9
Carbon dioxide (CO_2)	31.0	73.0
Ethanol (C_2H_5OH)	243	63.0
Diethyl ether ($C_2H_5OC_2H_5$)	192.6	35.6
Mercury (Hg)	1462	1036
Methane (CH_4)	−83.0	45.6
Molecular hydrogen (H_2)	−239.9	12.8
Molecular nitrogen (N_2)	−147.1	33.5
Molecular oxygen (O_2)	−118.8	49.7
Sulfur hexafluoride (SF_6)	45.5	37.6
Water (H_2O)	374.4	219.5

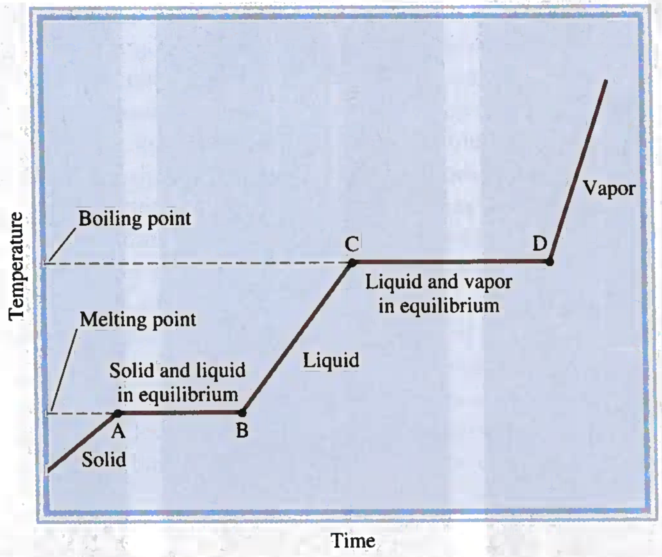


Figure 11.38 *A typical heating curve, from the solid phase through the liquid phase to the gas phase of a substance. Because ΔH_{fus} is smaller than ΔH_{vap}, a substance melts in less time than it takes to boil. This explains why AB is shorter than CD. The steepness of the solid, liquid, and vapor heating lines is determined by the specific heat of the substance in each state.*

may freeze, thus joining the cubes together. This is not a true dynamic equilibrium; because the glass is not kept at 0°C, all the ice cubes will eventually melt away.

Because molecules are more strongly held in the solid phase than in the liquid phase, heat is required to bring about the solid-liquid phase transition. Looking at the heating curve shown in Figure 11.38, we see that when a solid is heated, its temperature increases gradually until point A is reached. At this point, the solid begins to melt. During the melting period (A ⟶ B), the first flat portion of the curve in Figure 11.38, heat is being absorbed by the system, yet its temperature remains constant. The heat helps the molecules to overcome the attractive forces in the solid. Once the sample has melted completely (point B), the heat absorbed increases the average kinetic energy of the liquid molecules, and the liquid temperature rises (B ⟶ C). The vaporization process (C ⟶ D) can be explained similarly. The temperature remains constant during the period when the increased kinetic energy is used to overcome the cohesive forces in the liquid. When all molecules are in the gas phase, the temperature rises again.

Molar heat of fusion (ΔH_{fus}) is *the energy* (usually in kilojoules) *required to melt 1 mole of a solid.* Table 11.8 shows the molar heats of fusion for the substances listed in Table 11.6. A comparison of the data in the two tables shows that for each substance ΔH_{fus} is smaller than ΔH_{vap}. This is consistent with the fact that molecules in a liquid are still fairly closely packed together, so that some energy is needed to bring about the rearrangement from solid to liquid. On the other hand, when a liquid evaporates, its molecules become completely separated from one another and considerably more energy is required to overcome the attractive force.

As we would expect, *cooling* a substance has the opposite effect of heating it. If we remove heat from a gas sample at a steady rate, its temperature decreases. As the liquid is being formed, heat is given off by the system, because its potential energy is decreasing. For this reason, the temperature of the system remains constant over the condensation period (D ⟶ C). After all the vapor has condensed, the temperature of the liquid begins to drop. Continued cooling of the liquid finally leads to freezing (B ⟶ A).

TABLE 11.8 Molar Heats of Fusion for Selected Substances

Substance	Melting Point* (°C)	ΔH_{fus} (kJ/mol)
Argon (Ar)	−190	1.3
Benzene (C_6H_6)	5.5	10.9
Ethanol (C_2H_5OH)	−117.3	7.61
Diethyl ether ($C_2H_5OC_2H_5$)	−116.2	6.90
Mercury (Hg)	−39	23.4
Methane (CH_4)	−183	0.84
Water (H_2O)	0	6.01

*Measured at 1 atm.

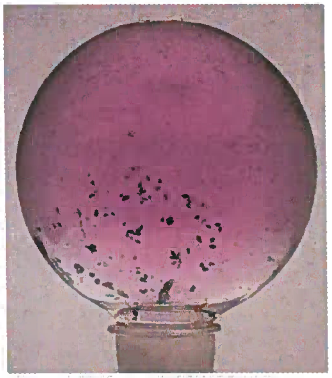
The phenomenon known as ***supercooling*** refers to the situation in which *a liquid can be temporarily cooled to below its freezing point.* Supercooling occurs when heat is removed from a liquid so rapidly that the molecules literally have no time to assume the ordered structure of a solid. A supercooled liquid is unstable; gentle stirring or the addition to it of a small "seed" crystal of the same substance will cause it to solidify quickly.

Solid-Vapor Equilibrium

Solids, too, undergo evaporation and, therefore, possess a vapor pressure. Consider the following dynamic equilibrium:

$$\text{solid} \rightleftharpoons \text{vapor}$$

Sublimation is *the process in which molecules go directly from the solid into the vapor phase.* ***Deposition*** is the reverse process, that is, *molecules make the transition from vapor to solid directly.* Naphthalene, which is the substance used to make mothballs, has a fairly high (equilibrium) vapor pressure for a solid (1 mmHg at 53°C); thus, its pungent vapor quickly permeates an enclosed space. Iodine also sublimes. At room temperature, the violet color of iodine vapor is easily visible in a closed container.



Solid iodine in equilibrium with its vapor.

Because molecules are more tightly held in a solid, the vapor pressure of a solid is generally much less than that of the corresponding liquid. ***Molar heat of sublimation (ΔH_{sub})*** of a substance is *the energy* (usually in kilojoules) *required to sublime 1 mole of a solid.* It is equal to the sum of the molar heats of fusion and vaporization:

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap} \tag{11.6}$$

Equation (11.6) is an illustration of Hess's law (see Section 6.6). The enthalpy, or heat change, for the overall process is the same whether the substance changes directly from the solid to the vapor form or from the solid to the liquid and then to the vapor. Note that Equation (11.6) holds only if all the phase changes occur at the *same* temperature. If not, the equation can be used only as an approximation.

Figure 11.39 summarizes the types of phase changes discussed in this section.

When a substance is heated, its temperature will rise and eventually it will undergo a phase transition. To calculate the total energy change for such a process we must include all of the steps, shown in Example 11.8.

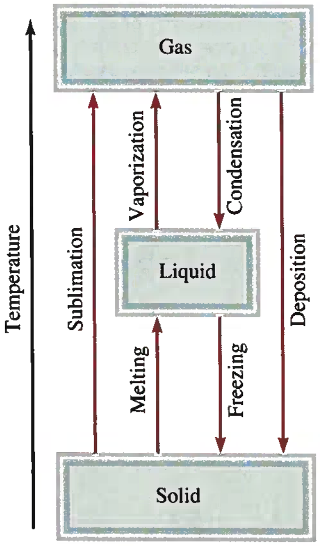


Figure 11.39 *The various phase changes that a substance can undergo.*

Example 11.8

Calculate the amount of energy (in kilojoules) needed to heat 346 g of liquid water from 0°C to 182°C. Assume that the specific heat of water is 4.184 J/g · °C over the entire liquid range and that the specific heat of steam is 1.99 J/g · °C.

Strategy The heat change (q) at each stage is given by $q = ms\Delta t$, where m is the mass of water, s is the specific heat, and Δt is the temperature change. If there is a phase change, such as vaporization, then q is given by $n\Delta H_{\text{vap}}$, where n is the number of moles of water.

Solution The calculation can be broken down in three steps.

Step 1: Heating water from 0°C to 100°C
Using Equation (6.12) we write

$$\begin{aligned} q_1 &= ms\Delta t \\ &= (346\text{ g})(4.184\text{ J/g}\cdot{}^\circ\text{C})(100^\circ\text{C} - 0^\circ\text{C}) \\ &= 1.45 \times 10^5\text{ J} \\ &= 145\text{ kJ} \end{aligned}$$

Step 2: Evaporating 346 g of water at 100°C (a phase change)
In Table 11.6 we see $\Delta H_{\text{vap}} = 40.79$ kJ/mol for water, so

$$\begin{aligned} q_2 &= 346\text{ g H}_2\text{O} \times \frac{1\text{ mol H}_2\text{O}}{18.02\text{ g H}_2\text{O}} \times \frac{40.79\text{ kJ}}{1\text{ mol H}_2\text{O}} \\ &= 783\text{ kJ} \end{aligned}$$

Step 3: Heating steam from 100°C to 182°C

$$\begin{aligned} q_3 &= ms\Delta t \\ &= (346\text{ g})(1.99\text{ J/g}\cdot{}^\circ\text{C})(182^\circ\text{C} - 100^\circ\text{C}) \\ &= 5.65 \times 10^4\text{ J} \\ &= 56.5\text{ kJ} \end{aligned}$$

The overall energy required is given by

$$\begin{aligned} q_{\text{overall}} &= q_1 + q_2 + q_3 \\ &= 145\text{ kJ} + 783\text{ kJ} + 56.5\text{ kJ} \\ &= \boxed{985\text{ kJ}} \end{aligned}$$

Check All the qs have a positive sign, which is consistent with the fact that heat is absorbed to raise the temperature from 0°C to 182°C. Also, as expected, much more heat is absorbed during phase transition.

Similar problem: 11.78.

Practice Exercise Calculate the heat released when 68.0 g of steam at 124°C is converted to water at 45°C.

11.9 Phase Diagrams

The overall relationships among the solid, liquid, and vapor phases are best represented in a single graph known as a phase diagram. A ***phase diagram*** summarizes *the conditions at which a substance exists as a solid, liquid, or gas.* In this section we will briefly discuss the phase diagrams of water and carbon dioxide.

Water

Figure 11.40(a) shows the phase diagram of water. The graph is divided into three regions, each of which represents a pure phase. The line separating any two regions

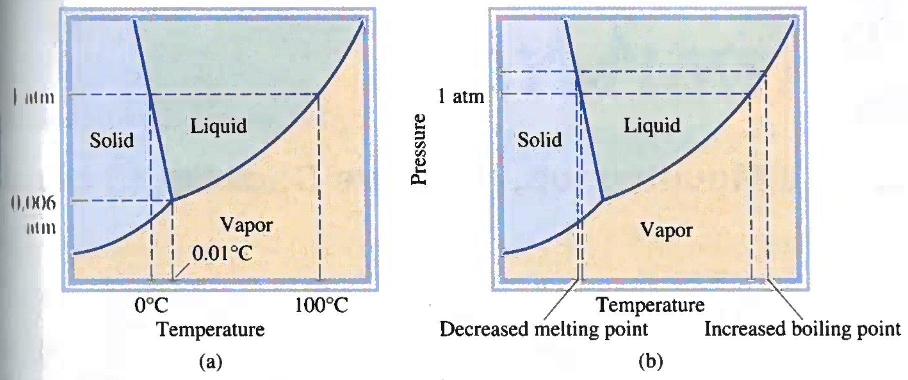


Figure 11.40 *(a) The phase diagram of water. Each solid line between two phases specifies the conditions of pressure and temperature under which the two phases can exist in equilibrium. The point at which all three phases can exist in equilibrium (0.006 atm and 0.01°C) is called the triple point. (b) This phase diagram tells us that increasing the pressure on ice lowers its melting point and that increasing the pressure of liquid water raises its boiling point.*

indicates conditions under which these two phases can exist in equilibrium. For example, the curve between the liquid and vapor phases shows the variation of vapor pressure with temperature. (Compare this curve with Figure 11.35.) The other two curves similarly indicate conditions for equilibrium between ice and liquid water and between ice and water vapor. (Note that the solid-liquid boundary line has a negative slope.) The point at which all three curves meet is called the ***triple point,*** which is *the only condition under which all three phases can be in equilibrium with one another.* For water, this point is at 0.01°C and 0.006 atm.

Phase diagrams enable us to predict changes in the melting point and boiling point of a substance as a result of changes in the external pressure; we can also anticipate directions of phase transitions brought about by changes in temperature and pressure. The normal melting point and boiling point of water at 1 atm are 0°C and 100°C, respectively. What would happen if melting and boiling were carried out at some other pressure? Figure 11.40(b) shows that increasing the pressure above 1 atm will raise the boiling point and lower the melting point. A decrease in pressure will lower the boiling point and raise the melting point.

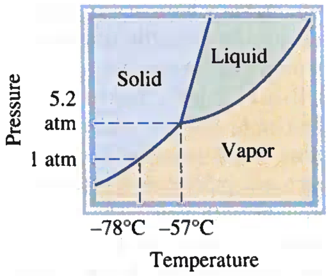


Figure 11.41 *The phase diagram of carbon dioxide. Note that the solid-liquid boundary line has a positive slope. The liquid phase is not stable below 5.2 atm, so that only the solid and vapor phases can exist under atmospheric conditions.*

Carbon Dioxide

The phase diagram of carbon dioxide (Figure 11.41) is generally similar to that of water, with one important exception—the slope of the curve between solid and liquid is positive. In fact, this holds true for almost all other substances. Water behaves differently because ice is *less* dense than liquid water. The triple point of carbon dioxide is at 5.2 atm and −57°C.

An interesting observation can be made about the phase diagram in Figure 11.41. As you can see, the entire liquid phase lies well above atmospheric pressure; therefore, it is impossible for solid carbon dioxide to melt at 1 atm. Instead, when solid CO_2 is heated to −78°C at 1 atm, it sublimes. In fact, solid carbon dioxide is called dry ice because it looks like ice and *does not melt* (Figure 11.42). Because of this property, dry ice is useful as a refrigerant.

Figure 11.42 *Under atmospheric conditions, solid carbon dioxide does not melt; it can only sublime. The cold carbon dioxide gas causes nearby water vapor to condense and form a fog.*

CHEMISTRY *in Action*

Hard-Boiling an Egg on a Mountaintop, Pressure Cookers, and Ice Skating

Phase equilibria are affected by external pressure. Depending on atmospheric conditions, the boiling point and freezing point of water may deviate appreciably from 100°C and 0°C, respectively, as we see below.

Hard-Boiling an Egg on a Mountaintop

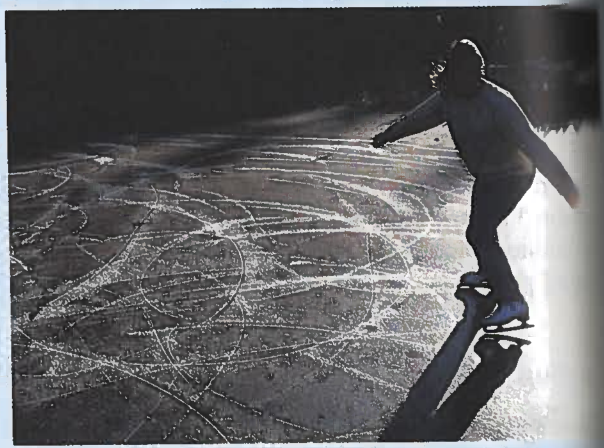
Suppose you have just scaled Pike's Peak in Colorado. To help regain your strength following the strenuous work, you decide to hard-boil an egg and eat it. To your surprise, water seems to boil more quickly than usual, but after 10 min in boiling water, the egg is still not cooked. A little knowledge of phase equilibria could have saved you the disappointment of cracking open an uncooked egg (especially if it is the only egg you brought with you). The summit of Pike's Peak is 14,000 ft above sea level. At this altitude, the atmospheric pressure is only about 0.6 atm. From Figure 11.40(b), we see that the boiling point of water decreases with decreasing pressure, so at the lower pressure water will boil at about 86°C. However, it is not the boiling action but the amount of heat delivered to the egg that does the actual cooking, and the amount of heat delivered is proportional to the temperature of the water. For this reason, it would take considerably longer, perhaps 30 min, to hard-cook your egg.

Pressure Cookers

The effect of pressure on boiling point also explains why pressure cookers save time in the kitchen. A pressure cooker is a sealed container that allows steam to escape only when it exceeds a certain pressure. The pressure above the water in the cooker is the sum of the atmospheric pressure and the pressure of the steam. Consequently, the water in the pressure cooker will boil at a higher temperature than 100°C and the food in it will be hotter and cook faster.

Ice Skating

Let us now turn to the ice-water equilibrium. The negative slope of the solid-liquid curve means that the melting point of ice decreases with increasing external pressure, as shown in Figure 11.40(b). This phenomenon helps to make ice skating possible. Because skates have very thin runners, a 130-lb person can exert a pressure equivalent to 500 atm on the ice. (Remember that pressure is defined as force per unit area.) Consequently, at a temperature lower than 0°C, the ice under the skates melts and the film of water formed under the runners facilitates the movement of the skater over ice. Calculations show that the melting point of ice decreases by 7.4 × 10 when the pressure increases by 1 atm. Thus, when the pressure exerted on the ice by the skater is 500 atm, the melting point falls to $-(500 \times 7.4 \times 10^{-3})$, or −3.7°C. Actually, it turns out that friction between the blades and the ice is the major cause for melting the ice. This explains why it is possible to skate outdoors even when the temperature drops below −20°C.



The pressure exerted by the skater on ice lowers its melting point, and the film of water formed under the blades acts as a lubricant between the and the ice.

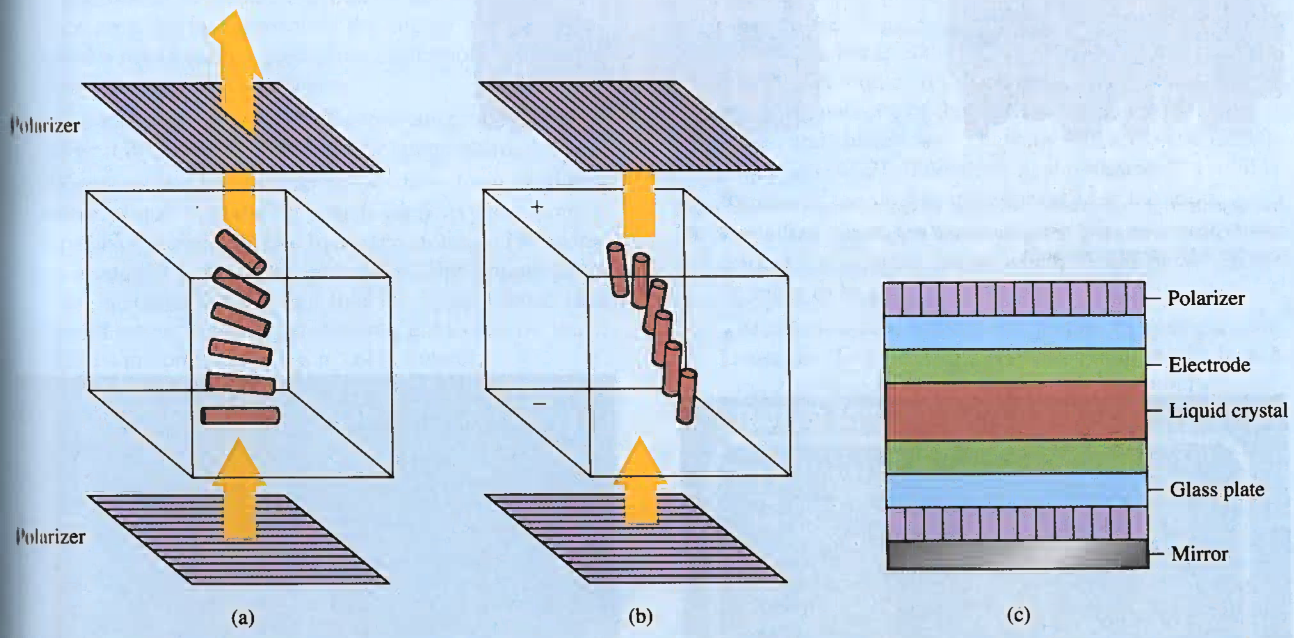
CHEMISTRY *in Action*

Liquid Crystals

Ordinarily, there is a sharp distinction between the highly ordered state of a crystalline solid and the more random molecular arrangement of liquids. Crystalline ice and liquid water, for example, differ from each other in this respect. One class of substances, however, tends so greatly toward an ordered arrangement that a melting crystal first forms a milky liquid, called the *paracrystalline state,* with characteristically crystalline properties. At higher temperatures, this milky fluid changes sharply into a clear liquid that behaves like an ordinary liquid. Such substances are known as *liquid crystals.*

Molecules that exhibit liquid crystallinity are usually long and rodlike. An important class of liquid crystals is called thermotropic liquid crystals, which form when the solid is heated. The two common structures of thermotropic liquid crystals are nematic and smectic. In smectic liquid crystals, the long axes of the molecules are perpendicular to the plane of the layers. The layers are free to slide over one another so that the substance has the mechanical properties of a two-dimensional solid. Nematic liquid crystals are less ordered. Although the molecules in nematic liquid crystals are aligned with their long axes parallel to one another, they are not separated into layers.

Thermotropic liquid crystals have many applications in science, technology, and medicine. The familiar black-and-white displays in timepieces and calculators are based on the properties of these substances. Transparent aligning agents made of tin oxide (SnO_2) applied to the lower and upper inside surfaces of the liquid crystal cell preferentially orient the molecules in the nematic phase by 90° relative to each other. In this way, the molecules become "twisted" through the liquid crystal phase. When properly adjusted, this twist rotates the plane of polarization by 90°



(a) (b) (c)

A liquid crystal display (LCD) using nematic liquid crystals. Molecules in contact with the bottom and top cell surfaces are aligned at right angles to one another. (a) The extent of twist in the molecular orientation between the surfaces is adjusted so as to rotate the plane of polarized light by 90°, allowing it to pass through the top polarizer. Consequently, the cell appears clear. (b) When the electric field is on, molecules orient along the direction of the field, the plane of polarized light can no longer pass through the top polarizer, and the cell appears black. (c) A cross section of a LCD such as that used in watches and calculators.

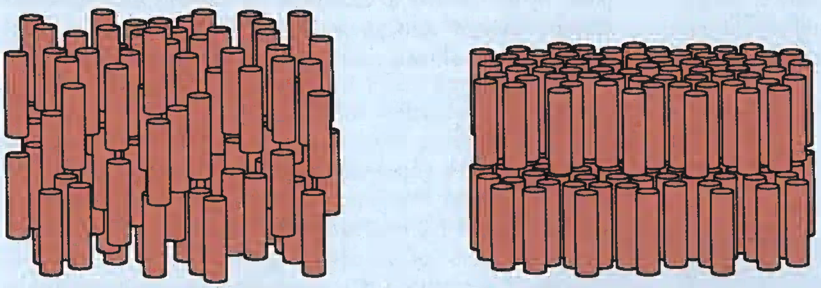
(Continued)

CHEMISTRY *in Action*

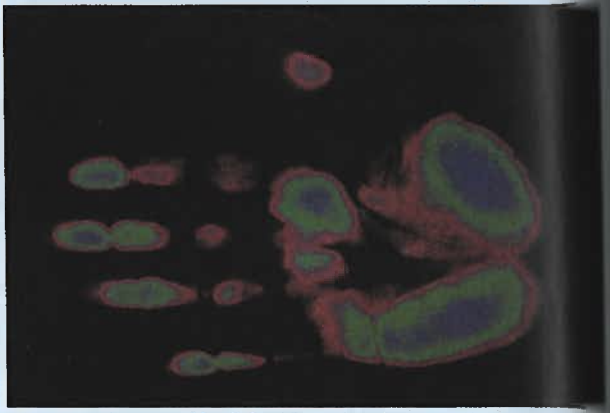
(Continued)

and allows the light to pass through the two polarizers (arranged at 90° to each other). When an electric field is applied, the nematic molecules experience a torque (a torsion or rotation) that forces them to align along the direction of the field. Now the incident polarized light cannot pass through the top polarizer. In watches and calculators, a mirror is placed under the bottom polarizer. In the absence of an electric field, the reflected light goes through both polarizers and the cell looks clear from the top. When the electric field is turned on, the incident light from the top cannot pass through the bottom polarizer to reach the reflector and the cell becomes dark. Typically a few volts are applied across a nematic layer about 10 μm thick ($1 \mu m = 10^{-6}$ m). The response time for molecules to align and relax when the electric field is turned on and off is in the ms range ($1 ms = 10^{-3}$ s).

Another type of thermotropic liquid crystals is called cholesteric liquid crystals. The color of cholesteric liquid crystals changes with temperature and therefore they are suitable for use as sensitive thermometers. In metallurgy, for example, they are used to detect metal stress, heat sources, and corrosion paths. Medically, the temperature of the body at specific sites can be determined with the aid of liquid crystals. This technique has become an important diagnostic tool in treating infection and tumor growth (for example, breast tumors). Because localized infections and tumors increase metabolic rates and hence temperature in the affected tissues, a thin film of liquid crystal can help a physician see whether an infection or tumor is present by responding to a temperature difference with a change of color.



The alignment of molecules in two types of liquid crystals. Nematic liquid crystals behave like a one-dimensional solid and smectic liquid crystals behave like a two-dimensional solid.



A liquid crystal thermogram. The red color represents the highest temperature and the blue color the lowest temperature.

Summary of Facts and Concepts

1. All substances exist in one of three states: gas, liquid, or solid. The major difference between the condensed state and the gaseous state is the distance separating molecules.
2. Intermolecular forces act between molecules or between molecules and ions. Generally, these attractive forces are much weaker than bonding forces.
3. Dipole-dipole forces and ion-dipole forces attract molecules with dipole moments to other polar molecules or ions.
4. Dispersion forces are the result of temporary dipole moments induced in ordinarily nonpolar molecules. The extent to which a dipole moment can be induced in a molecule is called its polarizability. The term "van der Waals forces" refers to dipole-dipole, dipole-induced dipole, and dispersion forces.
5. Hydrogen bonding is a relatively strong dipole-dipole interaction between a polar bond containing a hydrogen atom and an electronegative O, N, or F atom. Hydrogen bonds between water molecules are particularly strong.
6. Liquids tend to assume a geometry that minimizes surface area. Surface tension is the energy needed to expand a liquid surface area; strong intermolecular forces lead to greater surface tension.
7. Viscosity is a measure of the resistance of a liquid to flow; it decreases with increasing temperature.
8. Water molecules in the solid state form a three-dimensional network in which each oxygen atom is covalently bonded to two hydrogen atoms and is hydrogen-bonded to two hydrogen atoms. This unique structure accounts for the fact that ice is less dense than liquid water, a property that allows life to survive under the ice in ponds and lakes in cold climates.
9. Water is also ideally suited for its ecological role by its high specific heat, another property imparted by its strong hydrogen bonding. Large bodies of water are able to moderate Earth's climate by giving off and absorbing substantial amounts of heat with only small changes in the water temperature.
10. All solids are either crystalline (with a regular structure of atoms, ions, or molecules) or amorphous (without a regular structure). Glass is an example of an amorphous solid.
11. The basic structural unit of a crystalline solid is the unit cell, which is repeated to form a three-dimensional crystal lattice. X-ray diffraction has provided much of our knowledge about crystal structure.
12. The four types of crystals and the forces that hold their particles together are ionic crystals, held together by ionic bonding; covalent crystals, covalent bonding; molecular crystals, van der Waals forces and/or hydrogen bonding; and metallic crystals, metallic bonding.
13. A liquid in a closed vessel eventually establishes a dynamic equilibrium between evaporation and condensation. The vapor pressure over the liquid under these conditions is the equilibrium vapor pressure, which is often referred to simply as "vapor pressure."
14. At the boiling point, the vapor pressure of a liquid equals the external pressure. The molar heat of vaporization of a liquid is the energy required to vaporize one mole of the liquid. It can be determined by measuring the vapor pressure of the liquid as a function of temperature and using the Clausius-Clapeyron equation [Equation (11.2)]. The molar heat of fusion of a solid is the energy required to melt one mole of the solid.
15. For every substance there is a temperature, called the critical temperature, above which its gas phase cannot be made to liquefy.
16. The relationships among the phases of a single substance are illustrated by a phase diagram, in which each region represents a pure phase and the boundaries between the regions show the temperatures and pressures at which the two phases are in equilibrium. At the triple point, all three phases are in equilibrium.

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Questions and Problems

Intermolecular Forces

Review Questions

11.1 Give an example for each type of intermolecular forces. (a) dipole-dipole interaction, (b) dipole-induced dipole interaction, (c) ion-dipole interaction, (d) dispersion forces, (e) van der Waals forces

11.2 Explain the term "polarizability." What kind of molecules tend to have high polarizabilities? What is the relationship between polarizability and intermolecular forces?

11.3 Explain the difference between a temporary dipole moment and the permanent dipole moment.

11.4 Give some evidence that all atoms and molecules exert attractive forces on one another.

11.5 What physical properties should you consider in comparing the strength of intermolecular forces in solids and in liquids?

11.6 Which elements can take part in hydrogen bonding? Why is hydrogen unique in this kind of interaction?

Problems

11.7 The compounds Br_2 and ICl have the same number of electrons, yet Br_2 melts at −7.2°C and ICl melts at 27.2°C. Explain.

11.8 If you lived in Alaska, which of the following natural gases would you keep in an outdoor storage tank in winter? Explain why. methane (CH_4), propane (C_3H_8), or butane (C_4H_{10})

11.9 The binary hydrogen compounds of the Group 4A elements and their boiling points are: CH_4, −162°C; SiH_4, −112°C; GeH_4, −88°C; and SnH_4, −52°C. Explain the increase in boiling points from CH_4 to SnH_4.

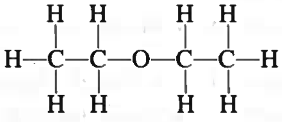
11.10 List the types of intermolecular forces that exist between molecules (or basic units) in each of the following species: (a) benzene (C_6H_6), (b) CH_3Cl, (c) PF_3, (d) NaCl, (e) CS_2.

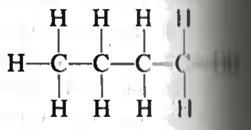
11.11 Ammonia is both a donor and an acceptor of hydrogen in hydrogen-bond formation. Draw a diagram showing the hydrogen bonding of an ammonia molecule with two other ammonia molecules.

11.12 Which of the following species are capable of hydrogen-bonding among themselves? (a) C (b) HI, (c) KF, (d) BeH_2, (e) CH_3COOH

11.13 Arrange the following in order of increasing boiling point: RbF, CO_2, CH_3OH, CH_3Br. Explain your reasoning.

11.14 Diethyl ether has a boiling point of 34.5°C, and 1-butanol has a boiling point of 117°C:


diethyl ether


1-butanol

Both of these compounds have the same number and types of atoms. Explain the difference in their boiling points.

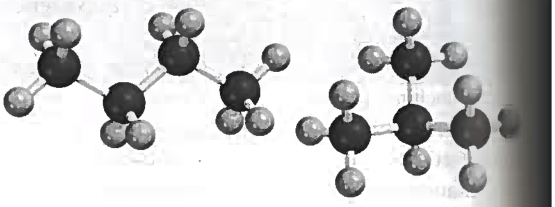
11.15 Which member of each of the following pairs of substances would you expect to have a higher boiling point? (a) O_2 and Cl_2, (b) SO_2 and CO_2, (c) HF and HI

11.16 Which substance in each of the following pairs would you expect to have the higher boiling point? Explain why. (a) Ne or Xe, (b) CO_2 or CS_2, (c) C or Cl_2, (d) F_2 or LiF, (e) NH_3 or PH_3

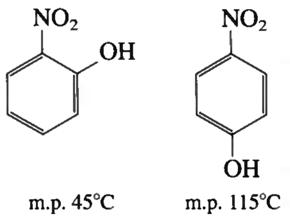
11.17 Explain in terms of intermolecular forces why (a) NH_3 has a higher boiling point than CH_4 and (b) KCl has a higher melting point than I_2.

11.18 What kind of attractive forces must be overcome in order to (a) melt ice, (b) boil molecular bromine, (c) melt solid iodine, and (d) dissociate F_2 into atoms?

11.19 The following compounds have the same molecular formulas (C_4H_{10}). Which one would you expect to have a higher boiling point?



11.20 Explain the difference in the melting points of the following compounds:



(*Hint:* Only one of the two can form intramolecular hydrogen bonds.)

Properties of Liquids

Review Questions

11.21 Explain why liquids, unlike gases, are virtually incompressible.

11.22 What is surface tension? What is the relationship between intermolecular forces and surface tension? How does surface tension change with temperature?

11.23 Despite the fact that stainless steel is much denser than water, a stainless-steel razor blade can be made to float on water. Why?

11.24 Use water and mercury as examples to explain adhesion and cohesion.

11.25 A glass can be filled slightly above the rim with water. Explain why the water does not overflow.

11.26 Draw diagrams showing the capillary action of (a) water and (b) mercury in three tubes of different radii.

11.27 What is viscosity? What is the relationship between intermolecular forces and viscosity?

11.28 Why does the viscosity of a liquid decrease with increasing temperature?

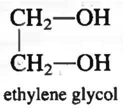
11.29 Why is ice less dense than water?

11.30 Outdoor water pipes have to be drained or insulated in winter in a cold climate. Why?

Problems

11.31 Predict which of the following liquids has greater surface tension: ethanol (C_2H_5OH) or dimethyl ether (CH_3OCH_3).

11.32 Predict the viscosity of ethylene glycol relative to that of ethanol and glycerol (see Table 11.3).



$$\begin{array}{c} CH_2{-}OH \\ | \\ CH_2{-}OH \end{array}$$

ethylene glycol

Crystal Structure

Review Questions

11.33 Define the following terms: crystalline solid, lattice point, unit cell, coordination number, closest packing.

11.34 Describe the geometries of the following cubic cells: simple cubic, body-centered cubic, face-centered cubic. Which of these structures would give the highest density for the same type of atoms? Which the lowest?

11.35 Classify the solid states in terms of crystal types of the elements in the third period of the periodic table. Predict the trends in their melting points and boiling points.

11.36 The melting points of the oxides of the third-period elements are given in parentheses: Na_2O (1275°C), MgO (2800°C), Al_2O_3 (2045°C), SiO_2 (1610°C), P_4O_{10} (580°C), SO_3 (16.8°C), Cl_2O_7 (−91.5°C). Classify these solids in terms of crystal types.

Problems

11.37 What is the coordination number of each sphere in (a) a simple cubic cell, (b) a body-centered cubic cell, and (c) a face-centered cubic cell? Assume the spheres are all the same.

11.38 Calculate the number of spheres that would be found within a simple cubic, a body-centered cubic, and a face-centered cubic cell. Assume that the spheres are the same.

11.39 Metallic iron crystallizes in a cubic lattice. The unit cell edge length is 287 pm. The density of iron is 7.87 g/cm^3. How many iron atoms are within a unit cell?

11.40 Barium metal crystallizes in a body-centered cubic lattice (the Ba atoms are at the lattice points only). The unit cell edge length is 502 pm, and the density of the metal is 3.50 g/cm^3. Using this information, calculate Avogadro's number. [*Hint:* First calculate the volume (in cm^3) occupied by 1 mole of Ba atoms in the unit cells. Next calculate the volume (in cm^3) occupied by one Ba atom in the unit cell. Assume that 68% of the unit cell is occupied by Ba atoms.]

11.41 Vanadium crystallizes in a body-centered cubic lattice (the V atoms occupy only the lattice points). How many V atoms are present in a unit cell?

11.42 Europium crystallizes in a body-centered cubic lattice (the Eu atoms occupy only the lattice points). The density of Eu is 5.26 g/cm^3. Calculate the unit cell edge length in pm.

11.43 Crystalline silicon has a cubic structure. The unit cell edge length is 543 pm. The density of the solid is 2.33 g/cm^3. Calculate the number of Si atoms in one unit cell.

11.44 A face-centered cubic cell contains 8 X atoms at the corners of the cell and 6 Y atoms at the faces. What is the empirical formula of the solid?

X-Ray Diffraction of Crystals

Review Questions

11.45 Define X-ray diffraction. What are the typical wavelengths (in nanometers) of X rays (see Figure 7.4).

11.46 Write the Bragg equation. Define every term and describe how this equation can be used to measure interatomic distances.

Problems

11.47 When X rays of wavelength 0.090 nm are diffracted by a metallic crystal, the angle of first-order diffraction ($n = 1$) is measured to be 15.2°. What is the distance (in pm) between the layers of atoms responsible for the diffraction?

11.48 The distance between layers in a NaCl crystal is 282 pm. X rays are diffracted from these layers at an angle of 23.0°. Assuming that $n = 1$, calculate the wavelength of the X rays in nm.

Types of Crystals

Review Questions

11.49 Describe and give examples of the following types of crystals: (a) ionic crystals, (b) covalent crystals, (c) molecular crystals, (d) metallic crystals.

11.50 Why are metals good conductors of heat and electricity? Why does the ability of a metal to conduct electricity decrease with increasing temperature?

Problems

11.51 A solid is hard, brittle, and electrically nonconducting. Its melt (the liquid form of the substance) and an aqueous solution containing the substance conduct electricity. Classify the solid.

11.52 A solid is soft and has a low melting point (below 100°C). The solid, its melt, and an aqueous solution containing the substance are all nonconductors of electricity. Classify the solid.

11.53 A solid is very hard and has a high melting point. Neither the solid nor its melt conducts electricity. Classify the solid.

11.54 Which of the following are molecular solids and which are covalent solids? Se_8, HBr, Si, CO_2, C, P_4O_6, SiH_4

11.55 Classify the solid state of the following substances as ionic crystals, covalent crystals, molecular crystals, or metallic crystals: (a) CO_2, (b) B_{12}, (c) S_8, (d) KBr, (e) Mg, (f) SiO_2, (g) LiCl, (h) Cr.

11.56 Explain why diamond is harder than graphite. Why is graphite an electrical conductor but diamond is not?

Amorphous Solids

Review Questions

11.57 What is an amorphous solid? How does it differ from crystalline solid?

11.58 Define glass. What is the chief component of glass? Name three types of glass.

Phase Changes

Review Questions

11.59 What is a phase change? Name all possible changes that can occur among the vapor, liquid, and solid phases of a substance.

11.60 What is the equilibrium vapor pressure of a liquid? How is it measured and how does it change with temperature?

11.61 Use any one of the phase changes to explain what is meant by dynamic equilibrium.

11.62 Define the following terms: (a) molar heat of vaporization, (b) molar heat of fusion, (c) molar heat of sublimation. What are their units?

11.63 How is the molar heat of sublimation related to the molar heats of vaporization and fusion? On what law are these relationships based?

11.64 What can we learn about the intermolecular forces in a liquid from the molar heat of vaporization?

11.65 The greater the molar heat of vaporization of a liquid, the greater its vapor pressure. True or false?

11.66 Define boiling point. How does the boiling point of a liquid depend on external pressure? Referring to Table 5.3, what is the boiling point of water when the external pressure is 187.5 mmHg?

11.67 As a liquid is heated at constant pressure, its temperature rises. This trend continues until the boiling point of the liquid is reached. No further rise in temperature of the liquid can be induced by heating. Explain.

11.68 What is critical temperature? What is the significance of critical temperature in liquefaction of gases?

11.69 What is the relationship between intermolecular forces in a liquid and the liquid's boiling point and critical temperature? Why is the critical temperature of water greater than that of most other substances?

11.70 How do the boiling points and melting points of water and carbon tetrachloride vary with pressure? Explain any difference in behavior of these two substances.

11.71 Why is solid carbon dioxide called dry ice?

11.72 The vapor pressure of a liquid in a closed container depends on which of the following? (a) the volume above the liquid, (b) the amount of liquid present, (c) temperature, (d) intermolecular forces between the molecules in the liquid

11.73 Referring to Figure 11.35, estimate the boiling points of diethyl ether, water, and mercury at 0.5 atm.

11.74 Wet clothes dry more quickly on a hot, dry day than on a hot, humid day. Explain.

11.75 Which of the following phase transitions gives off more heat? (a) 1 mole of steam to 1 mole of water at 100°C, or (b) 1 mole of water to 1 mole of ice at 0°C.

11.76 A beaker of water is heated to boiling by a Bunsen burner. Would adding another burner raise the boiling point of water? Explain.

Problems

11.77 Calculate the amount of heat (in kJ) required to convert 74.6 g of water to steam at 100°C.

11.78 How much heat (in kJ) is needed to convert 866 g of ice at −10°C to steam at 126°C? (The specific heats of ice and steam are 2.03 J/g · °C and 1.99 J/g · °C, respectively.)

11.79 How is the rate of evaporation of a liquid affected by (a) temperature, (b) the surface area of a liquid exposed to air, (c) intermolecular forces?

11.80 The molar heats of fusion and sublimation of molecular iodine are 15.27 kJ/mol and 62.30 kJ/mol, respectively. Estimate the molar heat of vaporization of liquid iodine.

11.81 The following compounds, listed with their boiling points, are liquid at −10°C: butane, −0.5°C; ethanol, 78.3°C; toluene, 110.6°C. At −10°C, which of these liquids would you expect to have the highest vapor pressure? Which the lowest? Explain.

11.82 Freeze-dried coffee is prepared by freezing brewed coffee and then removing the ice component with a vacuum pump. Describe the phase changes taking place during these processes.

11.83 A student hangs wet clothes outdoors on a winter day when the temperature is −15°C. After a few hours, the clothes are found to be fairly dry. Describe the phase changes in this drying process.

11.84 Steam at 100°C causes more serious burns than water at 100°C. Why?

11.85 Vapor pressure measurements at several different temperatures are shown below for mercury. Determine graphically the molar heat of vaporization for mercury.

t (°C)	200	250	300	320	340
P (mmHg)	17.3	74.4	246.8	376.3	557.9

11.86 The vapor pressure of benzene, C_6H_6, is 40.1 mmHg at 7.6°C. What is its vapor pressure at 60.6°C? The molar heat of vaporization of benzene is 31.0 kJ/mol.

11.87 The vapor pressure of liquid X is lower than that of liquid Y at 20°C, but higher at 60°C. What can you deduce about the relative magnitude of the molar heats of vaporization of X and Y?

11.88 Estimate the molar heat of vaporization of a liquid whose vapor pressure doubles when the temperature is raised from 85°C to 95°C.

Phase Diagrams

Review Questions

11.89 What is a phase diagram? What useful information can be obtained from study of a phase diagram?

11.90 Explain how water's phase diagram differs from those of most substances. What property of water causes the difference?

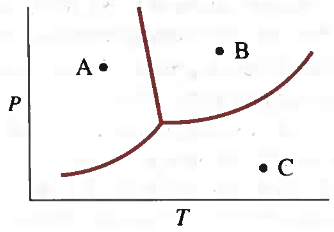
Problems

11.91 The blades of ice skates are quite thin, so that the pressure exerted on ice by a skater can be substantial. Explain how this fact enables a person to skate on ice.

11.92 A length of wire is placed on top of a block of ice. The ends of the wire extend over the edges of the ice, and a heavy weight is attached to each end. It is found that the ice under the wire gradually melts, so that the wire slowly moves through the ice block. At the same time, the water above the wire refreezes. Explain the phase changes that accompany this phenomenon.

11.93 The boiling point and freezing point of sulfur dioxide are −10°C and −72.7°C (at 1 atm), respectively. The triple point is −75.5°C and 1.65 × 10^{-3} atm, and its critical point is at 157°C and 78 atm. On the basis of this information, draw a rough sketch of the phase diagram of SO_2.

11.94 A phase diagram of water is shown at the end of this problem. Label the regions. Predict what would happen as a result of the following changes: (a) Starting at A, we raise the temperature at constant pressure. (b) Starting at C, we lower the temperature at constant pressure. (c) Starting at B, we lower the pressure at constant temperature.



Additional Problems

11.95 Name the kinds of attractive forces that must be overcome in order to (a) boil liquid ammonia, (b) melt solid phosphorus (P_4), (c) dissolve CsI in liquid HF, (d) melt potassium metal.

11.96 Which of the following properties indicates very strong intermolecular forces in a liquid? (a) very low surface tension, (b) very low critical temperature, (c) very low boiling point, (d) very low vapor pressure

11.97 At −35°C, liquid HI has a higher vapor pressure than liquid HF. Explain.

11.98 Based on the following properties of elemental boron, classify it as one of the crystalline solids discussed in Section 11.6: high melting point (2300°C), poor conductor of heat and electricity, insoluble in water, very hard substance.

11.99 Referring to Figure 11.41, determine the stable phase of CO_2 at (a) 4 atm and −60°C and (b) 0.5 atm and −20°C.

11.100 Which of the following substances has the highest polarizability? CH_4, H_2, CCl_4, SF_6, H_2S

11.101 A CO_2 fire extinguisher is located on the outside of a building in Massachusetts. During the winter months, one can hear a sloshing sound when the extinguisher is gently shaken. In the summertime there is often no sound when it is shaken. Explain. Assume that the extinguisher has no leaks and that it has not been used.

11.102 What is the vapor pressure of mercury at its normal boiling point (357°C)?

11.103 A flask of water is connected to a powerful vacuum pump. When the pump is turned on, the water begins to boil. After a few minutes, the same water begins to freeze. Eventually, the ice disappears. Explain what happens at each step.

11.104 The liquid-vapor boundary line in the phase diagram of any substance always stops abruptly at a certain point. Why?

11.105 The interionic distance of several alkali halide crystals are:

NaCl	NaBr	NaI	KCl	KBr	KI
282 pm	299 pm	324 pm	315 pm	330 pm	353 pm

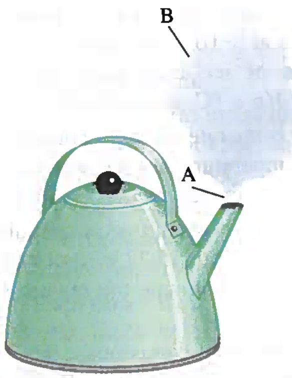
Plot lattice energy versus the reciprocal interionic distance. How would you explain the plot in terms of the dependence of lattice energy on distance of separation between ions? What law governs this interaction? (For lattice energies, see Table 9.1.)

11.106 Which has a greater density, crystalline SiO_2 or amorphous SiO_2? Why?

11.107 A student is given four solid samples labeled W, X, Y, and Z. All except Z have a metallic luster. She is told that the solids could be gold, lead sulfide, quartz (SiO_2), and iodine. The results of her investigations are: (a) W is a good electrical conductor; X, Y, and Z are poor electrical conductors. (b) When the solids are hit with a hammer, W flattens out, X shatters into many pieces, Y is smashed into a powder, and Z is cracked. (c) When the solids are heated with a Bunsen burner, Y melts with some sublimation, but X, W, and Z do not melt. (d) In t with 6 M HNO_3, X dissolves; there is no ef W, Y, or Z. On the basis of these test results, the solids.

11.108 Which of the following statements are fal Dipole-dipole interactions between molec greatest if the molecules possess only tem dipole moments. (b) All compounds contain drogen atoms can participate in hydrogen b mation. (c) Dispersion forces exist betw atoms, molecules, and ions. (d) The extent of induced dipole interaction depends only charge on the ion.

11.109 The diagram below shows a kettle of boilin on a stove. Identify the phases in regions A an



11.110 The south pole of Mars is covered with dry which partly sublimes during the summer. The vapor recondenses in the winter when the temp ture drops to 150 K. Given that the heat of subli tion of CO_2 is 25.9 kJ/mol, calculate the spheric pressure on the surface of Mars. [*Hint* Figure 11.41 to determine the normal sublima temperature of dry ice and Equation (11.5), wh also applies to sublimations.]

11.111 The properties of gases, liquids, and solids diff a number of respects. How would you use the netic molecular theory (see Section 5.7) to expl the following observations? (a) Ease of compr ibility decreases from gas to liquid to solid Solids retain a definite shape, but gases and liqu do not. (c) For most substances, the volume of given amount of material increases as it chan from solid to liquid to gas.

11.112 Select the substance in each pair that should h the higher boiling point. In each case identify th principal intermolecular forces involved and count briefly for your choice. (a) K_2S or (CH (b) Br_2 or $CH_3CH_2CH_2CH_3$

11.113 A small drop of oil in water assumes a spher shape. Explain. (*Hint:* Oil is made up of nonp molecules, which tend to avoid contact with wat

11.114 Under the same conditions of temperature and density, which of the following gases would you expect to behave less ideally: CH_4, SO_2? Explain.

11.115 The fluorides of the second-period elements and their melting points are: LiF, 845°C; BeF_2, 800°C; BF_3, −126.7°C; CF_4, −184°C; NF_3, −206.6°C; OF_2, −223.8°C; F_2, −219.6°C. Classify the type(s) of intermolecular forces present in each compound.

11.116 The standard enthalpy of formation of gaseous molecular iodine is 62.4 kJ/mol. Use this information to calculate the molar heat of sublimation of molecular iodine at 25°C.

11.117 The distance between Li^+ and Cl^- is 257 pm in solid LiCl and 203 pm in a LiCl unit in the gas phase. Explain the difference in the bond lengths.

11.118 Heat of hydration, that is, the heat change that occurs when ions become hydrated in solution, is largely due to ion-dipole interactions. The heats of hydration for the alkali metal ions are Li^+, −520 kJ/mol; Na^+, −405 kJ/mol; K^+, −321 kJ/mol. Account for the trend in these values.

11.119 If water were a linear molecule, (a) would it still be polar, and (b) would the water molecules still be able to form hydrogen bonds with one another?

11.120 Calculate the $\Delta H°$ for the following processes at 25°C: (a) $Br_2(l) \longrightarrow Br_2(g)$ and (b) $Br_2(g) \longrightarrow 2Br(g)$. Comment on the relative magnitudes of these $\Delta H°$ values in terms of the forces involved in each case. {*Hint:* See Table 9.4, and given that $\Delta H_f^\circ[Br_2(g)] = 30.7$ kJ/mol.}

11.121 Which liquid would you expect to have a greater viscosity, water or diethyl ether? The structure of diethyl ether is shown in Problem 11.14.

11.122 A beaker of water is placed in a closed container. Predict the effect on the vapor pressure of the water when (a) its temperature is lowered, (b) the volume of the container is doubled, (c) more water is added to the beaker.

11.123 Ozone (O_3) is a strong oxidizing agent that can oxidize all the common metals except gold and platinum. A convenient test for ozone is based on its action on mercury. When exposed to ozone, mercury becomes dull looking and sticks to glass tubing (instead of flowing freely through it). Write a balanced equation for the reaction. What property of mercury is altered by its interaction with ozone?

11.124 A sample of limestone ($CaCO_3$) is heated in a closed vessel until it is partially decomposed. Write an equation for the reaction and state how many phases are present.

11.125 Silicon used in computer chips must have an impurity level below 10^{-9} (that is, fewer than one impurity atom for every 10^9 Si atoms). Silicon is prepared by the reduction of quartz (SiO_2) with coke (a form of carbon made by the destructive distillation of coal) at about 2000°C:

$$SiO_2(s) + 2C(s) \longrightarrow Si(l) + 2CO(g)$$

Next, solid silicon is separated from other solid impurities by treatment with hydrogen chloride at 350°C to form gaseous trichlorosilane ($SiCl_3H$):

$$Si(s) + 3HCl(g) \longrightarrow SiCl_3H(g) + H_2(g)$$

Finally, ultrapure Si can be obtained by reversing the above reaction at 1000°C:

$$SiCl_3H(g) + H_2(g) \longrightarrow Si(s) + 3HCl(g)$$

(a) Trichlorosilane has a vapor pressure of 0.258 atm at −2°C. What is its normal boiling point? Is trichlorosilane's boiling point consistent with the type of intermolecular forces that exist among its molecules? (The molar heat of vaporization of trichlorosilane is 28.8 kJ/mol.) (b) What types of crystals do Si and SiO_2 form? (c) Silicon has a diamond crystal structure (see Figure 11.28). Each cubic unit cell (edge length $a = 543$ pm) contains eight Si atoms. If there are 1.0×10^{13} boron atoms per cubic centimeter in a sample of pure silicon, how many Si atoms are there for every B atom in the sample? Does this sample satisfy the 10^{-9} purity requirement for the electronic grade silicon?

11.126 Carbon and silicon belong to Group 4A of the periodic table and have the same valence electron configuration (ns^2np^2). Why does silicon dioxide (SiO_2) have a much higher melting point than carbon dioxide (CO_2)?

11.127 A pressure cooker is a sealed container that allows steam to escape when it exceeds a predetermined pressure. How does this device reduce the time needed for cooking?

11.128 A 1.20-g sample of water is injected into an evacuated 5.00-L flask at 65°C. What percentage of the water will be vapor when the system reaches equilibrium? Assume ideal behavior of water vapor and that the volume of liquid water is negligible. The vapor pressure of water at 65°C is 187.5 mmHg.

11.129 What are the advantages of cooking the vegetable broccoli with steam instead of boiling it in water?

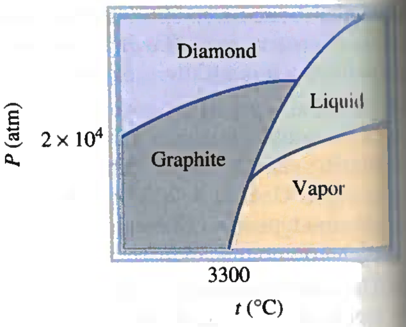
11.130 A quantitative measure of how efficiently spheres pack into unit cells is called *packing efficiency*, which is the percentage of the cell space occupied by the spheres. Calculate the packing efficiencies of a simple cubic cell, a body-centered cubic cell, and a face-centered cubic cell. (*Hint:* Refer to Figure 11.22 and use the relationship that the volume of a sphere is $\frac{4}{3}\pi r^3$, where r is the radius of the sphere.)

11.131 Provide an explanation for each of the following phenomena: (a) Solid argon (m.p. −189.2°C; b.p. −185.7°C) can be prepared by immersing a flask containing argon gas in liquid nitrogen (b.p. −195.8°C) until it liquefies and then connecting the flask to a vacuum pump. (b) The melting point of cyclohexane (C_6H_{12}) increases with increasing pressure exerted on the solid cyclohexane. (c) Certain high-altitude clouds contain water droplets at −10°C. (d) When a piece of dry ice is added to a beaker of water, fog forms above the water.

11.132 Argon crystallizes in the face-centered cubic arrangement at 40 K. Given that the atomic radius of argon is 191 pm, calculate the density of solid argon.

11.133 A chemistry instructor performed the following mystery demonstration. Just before the students arrived in class, she heated some water to boiling in an Erlenmeyer flask. She then removed the flask from the flame and closed the flask with a rubber stopper. After the class commenced, she held the flask in front of the students and announced that she could make the water boil simply by rubbing an ice cube on the outside walls of the flask. To the amazement of everyone, it worked. Give an explanation for this phenomenon.

11.134 Given the phase diagram of carbon shown, answer the following questions: (a) How many triple points are there and what are the phases that can coexist at each triple point? (b) Which has a higher density, graphite or diamond? (c) Synthetic diamond can be made from graphite. Using the phase diagram, how would you go about making diamond?



11.135 Swimming coaches sometimes suggest that
of alcohol (ethanol) placed in an ear plugged
water "draws out the water." Explain this
from a molecular point of view.

11.136 Use the concept of intermolecular forces to
why the far end of a walking cane rises when
raises the handle.

11.137 Why do citrus growers spray their trees with
to protect them from freezing?

11.138 What is the origin of dark spots on the inner
walls of an old tungsten lightbulb? What is the
pose of filling these lightbulbs with argon gas?

11.139 The compound dichlorodifluoromethane (CCl
has a normal boiling point of −30°C, a critical
perature of 112°C, and a corresponding
pressure of 40 atm. If the gas is compressed
18 atm at 20°C, will the gas condense? Your
should be based on a graphical interpretation.

11.140 A student heated a beaker of cold water (on a
with a Bunsen burner. When the gas is ignited,
noticed that there was water condensed on the
side of the beaker. Explain what happened.

Special Problems

11.141 Sketch the cooling curves of water from about 110°C to about −10°C. How would you also show the formation of supercooled liquid below 0°C which then freezes to ice? The pressure is at 1 atm throughout the process. The curves need not be drawn quantitatively.

11.142 Iron crystallizes in a body-centered cubic lattice
The cell length as determined by X-ray diffraction
is 286.7 pm. Given that the density of iron
7.874 g/cm^3, calculate Avogadro's number.

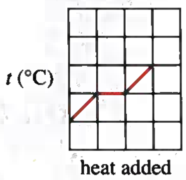
11.143 The boiling point of methanol is 65.0°C and
standard enthalpy of formation of methanol vapor

−201.2 kJ/mol. Calculate the vapor pressure of methanol (in mmHg) at 25°C. (*Hint:* See Appendix 3 for other thermodynamic data of methanol.)

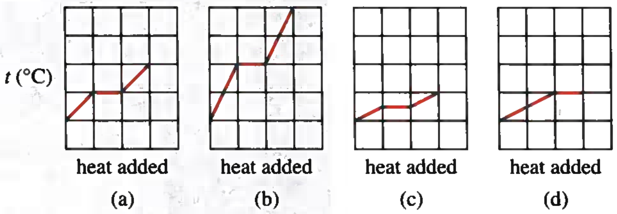
11.144 An alkali metal in the form of a cube of edge length 0.171 cm is vaporized in a 0.843-L container at 1235 K. The vapor pressure is 19.2 mmHg. Identify the metal by calculating the atomic radius in picometers and the density. (*Hint:* You need to consult Figures 8.5, 11.22, 11.29, and a chemistry handbook.)

11.145 A closed vessel of volume 9.6 L contains 2.0 g of water. Calculate the temperature (in °C) at which only half of the water remains in the liquid phase. (See Table 5.3 for vapor pressures of water at different temperatures.)

11.146 A sample of water shows the following behavior as it is heated at a constant rate:



If twice the mass of water has the same amount of heat transferred to it, which of the following graphs best describes the temperature variation? Note that the scales for all the graphs are the same.



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Answers to Practice Exercises

11.1 (a) Ionic and dispersion forces, (b) dispersion forces, (c) dipole-dipole and dispersion forces. **11.2** Only (c). **11.3** 10.50 g/cm^3. **11.4** 315 pm. **11.5** Two. **11.6** 361 pm. **11.7** 369 mmHg. **11.8** 173 kJ.