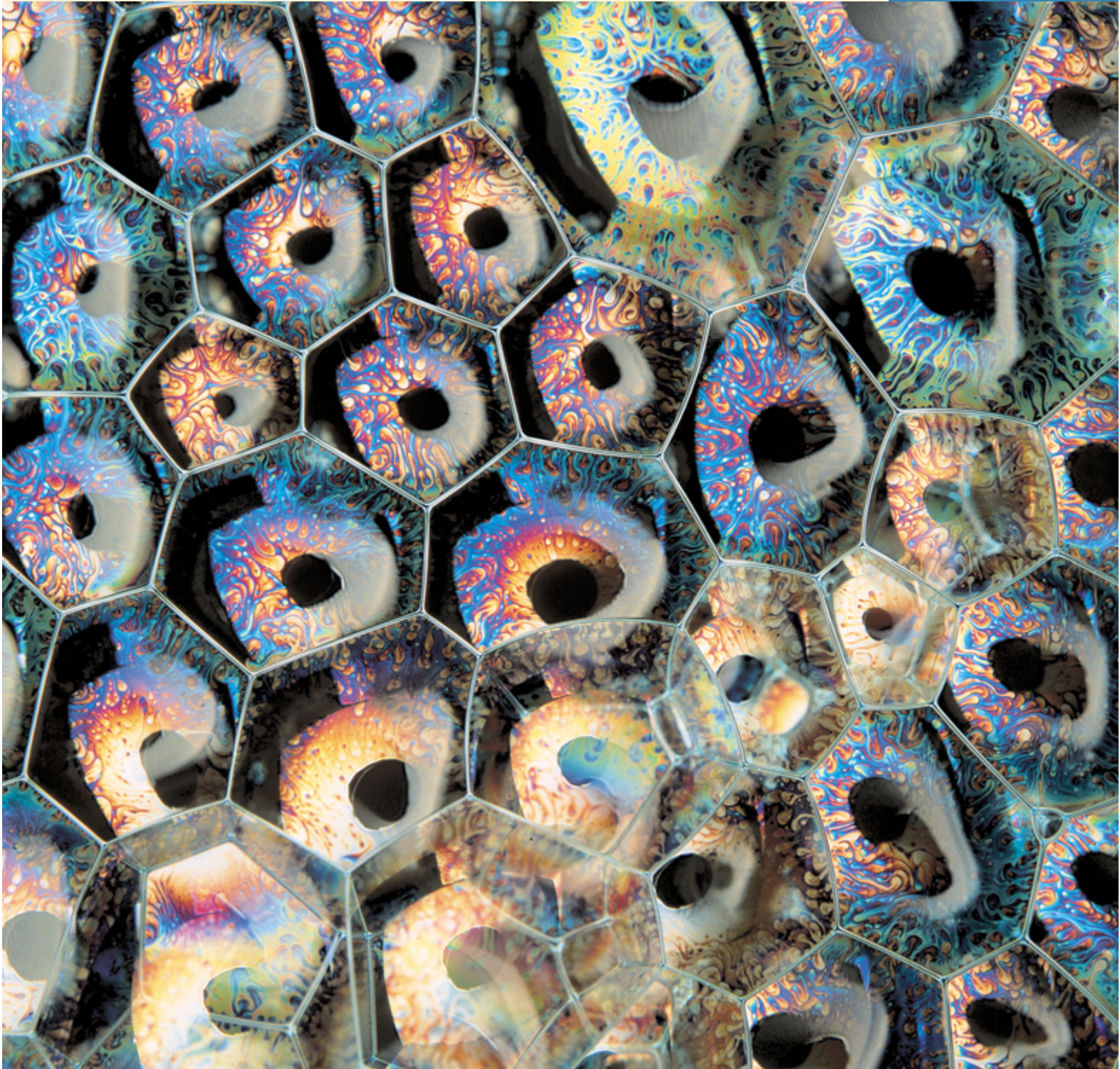
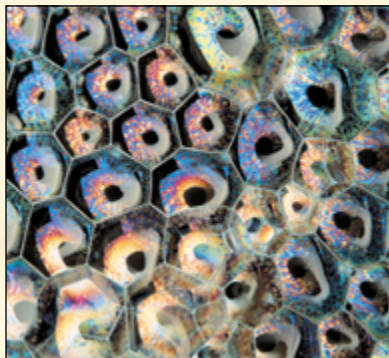


Liquids and Solids

13





The shapes of soap bubbles are due to surface tension, an important physical property of liquids. White light striking the bubbles gives brightly colored interference patterns.

OUTLINE

- 13-1 Kinetic–Molecular Description of Liquids and Solids
- 13-2 Intermolecular Attractions and Phase Changes

The Liquid State

- 13-3 Viscosity
- 13-4 Surface Tension
- 13-5 Capillary Action
- 13-6 Evaporation
- 13-7 Vapor Pressure
- 13-8 Boiling Points and Distillation
- 13-9 Heat Transfer Involving Liquids

The Solid State

- 13-10 Melting Point
- 13-11 Heat Transfer Involving Solids
- 13-12 Sublimation and the Vapor Pressure of Solids
- 13-13 Phase Diagrams (P versus T)
- 13-14 Amorphous Solids and Crystalline Solids
- 13-15 Structures of Crystals
- 13-16 Bonding in Solids
- 13-17 Band Theory of Metals

OBJECTIVES

After you have studied this chapter, you should be able to

- Describe the properties of liquids and solids and how they differ from gases
- Understand the kinetic–molecular description of liquids and solids, and show how this description differs from that for gases
- Use the terminology of phase changes
- Understand various kinds of intermolecular attractions and how they are related to physical properties such as vapor pressure, viscosity, melting point, and boiling point
- Describe evaporation, condensation, and boiling in molecular terms
- Calculate the heat transfer involved in warming or cooling without change of phase
- Calculate the heat transfer involved in phase changes
- Describe melting, solidification, sublimation, and deposition in molecular terms
- Interpret P versus T phase diagrams
- Describe the regular structure of crystalline solids
- Describe various types of solids
- Relate the properties of different types of solids to the bonding or interactions among particles in these solids
- Visualize some common simple arrangements of atoms in solids
- Carry out calculations relating atomic arrangement, density, unit cell size, and ionic or atomic radii in some simple crystalline arrangements
- Describe the bonding in metals
- Explain why some substances are conductors, some are insulators, and others are semiconductors

The molecules of most gases are so widely separated at ordinary temperatures and pressures that they do not interact with one another significantly. The physical properties of gases are reasonably well described by the simple relationships in Chapter 12. In liquids and solids, the so-called **condensed phases**, the particles are close together so they interact strongly. Although the properties of liquids and solids can be described, they cannot be adequately explained by simple mathematical relationships. Table 13-1 and Figure 13-1 summarize some of the characteristics of gases, liquids, and solids.

See the *Saunders Interactive General Chemistry CD-ROM*, Screen 13.2, Phases of Matter; the Kinetic-Molecular Theory. This screen contains an animated version of Figure 13-1.

TABLE 13-1 Some Characteristics of Solids, Liquids, and Gases

Solids	Liquids	Gases
<ol style="list-style-type: none"> 1. Have definite shape (resist deformation) 2. Are nearly incompressible 3. Usually have higher density than liquids 4. Are not fluid 5. Diffuse only very slowly through solids 6. Have an ordered arrangement of particles that are very close together; particles have vibrational motion only 	<ol style="list-style-type: none"> 1. Have no definite shape (assume shapes of containers) 2. Have definite volume (are only very slightly compressible) 3. Have high density 4. Are fluid 5. Diffuse through other liquids 6. Consist of disordered clusters of particles that are quite close together; particles have random motion in three dimensions 	<ol style="list-style-type: none"> 1. Have no definite shape (fill containers completely) 2. Are compressible 3. Have low density 4. Are fluid 5. Diffuse rapidly 6. Consist of extremely disordered particles with much empty space between them; particles have rapid, random motion in three dimensions

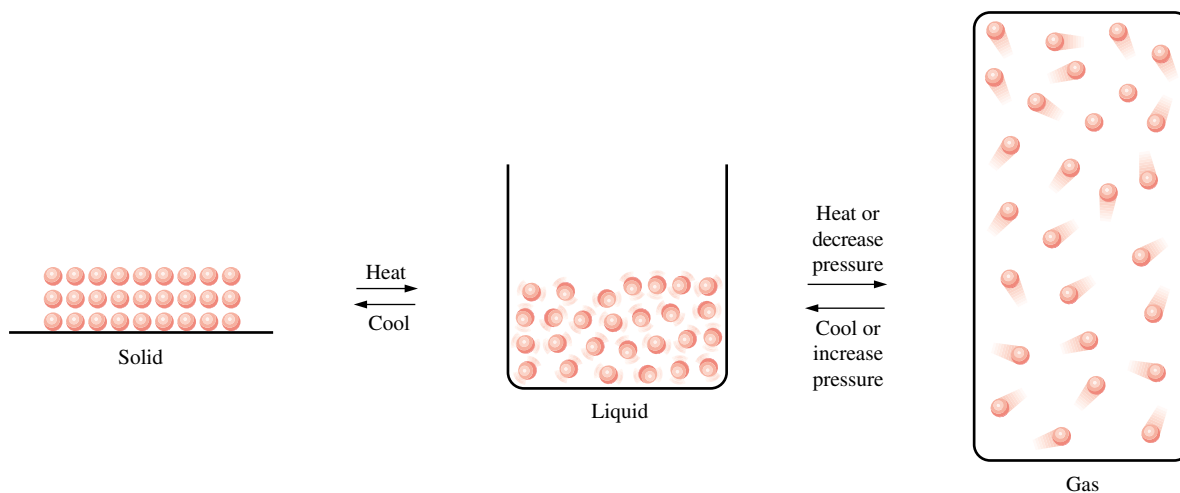


Figure 13-1 Representations of the kinetic-molecular description of the three phases of matter.

13-1 KINETIC–MOLECULAR DESCRIPTION OF LIQUIDS AND SOLIDS

Intermolecular attractions are those between different molecules or ions. Intramolecular attractions are those between atoms within a single molecule or ion.

The miscibility of two liquids refers to their ability to mix and produce a homogeneous solution.

Solidification and crystallization refer to the process in which a liquid changes to a solid.

The properties listed in Table 13-1 can be qualitatively explained in terms of the kinetic–molecular theory of Chapter 12. We saw in Section 12-13 that the average kinetic energy of a collection of gas molecules decreases as the temperature is lowered. As a sample of gas is cooled and compressed, the rapid, random motion of gaseous molecules decreases. The molecules approach one another, and the intermolecular attractions increase. Eventually, these increasing intermolecular attractions overcome the reduced kinetic energies. At this point condensation (liquefaction) occurs. The temperatures and pressures required for condensation vary from gas to gas, because different kinds of molecules have different attractive forces.

In the liquid state the forces of attraction among particles are great enough that disordered clustering occurs. The particles are so close together that very little of the volume occupied by a liquid is empty space. As a result, it is very hard to compress a liquid. Particles in liquids have sufficient energy of motion to overcome partially the attractive forces among them. They are able to slide past one another so that liquids assume the shapes of their containers up to the volume of the liquid.

Liquids diffuse into other liquids with which they are *miscible*. For example, when a drop of red food coloring is added to a glass of water, the water becomes red throughout after diffusion is complete. The natural diffusion rate is slow at normal temperatures. Because the average separations among particles in liquids are far less than those in gases, the densities of liquids are much higher than the densities of gases (Table 12-1).

Cooling a liquid lowers its molecular kinetic energy and causes its molecules to slow down even more. If the temperature is lowered sufficiently, at ordinary pressures, stronger but shorter-range attractive interactions overcome the reduced kinetic energies of the molecules to cause *solidification*. The temperature required for *crystallization* at a given pressure depends on the nature of short-range interactions among the particles and is characteristic of each substance.

Most solids have ordered arrangements of particles with a very restricted range of motion. Particles in the solid state cannot move freely past one another so they only vibrate about fixed positions. Consequently, solids have definite shapes and volumes. Because the particles are so close together, solids are nearly incompressible and are very dense relative to gases. Solid particles do not diffuse readily into other solids. However, analysis of

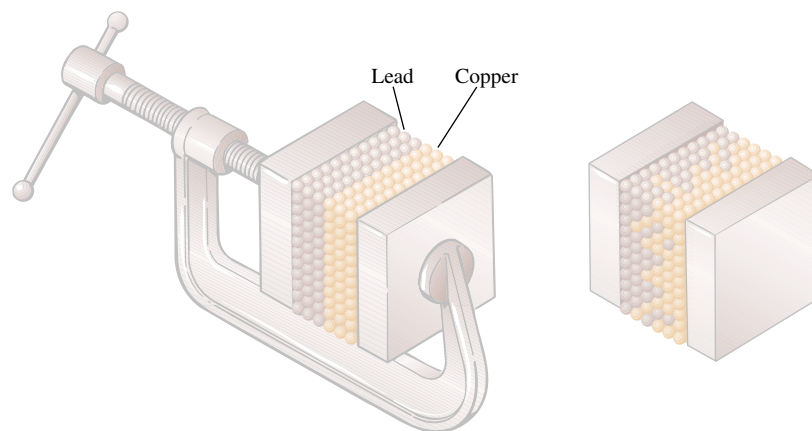


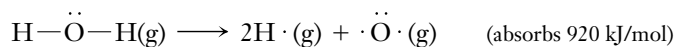
Figure 13-2 A representation of diffusion in solids. When blocks of two different metals are clamped together for a long time, a few atoms of each metal diffuse into the other metal.

two blocks of different solids, such as copper and lead, that have been pressed together for a period of years shows that each block contains some atoms of the other element. This demonstrates that solids do diffuse, but very slowly (Figure 13-2).

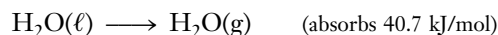
13-2 INTERMOLECULAR ATTRACTIONS AND PHASE CHANGES

We have seen (Section 12-15) how the presence of strong attractive forces between gas molecules can cause gas behavior to become nonideal when the molecules get close together. In liquids and solids the molecules are much closer together than in gases. As a result, properties of liquids, such as boiling point, vapor pressure, viscosity, and heat of vaporization, depend markedly on the strengths of the intermolecular attractive forces. These forces are also directly related to the properties of solids, such as melting point and heat of fusion. Let us preface our study of these condensed phases with a discussion of the types of attractive forces that can exist between molecules and ions.

Intermolecular forces refer to the forces *between* individual particles (atoms, molecules, ions) of a substance. These forces are quite weak relative to *intramolecular forces*, that is, covalent and ionic bonds *within* compounds. For example, 920 kJ of energy is required to decompose one mole of water vapor into H and O atoms. This reflects the strength of intramolecular forces (covalent bonds).



Only 40.7 kJ is required to convert one mole of liquid water into steam at 100°C.



This reflects the strength of the intermolecular forces of attraction between the water molecules, mainly *hydrogen bonding*.

If it were not for the existence of intermolecular attractions, condensed phases (liquids and solids) could not exist. These are the forces that hold the particles close to one another in liquids and solids. As we shall see, the effects of these attractions on melting points of solids parallel those on boiling points of liquids. High boiling points are associated with compounds that have strong intermolecular attractions. Let us consider the effects of the general types of forces that exist among ionic, covalent, and monatomic species.


Ion–Ion Interactions

According to Coulomb's Law, the *force of attraction* between two oppositely charged ions is directly proportional to the charges on the ions, q^+ and q^- , and inversely proportional to the square of the distance between them, d .

$$F \propto \frac{q^+ q^-}{d^2}$$

Energy has the units of force \times distance, $F \times d$, so the *energy of attraction* between two oppositely charged ions is directly proportional to the charges on the ions and inversely proportional to the distance of separation.

$$E \propto \frac{q^+ q^-}{d}$$

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 13.3, Intermolecular Forces (1).

It is important to be able to tell whether a substance is ionic, nonpolar covalent, or polar covalent. You should review the discussion of bonding in Chapters 7 and 8.

When oppositely charged ions are close together, d (the denominator) is small, so F , the attractive force between them, is large.

Ionic bonding may be thought of as both *inter-* and *intramolecular* bonding.

Ionic compounds such as NaCl, CaBr₂, and K₂SO₄ exist as extended arrays of discrete ions in the solid state. As we shall see in Section 13-16, the oppositely charged ions in these arrays are quite close together. As a result of these small distances, d , the energies of attraction in these solids are substantial. Most ionic bonding is strong, and as a result most ionic compounds have relatively high melting points (Table 13-2). At high enough temperatures, ionic solids melt as the added heat energy overcomes the potential energy associated with the attraction of oppositely charged ions. The ions in the resulting liquid samples are free to move about, which accounts for the excellent electrical conductivity of molten ionic compounds.

For most substances, the liquid is less dense than the solid, but H₂O is one of the rare exceptions. Melting a solid nearly always produces greater average separations among the particles. This means that the forces (and energies) of attractions among the ions in an ionic liquid are less than in the solid state because the average d is greater in the melt. However, these energies of attraction are still much greater in magnitude than the energies of attraction among neutral species (molecules or atoms).

The product q^+q^- increases as the charges on ions increase. Ionic substances containing multiply charged ions, such as Al³⁺, Mg²⁺, O²⁻, and S²⁻ ions, *usually* have higher melting and boiling points than ionic compounds containing only singly charged ions, such as Na⁺, K⁺, F⁻, and Cl⁻. For a series of ions of similar charges, the closer approach of smaller ions results in stronger interionic attractive forces and higher melting points (compare NaF, NaCl, and NaBr in Table 13-2).

Dipole–Dipole Interactions

Permanent dipole–dipole interactions occur between polar covalent molecules because of the attraction of the δ^+ atoms of one molecule to the δ^- atoms of another molecule (Section 7-9).

Electrostatic forces between two ions decrease by the factor $1/d^2$ as their separation, d , increases. But dipole–dipole forces vary as $1/d^4$. Because of the higher power of d in the denominator, $1/d^4$ diminishes with increasing d much more rapidly than does $1/d^2$. As a result, dipole forces are effective only over very short distances. Furthermore, for dipole–dipole forces, q^+ and q^- represent only “partial charges,” so these forces are weaker than ion–ion forces. Average dipole–dipole interaction energies are approximately 4 kJ per mole of bonds. They are much weaker than ionic and covalent bonds, which have typical energies of about 400 kJ per mole of bonds. Substances in which permanent dipole–dipole interactions affect physical properties include bromine fluoride, BrF, and sulfur


 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 13.4, Intermolecular Forces (2), especially the subsection “Dipole–Dipole Forces.”

TABLE 13-2 *Melting Points of Some Ionic Compounds*

Compound	mp (°C)	Compound	mp (°C)	Compound	mp (°C)
NaF	993	CaF ₂	1423	MgO	2800
NaCl	801	Na ₂ S	1180	CaO	2580
NaBr	747	K ₂ S	840	BaO	1923
KCl	770				

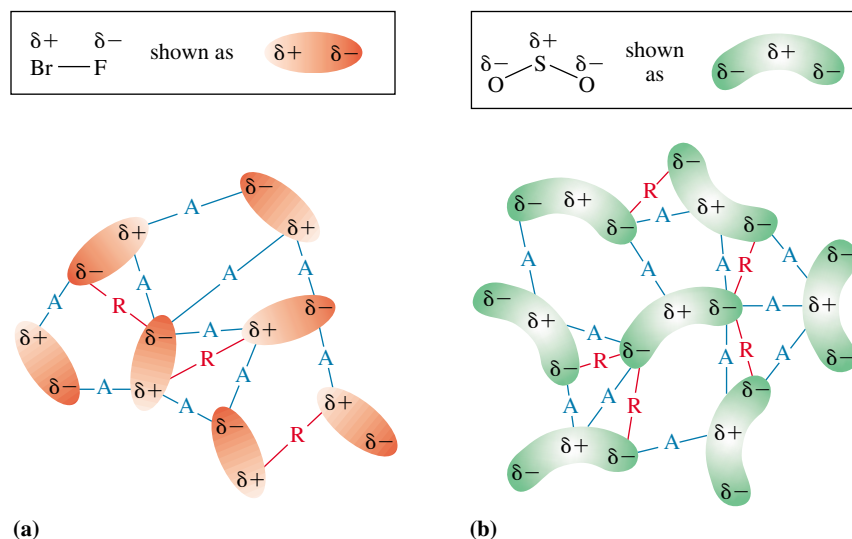



Figure 13-3 Dipole–dipole interactions among polar molecules. (a) Bromine fluoride, BrF. (b) Sulfur dioxide, SO_2 . Each polar molecule is shaded with regions of highest negative charge (δ^-) darkest and regions of highest positive charge (δ^+) lightest. Attractive forces are shown as —A—, and repulsive forces are shown as —R—. Molecules tend to arrange themselves to maximize attractions by bringing regions of opposite charge together while minimizing repulsions by separating regions of like charge.

dioxide, SO_2 . Dipole–dipole interactions are illustrated in Figure 13-3. All dipole–dipole interactions, including hydrogen bonding (discussed in the following section), are somewhat directional. An increase in temperature causes an increase in translational, rotational, and vibrational motion of molecules. This produces more random orientations of molecules relative to one another. Consequently, dipole–dipole interactions become less important as temperature increases. All these factors make compounds having only dipole–dipole interactions more volatile than ionic compounds.

Hydrogen Bonding

Hydrogen bonds are a special case of very strong dipole–dipole interaction. They are not really chemical bonds in the formal sense.

Strong hydrogen bonding occurs among polar covalent molecules containing H and one of the three small, highly electronegative elements—F, O, or N.

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 13.6, Hydrogen Bonding.

Like ordinary dipole–dipole interactions, hydrogen bonds result from the attractions between δ^+ atoms of one molecule, in this case H atoms, and the δ^- atoms of another molecule. The small sizes of the F, O, and N atoms, combined with their high electronegativities, concentrate the electrons of these molecules around these δ^- atoms. This causes an H atom bonded to one of these highly electronegative elements to become quite positive. The δ^+ H atom is attracted to a lone pair of electrons on an F, O, or N atom other than the atom to which it is covalently bonded (Figure 13-4). The molecule that contains the hydrogen-bonding δ^+ H atom is often referred to as the *hydrogen-bond donor*; the δ^- atom to which it is attracted is called the *hydrogen-bond acceptor*.

Recently, careful studies of light absorption and magnetic properties in solution and of the arrangements of molecules in solids have led to the conclusion that the same kind of attraction occurs (although more weakly) when H is bonded to carbon. In some cases, very weak $\text{C—H}\cdots\text{O}$ “hydrogen bonds” exist. Similar observations suggest the existence

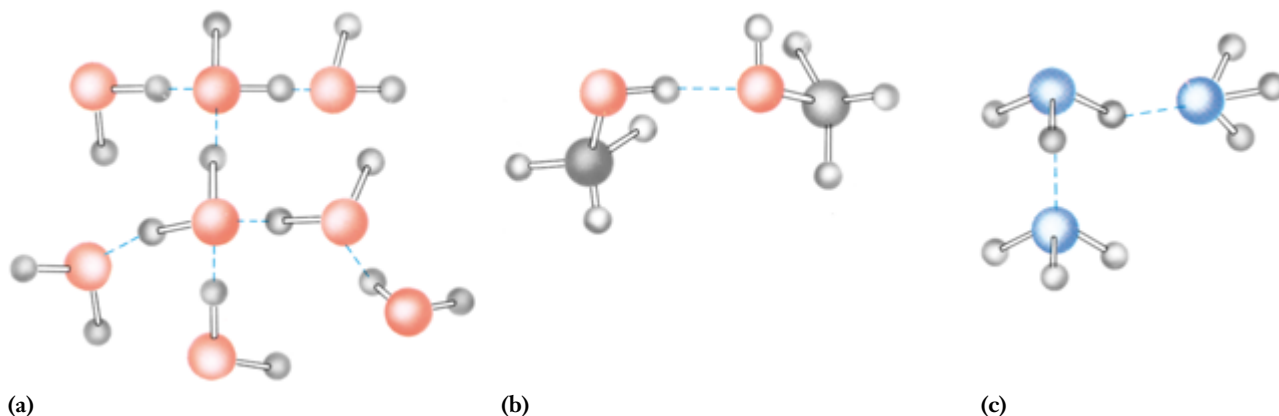


Figure 13-4 Hydrogen bonding (indicated by dashed lines) in (a) water, H_2O ; (b) methyl alcohol, CH_3OH ; and (c) ammonia, NH_3 . Hydrogen bonding is a special case of very strong dipole interaction.

of weak hydrogen bonds to chlorine atoms, such as $\text{O}-\text{H}\cdots\text{Cl}$. However, most chemists usually restrict usage of the term “hydrogen bonding” to compounds in which H is covalently bonded to F, O, or N, and we will do likewise throughout this text.

Typical hydrogen-bond energies are in the range 15 to 20 kJ/mol, which is four to five times greater than the energies of other dipole–dipole interactions. As a result, hydrogen bonds exert a considerable influence on the properties of substances. Hydrogen bonding is responsible for the unusually high melting and boiling points of compounds such as water, methyl alcohol, and ammonia compared with other compounds of similar molecular weight and molecular geometry (Figure 13-5). Hydrogen bonding between amino acid subunits is very important in establishing the three-dimensional structures of proteins.

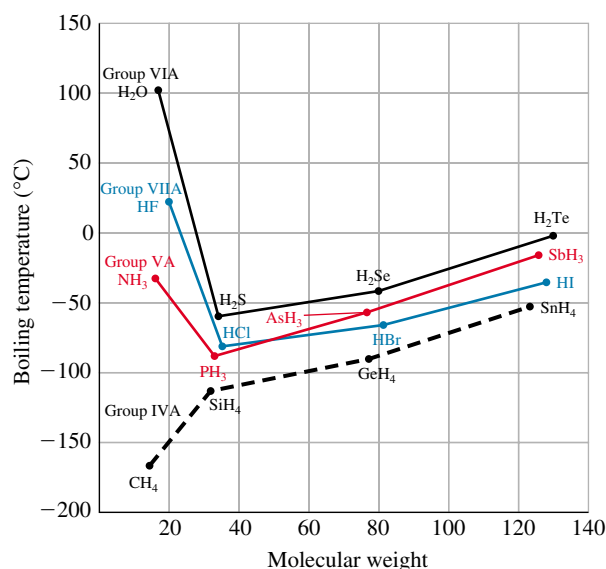


Figure 13-5 Boiling points of some hydrides as a function of molecular weight. The unusually high boiling points of NH_3 , H_2O , and HF compared with those of other hydrides of the same groups are due to hydrogen bonding. The electronegativity difference between H and C is small, and there are no unshared pairs on C; thus, CH_4 is not hydrogen bonded. Increasing molecular weight corresponds to increasing number of electrons; this makes the electron clouds easier to deform and causes increased dispersion forces, accounting for the increase in boiling points for the nonhydrogen-bonded members of each series.

Dispersion Forces

Dispersion forces are weak attractive forces that are important only over *extremely* short distances because they vary as $1/d^7$. They are present between all types of molecules in condensed phases but are weak for small molecules. Dispersion forces are the only kind of intermolecular forces present among symmetrical nonpolar substances such as SO_3 , CO_2 , O_2 , N_2 , Br_2 , H_2 , and monatomic species such as the noble gases. Without dispersion forces, such substances could not condense to form liquids or solidify to form solids. Condensation of some substances occurs only at very low temperatures and/or high pressures.

Dispersion forces result from the attraction of the positively charged nucleus of one atom for the electron cloud of an atom in nearby molecules. This induces *temporary* dipoles in neighboring atoms or molecules. As electron clouds become larger and more diffuse, they are attracted less strongly by their own (positively charged) nuclei. Thus, they are more easily distorted, or *polarized*, by adjacent nuclei.

Polarizability increases with increasing numbers of electrons and therefore with increasing sizes of molecules. Therefore, dispersion forces are generally stronger for molecules that have more electrons or are larger.

Dispersion forces are often called London forces, after the German-born physicist Fritz London (1900–1954). He initially postulated their existence in 1930, on the basis of quantum theory.

Although the term “van der Waals forces” usually refers to all intermolecular attractions, it is also often used interchangeably with “dispersion forces,” as are the terms “London forces” and “dipole-induced dipole forces.”

Dispersion forces are depicted in Figure 13-6. They exist in all substances.

Figure 13-5 shows that polar covalent compounds with hydrogen bonding (H_2O , HF , NH_3) boil at higher temperatures than analogous polar compounds without hydrogen bonding (H_2S , HCl , PH_3). Symmetrical, nonpolar compounds (CH_4 , SiH_4) of compa-

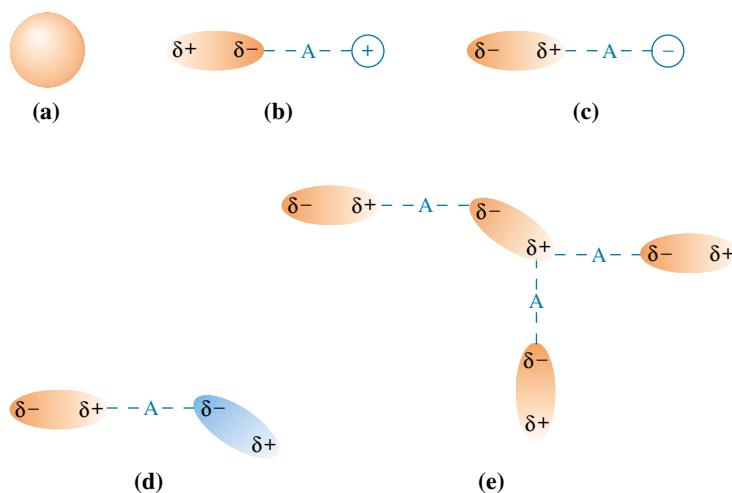


Figure 13-6 An illustration of how a temporary dipole can be induced in an atom. (a) An isolated argon atom, with spherical charge distribution (no dipole). (b) When a cation approaches the argon atom, the outer portion of the electron cloud is weakly attracted by the ion's positive charge. This induces a weak *temporary* dipole in the argon atom. (c) A temporary dipole can also be induced if the argon atom is approached by an anion. (d) The approach of a molecule with a permanent dipole (for instance, HF) could also temporarily polarize the argon atom. (e) Even in pure argon, the close approach of one argon atom to another results in temporary dipole formation in both atoms as each atom's electron cloud is attracted by the nucleus of the other atom or is repelled by the other atom's electron cloud. The resulting temporary dipoles cause weak attractions among the argon atoms. Molecules are even more easily polarized than isolated atoms.


 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 13.5, Intermolecular Forces (3).

TABLE 13-3 *Approximate Contributions to the Total Energy of Interaction Between Molecules, in kJ/mol*

Molecule	Permanent Dipole Moment (D)	Permanent Dipole–Dipole Energy	Dispersion Energy	Total Energy	Molar Heat of Vaporization (kJ/mol)
Ar	0	0	8.5	8.5	6.7
CO	0.1	≈0	8.7	8.7	8.0
HCl	1.03	3.3	17.8	21	16.2
NH ₃	1.47	13*	16.3	29	27.4
H ₂ O	1.85	36*	10.9	47	40.7

*Hydrogen-bonded.

rable molecular weight boil at lower temperatures. In the absence of hydrogen bonding, boiling points of analogous substances (CH₄, SiH₄, GeH₄, SnH₄) increase fairly regularly with increasing number of electrons and molecular size (molecular weight). This is due to increasing effectiveness of dispersion forces of attraction in the larger molecules and occurs even in the case of some polar covalent molecules. The increasing effectiveness of dispersion forces, for example, accounts for the increase in boiling points in the sequences HCl < HBr < HI and H₂S < H₂Se < H₂Te, which involve nonhydrogen-bonded polar covalent molecules. The differences in electronegativities between hydrogen and other nonmetals *decrease* in these sequences, and the increasing dispersion forces override the decreasing permanent dipole–dipole forces. The *permanent* dipole–dipole interactions therefore have very little effect on the boiling point trend of these compounds.

Let us compare the magnitudes of the various contributions to the total energy of interactions in some simple molecules. Table 13-3 shows the permanent dipole moments and the energy contributions for five simple molecules. The contribution from dispersion forces is substantial in all cases. The permanent dipole–dipole energy is greatest for substances in which hydrogen bonding occurs. The variations of these total energies of interaction are closely related to molar heats of vaporization. As we shall see in Section 13-9, the heat of vaporization measures the amount of energy required to overcome the attractive forces that hold the molecules together in a liquid.

The properties of a liquid or a solid are often the result of many forces. The properties of an ionic compound are determined mainly by the very strong ion–ion interactions, even though other forces may also be present. In a polar covalent compound that contains N–H, O–H, or F–H bonds, strong hydrogen bonding is often the strongest force present. If hydrogen bonding is absent in a polar covalent compound, dispersion forces are likely to be the most important forces. In a slightly polar or nonpolar covalent compound or a monatomic nonmetal, the dispersion forces, though weak, are still the strongest ones present, so they determine the forces. For large molecules, even the very weak dispersion forces can total up to a considerable interactive force.

THE LIQUID STATE

We shall briefly describe several properties of the liquid state. These properties vary markedly among various liquids, depending on the nature and strength of the attractive forces among the particles (atoms, molecules, ions) making up the liquid.

The covalent bonding *within* a polyatomic ion such as NH₄⁺ or SO₄²⁻ is very strong, but the forces that hold the *entire substance* together are ionic. Thus a compound that contains a polyatomic ion is an ionic compound (see Section 7-10).

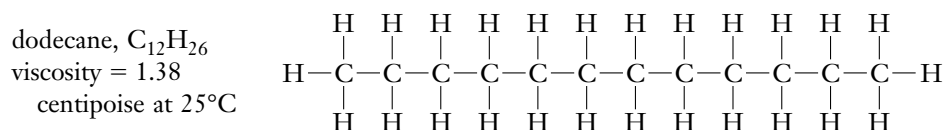
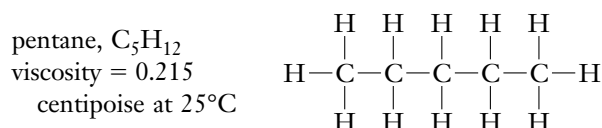


Honey is a very viscous liquid.

13-3 VISCOSITY

Viscosity is the resistance to flow of a liquid. Honey has a high viscosity at room temperature, and freely flowing gasoline has a low viscosity. The viscosity of a liquid can be measured with a viscometer such as the one in Figure 13-7.

For a liquid to flow, the molecules must be able to slide past one another. In general, the stronger the intermolecular forces of attraction, the more viscous the liquid is. Substances that have a great ability to form hydrogen bonds, especially involving several hydrogen-bonding sites per molecule, such as glycerine (margin), usually have high viscosities. Increasing the size and surface area of molecules generally results in increased viscosity, due to the increased dispersion forces. For example, the shorter-chain hydrocarbon pentane (a free-flowing liquid at room temperature) is less viscous than dodecane (an oily liquid at room temperature). The longer the molecules are, the more they can get “tangled up” with one another, and the harder it is for them to flow.

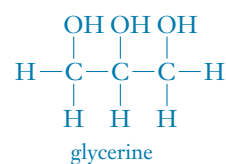


As temperature increases and the molecules move more rapidly, their kinetic energies are better able to overcome intermolecular attractions. Thus, viscosity decreases with increasing temperature, as long as no changes in composition occur.

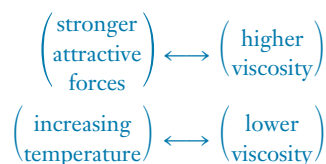
The *poise* is the unit used to express viscosity. The viscosity of water at $25^\circ C$ is 0.89 centipoise.



See the *Saunders Interactive General Chemistry CD-ROM*, Screen 13.11, Properties of Liquids (4): Surface Tension/Capillary Action/Viscosity.



Viscosity = 945 centipoise at $25^\circ C$



13-4 SURFACE TENSION

Molecules below the surface of a liquid are influenced by intermolecular attractions from all directions. Those on the surface are attracted only toward the interior (Figure 13-8); these attractions pull the surface layer toward the center. The most stable situation is one

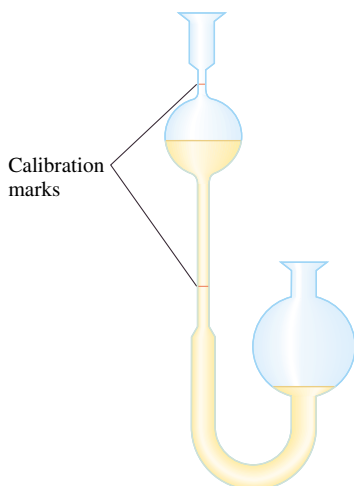


Figure 13-7 The Ostwald viscometer, a device used to measure viscosity of liquids. The time it takes for a known volume of a liquid to flow through a small neck of known size is measured. Liquids with low viscosities flow rapidly.

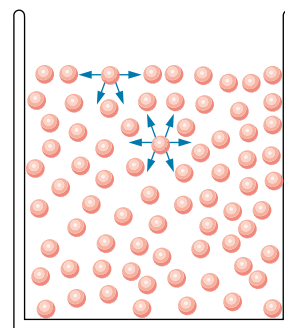
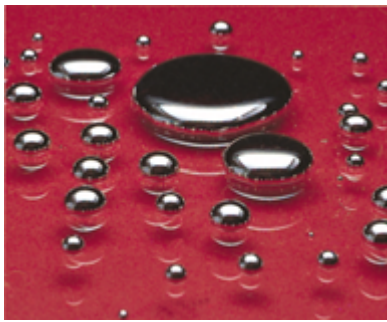


Figure 13-8 A molecular-level view of the attractive forces experienced by molecules at and below the surface of a liquid.



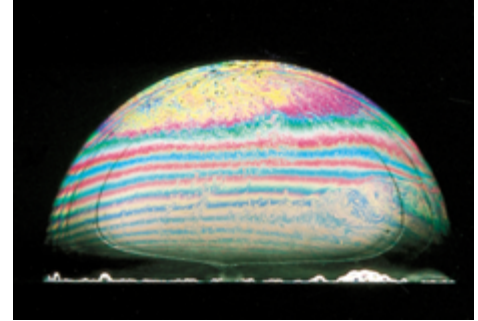
The surface tension of water supports this water strider. The nonpolar surfaces of its feet also help to repel the water.



Droplets of mercury lying on a glass surface. The small droplets are almost spherical, whereas the larger droplets are flattened due to the effects of gravity. This shows that surface tension has more influence on the shape of the small (lighter) droplets.



Figure 13-9 The meniscus, as observed in glass tubes with water and with mercury.



(Right) The shape of a soap bubble is due to the inward force (surface tension) that acts to minimize the surface area.

in which the surface area is minimal. For a given volume, a sphere has the least possible surface area, so drops of liquid tend to assume spherical shapes. **Surface tension** is a measure of the inward forces that must be overcome to expand the surface area of a liquid.

13-5 CAPILLARY ACTION

All forces holding a liquid together are called **cohesive forces**. The forces of attraction between a liquid and another surface are **adhesive forces**. The partial positive charges on the H atoms of water hydrogen bond strongly to the partial negative charges on the oxygen atoms at the surface of the glass. As a result, water *adheres* to glass, or is said to *wet* glass. As water creeps up the side of the glass tube, its favorable area of contact with the glass increases. The surface of the water, its **meniscus**, has a concave shape (Figure 13-9). On the other hand, mercury does not wet glass because its cohesive forces (due to dispersion forces) are much stronger than its attraction to glass. Thus, its meniscus is convex. **Capillary action** occurs when one end of a capillary tube, a glass tube with a small bore (inside diameter), is immersed in a liquid. If adhesive forces exceed cohesive forces, the liquid creeps up the sides of the tube until a balance is reached between adhesive forces and the weight of liquid. The smaller the bore, the higher the liquid climbs. Capillary action helps plant roots take up water and dissolved nutrients from the soil and transmit them up the stems. The roots, like glass, exhibit strong adhesive forces for water. Osmotic pressure (Section 14-15) also plays a major role in this process.



Coating glass with a silicone polymer greatly reduces the adhesion of water to the glass. The left side of each glass has been treated with Rain-X, which contains a silicone polymer. Water on the treated side forms droplets that are easily swept away.

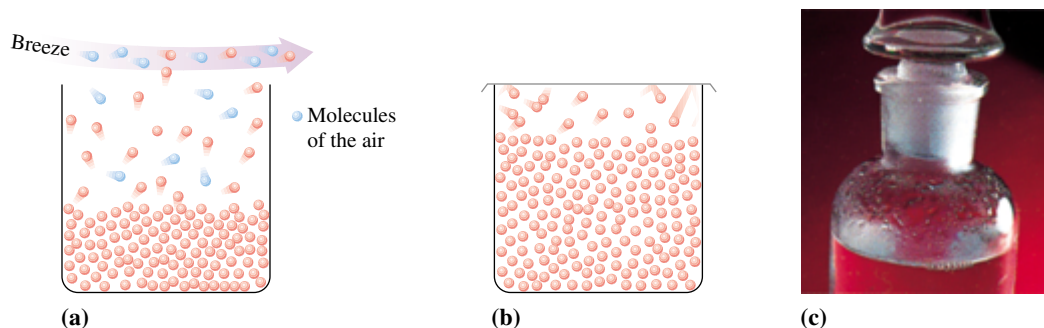


Figure 13-10 (a) Liquid continuously evaporates from an open vessel. (b) Equilibrium between liquid and vapor is established in a closed container in which molecules return to the liquid at the same rate as they leave it. (c) A bottle in which liquid–vapor equilibrium has been established. Note that droplets have condensed.

13-6 EVAPORATION

Evaporation, or vaporization, is the process by which molecules on the surface of a liquid break away and go into the gas phase (Figure 13-10). Kinetic energies of molecules in liquids depend on temperature in the same way as they do in gases. The distribution of kinetic energies among liquid molecules at two different temperatures is shown in Figure 13-11. To break away, the molecules must possess at least some minimum kinetic energy. Figure 13-11 shows that at a higher temperature, a greater fraction of molecules possess at least that minimum energy. The rate of evaporation increases as temperature increases.

Only the higher-energy molecules can escape from the liquid phase. The average molecular kinetic energy of the molecules remaining in the liquid state is thereby lowered, resulting in a lower temperature in the liquid. The liquid would then be cooler than its surroundings, so it absorbs heat from its surroundings. The cooling of your body by evaporation of perspiration is a familiar example of the cooling of the surroundings by evaporation of a liquid. This is called “cooling by evaporation.”



The dew on this spider web was formed by condensation of water vapor from the air.

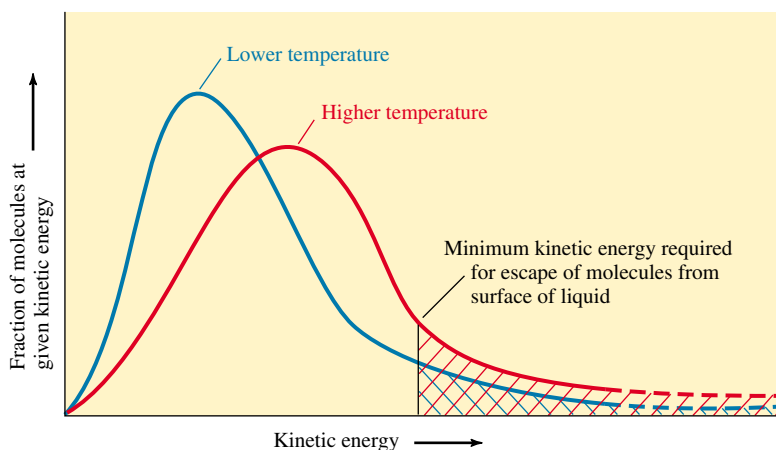



Figure 13-11 Distribution of kinetic energies of molecules in a liquid at different temperatures. At the lower temperature, a smaller fraction of the molecules have the energy required to escape from the liquid, so evaporation is slower and the equilibrium vapor pressure (Section 13-7) is lower.

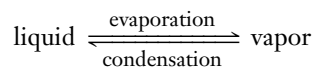
As an analogy, suppose that 30 students per minute leave a classroom, moving into the closed hallway outside, and 30 students per minute enter it. The total number of students in the room would remain constant, as would the total number of students outside the room.

This is one of the guiding principles that allows us to understand chemical equilibrium. It is discussed further in Chapter 17.

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 13.9, Properties of Liquids (2): Vapor Pressure; this screen contains an animation of the vaporization process.

As long as some liquid remains in contact with the vapor, the pressure does not depend on the volume or surface area of the liquid.

A molecule in the vapor may strike the liquid surface and be captured there. This process, the reverse of evaporation, is called **condensation**. As evaporation occurs in a closed container, the volume of liquid decreases and the number of gas molecules above the surface increases. Because more gas phase molecules can collide with the surface, the rate of condensation increases. The system composed of the liquid and gas molecules of the same substance eventually achieves a **dynamic equilibrium** in which the rate of evaporation equals the rate of condensation in the closed container.



The two opposing rates are not zero, but are equal to each other—hence we call this “dynamic,” rather than “static,” equilibrium. Even though evaporation and condensation are both continuously occurring, *no net change occurs* because the rates are equal.

However, if the vessel were left open to the air, this equilibrium could not be reached. Molecules would diffuse away, and slight air currents would also sweep some gas molecules away from the liquid surface. This would allow more evaporation to occur to replace the lost vapor molecules. Consequently, a liquid can eventually evaporate entirely if it is left uncovered. This situation illustrates **LeChatelier’s Principle**:

A system at equilibrium, or changing toward equilibrium, responds in the way that tends to relieve or “undo” any stress placed on it.

In this example the stress is the removal of molecules in the vapor phase. The response is the continued evaporation of the liquid.

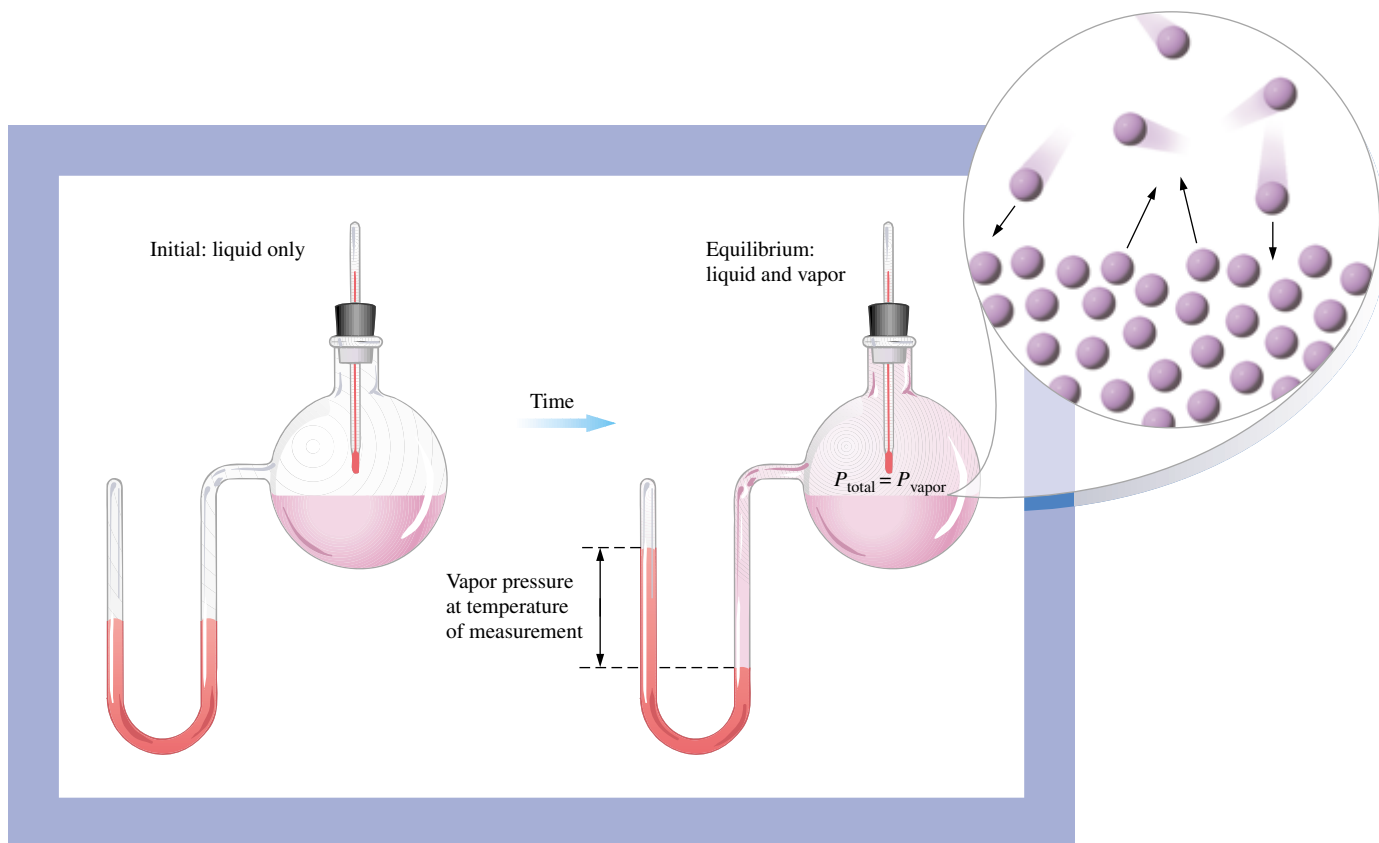
13-7 VAPOR PRESSURE

Vapor molecules cannot escape when vaporization of a liquid occurs in a closed container. As more molecules leave the liquid, more gaseous molecules collide with the walls of the container, with one another, and with the liquid surface, so more condensation occurs. This is responsible for the formation of liquid droplets that adhere to the sides of the vessel above a liquid surface and for the eventual establishment of equilibrium between liquid and vapor (see Figure 13-10b and c).

The partial pressure of vapor molecules above the surface of a liquid at equilibrium at a given temperature is the **vapor pressure (vp)** of the liquid at that temperature. Because the rate of evaporation increases with increasing temperature, vapor pressures of liquids *always* increase as temperature increases.

TABLE 13-4 Vapor Pressures (in torr) of Some Liquids

	0°C	25°C	50°C	75°C	100°C	125°C
water	4.6	23.8	92.5	300	760	1741
benzene	27.1	94.4	271	644	1360	
methyl alcohol	29.7	122	404	1126		
diethyl ether	185	470	1325	2680	4859	



Easily vaporized liquids are called **volatile** liquids, and they have relatively high vapor pressures. The most volatile liquid in Table 13-4 is diethyl ether. Water is the least volatile. Vapor pressures can be measured with manometers (Figure 13-12).

Stronger cohesive forces tend to hold molecules in the liquid state. Methyl alcohol molecules are strongly linked by hydrogen bonding, whereas diethyl ether molecules are not, so methyl alcohol has a lower vapor pressure than diethyl ether. The very strong hydrogen bonding in water accounts for its unusually low vapor pressure (see Table 13-4). Dispersion forces generally increase with increasing molecular size, so substances composed of larger molecules have lower vapor pressures.

Figure 13-12 A representation of the measurement of vapor pressure of a liquid at a given temperature. The container is evacuated before the liquid is added. At the instant the liquid is added to the container, there are no molecules in the gas phase so the pressure is zero. Some of the liquid then vaporizes until equilibrium is established. The difference in heights of the mercury column is a measure of the vapor pressure of the liquid at that temperature.

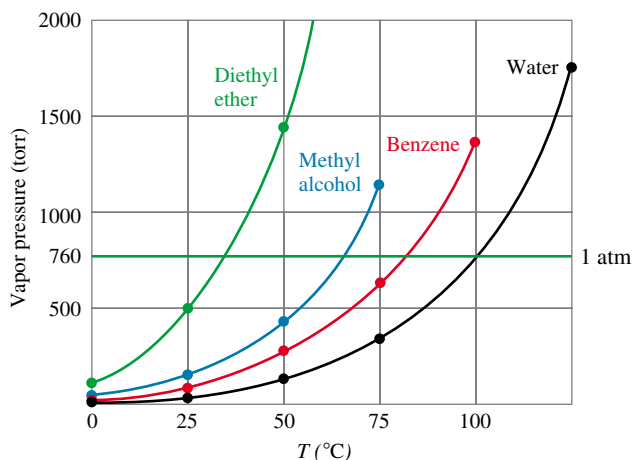
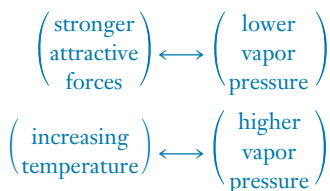


Figure 13-13 Plots of the vapor pressures of the liquids in Table 13-4. The *normal* boiling point of a liquid is the temperature at which its vapor pressure is equal to one atmosphere. Normal boiling points are: water, 100°C; benzene, 80.1°C; methyl alcohol, 65.0°C; and diethyl ether, 34.6°C. Notice that the increase in vapor pressure is *not* linear with temperature.



See the *Saunders Interactive General Chemistry CD-ROM*,

Screen 13.10, Properties of Liquids (3): Boiling Point.

As water is being heated, but before it boils, small bubbles may appear in the container. This is not boiling, but rather the formation of bubbles of dissolved gases such as CO_2 and O_2 whose solubilities in water decrease with increasing temperature.



Figure 13-14 A laboratory setup for distillation. During distillation of an impure liquid, nonvolatile substances remain in the distilling flask. The liquid is vaporized and condensed before being collected in the receiving flask. If any of the substances are flammable, using an open flame would be dangerous; in such a case, another source of heat, such as an electric heater, should be used.

We can understand the order of vapor pressures of the four liquids cited in Table 13-4 and Figure 13-13 by considering the strengths of their intermolecular attractions. Water has the lowest vapor pressure (strongest cohesive forces) because each molecule has two hydrogen atoms to act as hydrogen-bond donors and each molecule can accept hydrogen bonds from two other molecules. Methyl alcohol has only one potential hydrogen-bond donor, so its average cohesive forces are weaker than those in water and its vapor pressure is higher. In benzene and diethyl ether, the hydrogen atoms are all bonded to carbon, so strong hydrogen bonds are not possible. Electrons can move easily throughout the delocalized π -bonding orbitals of benzene, however, so benzene is quite polarizable and exhibits significant dispersion forces. In addition, the hydrogen atoms of benzene are more positive than most hydrogens that are bonded to carbon. The H atoms of benzene are attracted to the electron-rich π -bonding regions of nearby molecules. The accumulation of these forces gives benzene rather strong cohesive forces, resulting in a lower vapor pressure than we might expect for a hydrocarbon. The diethyl ether molecule is only slightly polar, resulting in weak dipole–dipole forces and a high vapor pressure.

13-8 BOILING POINTS AND DISTILLATION

When heat energy is added to a liquid, it increases the kinetic energy of the molecules, and the temperature of the liquid increases. Heating a liquid always increases its vapor pressure. When a liquid is heated to a sufficiently high temperature under a given applied (usually atmospheric) pressure, bubbles of vapor begin to form below the surface. If the vapor pressure inside the bubbles is less than the applied pressure on the surface of the liquid, the bubbles collapse as soon as they form. If the temperature is raised sufficiently, the vapor pressure is high enough that the bubbles can persist, rise to the surface, and burst, releasing the vapor into the air. This process is called *boiling* and is different from evaporation. The **boiling point** of a liquid is the temperature at which its vapor pressure equals the external pressure. The **normal boiling point** is the temperature at which the vapor pressure of a liquid is equal to exactly one atmosphere (760 torr). The vapor pressure of water is 760 torr at 100°C , its normal boiling point. As heat energy is added to a pure liquid *at its boiling point*, the temperature remains constant, because the energy is used to overcome the cohesive forces in the liquid to form vapor.

If the applied pressure is lower than 760 torr, say on the top of a mountain, water boils below 100°C . The chemical reactions involved in cooking food occur more slowly at the lower temperature, so it takes longer to cook food in boiling water at high altitudes than at sea level. A pressure cooker cooks food rapidly because water boils at higher temperatures under increased pressures. The higher temperature of the boiling water increases the rate of cooking.

Different liquids have different cohesive forces, so they have different vapor pressures and boil at different temperatures. A mixture of liquids with sufficiently different boiling points can often be separated into its components by **distillation**. In this process the mixture is heated slowly until the temperature reaches the point at which the most volatile liquid boils off. If this component is a liquid under ordinary conditions, it is subsequently recondensed in a water-cooled condensing column (Figure 13-14) and collected as a distillate. After enough heat has been added to vaporize all of the most volatile liquid, the temperature again rises slowly until the boiling point of the next substance is reached, and the process continues. Any nonvolatile substances dissolved in the liquid do not boil, but remain in the distilling flask. Impure water can be purified and separated from its dissolved salts by distillation. Compounds with similar boiling points, especially those that interact

very strongly with one another, are not effectively separated by simple distillation but require a modification called fractional distillation (Section 14-10).

13-9 HEAT TRANSFER INVOLVING LIQUIDS

Heat must be added to a liquid to raise its temperature (Section 1-13). The **specific heat** ($\text{J/g}\cdot^\circ\text{C}$) or **molar heat capacity** ($\text{J/mol}\cdot^\circ\text{C}$) of a liquid is the amount of heat that must be added to the stated mass of liquid to raise its temperature by one degree Celsius. If heat is added to a liquid under constant pressure, the temperature rises until its boiling point is reached. Then the temperature remains constant until enough heat has been added to boil away all the liquid. The **molar heat** (or **enthalpy**) **of vaporization** (ΔH_{vap}) of a liquid is the amount of heat that must be added to one mole of the liquid at its boiling point to convert it to vapor with no change in temperature. Heats of vaporization can also be expressed as energy per gram. For example, the heat of vaporization for water at its boiling point is 40.7 kJ/mol , or $2.26 \times 10^3 \text{ J/g}$.

$$\frac{\text{J}}{\text{g}} = \frac{40.7 \text{ kJ}}{\text{mol}} \times \frac{1000 \text{ J}}{\text{kJ}} \times \frac{1 \text{ mol}}{18.0 \text{ g}} = 2.26 \times 10^3 \text{ J/g}$$

Like many other properties of liquids, heats of vaporization reflect the strengths of intermolecular forces. Heats of vaporization generally increase as boiling points and intermolecular forces increase and as vapor pressures decrease. Table 13-5 illustrates this. The high heats of vaporization of water, ethylene glycol, and ethyl alcohol are due mainly to the strong hydrogen-bonding interactions in these liquids (see Section 13-2). The very high value for water makes it very effective as a coolant and, in the form of steam, as a source of heat.

Liquids can evaporate even below their boiling points. The water in perspiration is an effective coolant for our bodies. Each gram of water that evaporates absorbs 2.41 kJ of heat from the body. We feel even cooler in a breeze because perspiration evaporates faster, so heat is removed more rapidly.

The specific heat and heat capacity of a substance change somewhat with its temperature. For most substances, this variation is small enough to ignore.

Molar heats of vaporization (also called molar *enthalpies* of vaporization) are often expressed in kilojoules rather than joules. The units of heat of vaporization do *not* include temperature. This is because boiling occurs with *no change in temperature*.



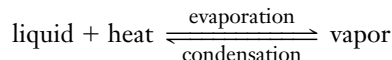
See the *Saunders Interactive General Chemistry CD-ROM*, Screen 13.8, Properties of Liquids (1): Enthalpy of Vaporization.

The heat of vaporization of water is higher at 37°C (normal body temperature) than at 100°C (2.41 kJ/g compared to 2.26 kJ/g).

TABLE 13-5 Heats of Vaporization, Boiling Points, and Vapor Pressures of Some Common Liquids

Liquid	Vapor Pressure (torr at 20°C)	Boiling Point at 1 atm ($^\circ\text{C}$)	Heat of Vaporization at Boiling Point	
			J/g	kJ/mol
water, H_2O	17.5	100.	2260	40.7
ethyl alcohol, $\text{CH}_3\text{CH}_2\text{OH}$	43.9	78.3	855	39.3
benzene, C_6H_6	74.6	80.1	395	30.8
diethyl ether, $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$	442.	34.6	351	26.0
carbon tetrachloride, CCl_4	85.6	76.8	213	32.8
ethylene glycol, $\text{CH}_2\text{OHCH}_2\text{OH}$	0.1	197.3	984	58.9

Condensation is the reverse of evaporation. The amount of heat that must be removed from a vapor to condense it (without change in temperature) is called the **heat of condensation**.



The heat of condensation of a liquid is equal in magnitude to the heat of vaporization. It is released by the vapor during condensation.

Because 2.26 kJ must be absorbed to vaporize one gram of water at 100°C, that same amount of heat must be released to the environment when one gram of steam at 100°C condenses to form liquid water at 100°C. In steam-heated radiators, steam condenses and releases 2.26 kJ of heat per gram as its molecules collide with the cooler radiator walls and condense there. The metallic walls conduct heat well. They transfer the heat to the air in contact with the outside walls of the radiator. The heats of condensation and vaporization of non-hydrogen-bonded liquids, such as benzene, have smaller magnitudes than those of hydrogen-bonded liquids (see Table 13-5). They are therefore much less effective as heating and cooling agents.

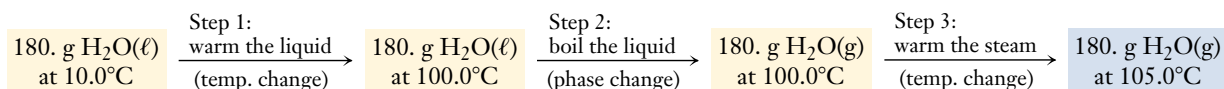
Because of the large amount of heat released by steam as it condenses, burns caused by steam at 100°C are much more severe than burns caused by liquid water at 100°C.

EXAMPLE 13-1 Heat of Vaporization

Calculate the amount of heat, in joules, required to convert 180. grams of water at 10.0°C to steam at 105.0°C.

Plan

The total amount of heat absorbed is the sum of the amounts required to (1) warm the liquid water from 10.0°C to 100.0°C, (2) convert the liquid water to steam at 100.0°C, and (3) warm the steam from 100.0°C to 105.0°C.



Steps 1 and 3 of this example involve warming with *no* phase change. Such calculations were introduced in Section 1-13.

Step 1: Temperature change only

Step 2: Phase change only

Step 3: Temperature change only

Steps 1 and 3 involve the specific heats of water and steam, 4.18 J/g·°C and 2.03 J/g·°C, respectively (Appendix E), whereas step 2 involves the heat of vaporization of water (2.26×10^3 J/g).

Solution

$$1. \quad \underline{\quad} \text{ J} = 180. \text{ g} \times \frac{4.18 \text{ J}}{\text{g} \cdot ^\circ\text{C}} \times (100.0^\circ\text{C} - 10.0^\circ\text{C}) = 6.77 \times 10^4 \text{ J} = 0.677 \times 10^5 \text{ J}$$

$$2. \quad \underline{\quad} \text{ J} = 180. \text{ g} \times \frac{2.26 \times 10^3 \text{ J}}{\text{g}} = 4.07 \times 10^5 \text{ J}$$

$$3. \quad \underline{\quad} \text{ J} = 180. \text{ g} \times \frac{2.03 \text{ J}}{\text{g} \cdot ^\circ\text{C}} \times (105.0^\circ\text{C} - 100.0^\circ\text{C}) = 1.8 \times 10^3 \text{ J} = 0.018 \times 10^5 \text{ J}$$

$$\text{Total amount of heat absorbed} = 4.76 \times 10^5 \text{ J}$$

You should now work Exercises 50 and 51.

Distillation is not an economical way to purify large quantities of water for public water supplies. The high heat of vaporization of water makes it too expensive to vaporize large volumes of water.

✓ **Problem-Solving Tip: Temperature Change or Phase Change?**

A problem such as Example 13-1 can be broken down into steps so that each involves *either* a temperature change *or* a phase change, but not both. A temperature change calculation uses the specific heat of the substance (steps 1 and 3 of Example 13-1); remember that each different phase has its own specific heat. A phase change always takes place with *no change* in temperature, so that calculation does not involve temperature (step 2 of Example 13-1).

EXAMPLE 13-2 Heat of Vaporization

Compare the amount of “cooling” experienced by an individual who drinks 400. mL of ice water (0.0°C) with the amount of “cooling” experienced by an individual who “sweats out” 400. mL of water. Assume that the sweat is essentially pure water and that all of it evaporates. The density of water is very nearly 1.00 g/mL at both 0.0°C and 37.0°C, average body temperature. The heat of vaporization of water is 2.41 kJ/g at 37.0°C.

Plan

In the case of drinking ice water, the body is cooled by the amount of heat required to raise the temperature of 400. mL (400. g) of water from 0.0°C to 37.0°C. The amount of heat lost by perspiration is equal to the amount of heat required to vaporize 400. g of water at 37.0°C.

Solution

Raising the temperature of 400. g of water from 0.0°C to 37.0°C requires

$$\underline{?} \text{ J} = (400. \text{ g})(4.18 \text{ J/g}\cdot^\circ\text{C})(37.0^\circ\text{C}) = 6.19 \times 10^4 \text{ J, or } \mathbf{61.9 \text{ kJ}}$$

Evaporating (i.e., “sweating out”) 400. mL of water at 37°C requires

$$\underline{?} \text{ J} = (400. \text{ g})(2.41 \times 10^3 \text{ J/g}) = 9.64 \times 10^5 \text{ J, or } \mathbf{964 \text{ kJ}}$$

Thus, we see that “sweating out” 400. mL of water removes 964 kJ of heat from one’s body, whereas drinking 400. mL of ice water cools it by only 61.9 kJ. Stated differently, sweating removes $(964/61.9) = 15.6$ times more heat than drinking ice water!

You should now work Exercise 55.



For health reasons, it is important to replace the water lost by perspiration.

The Clausius–Clapeyron Equation

We have seen (Figure 13-13) that vapor pressure increases with increasing temperature. Let us now discuss the quantitative expression of this relationship.

When the temperature of a liquid is changed from T_1 to T_2 , the vapor pressure of the liquid changes from P_1 to P_2 . These changes are related to the molar heat of vaporization, ΔH_{vap} , for the liquid by the **Clausius–Clapeyron equation**.

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

Although ΔH_{vap} changes somewhat with temperature, it is usually adequate to use the value tabulated at the normal boiling point of the liquid (Appendix E) unless more precise values are available. The units of R must be consistent with those of ΔH_{vap} .



The Clausius–Clapeyron equation is used for three types of calculations: (1) to predict the vapor pressure of a liquid at a specified temperature, as in Example 13-3; (2) to determine the temperature at which a liquid has a specified vapor pressure; and (3) to calculate ΔH_{vap} from measurement of vapor pressures at different temperatures.

*(Enrichment, continued)***EXAMPLE 13-3** *Vapor Pressure Versus Temperature*

The normal boiling point of ethanol, $\text{C}_2\text{H}_5\text{OH}$, is 78.3°C , and its molar heat of vaporization is 39.3 kJ/mol (Appendix E). What would be the vapor pressure, in torr, of ethanol at 50.0°C ?

Plan

The normal boiling point of a liquid is the temperature at which its vapor pressure is 760 torr, so we designate this as one of the conditions (subscript 1). We wish to find the vapor pressure at another temperature (subscript 2), and we know the molar heat of vaporization. We use the Clausius–Clapeyron equation to solve for P_2 .

Solution

$$\begin{aligned} P_1 &= 760 \text{ torr} & \text{at} & \quad T_1 = 78.3^\circ\text{C} + 273.2 = 351.5 \text{ K} \\ P_2 &= ? & \text{at} & \quad T_2 = 50.0^\circ\text{C} + 273.2 = 323.2 \text{ K} \\ \Delta H_{\text{vap}} &= 39.3 \text{ kJ/mol} & \text{or} & \quad 3.93 \times 10^4 \text{ J/mol} \end{aligned}$$

We solve for P_2 .

$$\ln\left(\frac{P_2}{760 \text{ torr}}\right) = \frac{3.93 \times 10^4 \text{ J/mol}}{\left(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)} \left(\frac{1}{351.5 \text{ K}} - \frac{1}{323.2 \text{ K}}\right)$$

$$\ln\left(\frac{P_2}{760 \text{ torr}}\right) = -1.18 \quad \text{so} \quad \left(\frac{P_2}{760 \text{ torr}}\right) = e^{-1.18} = 0.307$$

$$P_2 = 0.307(760 \text{ torr}) = \boxed{233 \text{ torr}} \quad (\text{lower vapor pressure at lower temperature})$$

You should now work Exercise 58.

TABLE 13-6 *General Effects of Intermolecular Attractions on Physical Properties of Liquids*

Property	Volatile Liquids (weak intermolecular attractions)	Nonvolatile Liquids (strong intermolecular attractions)
cohesive forces	low	high
viscosity	low	high
surface tension	low	high
specific heat	low	high
vapor pressure	high	low
rate of evaporation	high	low
boiling point	low	high
heat of vaporization	low	high

We have described many properties of liquids and discussed how they depend on intermolecular forces of attraction. The general effects of these attractions on the physical properties of liquids are summarized in Table 13-6. “High” and “low” are relative terms. Table 13-6 is intended to show only very general trends. Example 13-4 illustrates the use of intermolecular attractions to predict boiling points.

EXAMPLE 13-4 Boiling Points Versus Intermolecular Forces

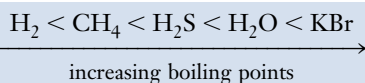
Predict the order of increasing boiling points for the following: H_2S ; H_2O ; CH_4 ; H_2 ; KBr .

Plan

We analyze the polarity and size of each substance to determine the kinds of intermolecular forces that are present. In general, the stronger the intermolecular forces, the higher is the boiling point of the substance.

Solution

KBr is ionic, so it boils at the highest temperature. Water exhibits hydrogen bonding and boils at the next highest temperature. Hydrogen sulfide is the only other polar covalent substance in the list, so it boils below H_2O but above the other two substances. Both CH_4 and H_2 are nonpolar. The larger CH_4 molecule is more easily polarized than the very small H_2 molecule, so dispersion forces are stronger in CH_4 . Thus, CH_4 boils at a higher temperature than H_2 .

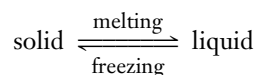


You should now work Exercise 24.

THE SOLID STATE

13-10 MELTING POINT

The **melting point (freezing point)** of a substance is the temperature at which its solid and liquid phases coexist in equilibrium.



The *melting point* of a solid is the same as the *freezing point* of its liquid. It is the temperature at which the rate of melting of a solid is the same as the rate of freezing of its liquid under a given applied pressure.

The **normal melting point** of a substance is its melting point at one atmosphere pressure. Changes in pressure have very small effects on melting points; they have large effects on boiling points.

13-11 HEAT TRANSFER INVOLVING SOLIDS

When heat is added to a solid below its melting point, its temperature rises. After enough heat has been added to bring the solid to its melting point, additional heat is required to convert the solid to liquid. During this melting process, the temperature remains constant

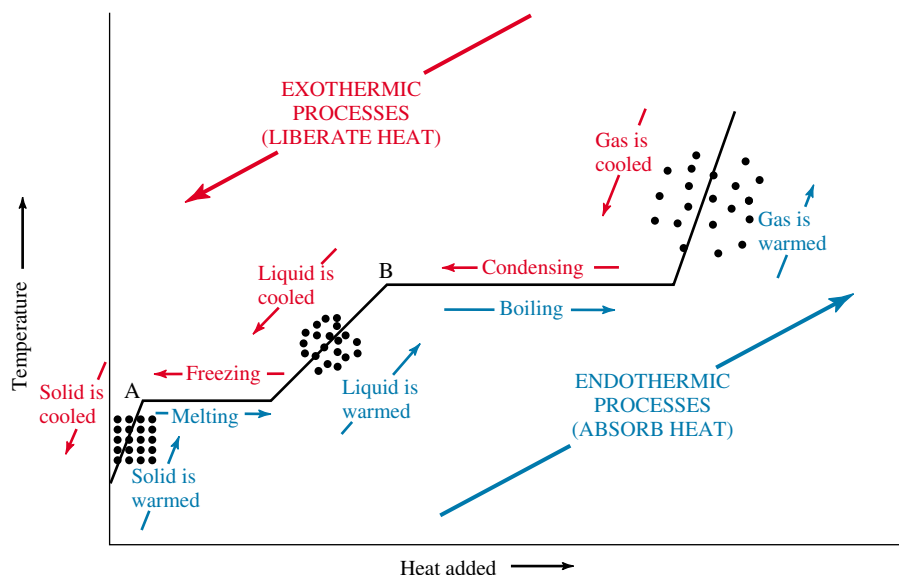


Figure 13-15 A typical heating curve at constant pressure. When heat energy is added to a solid below its melting point, the temperature of the solid rises until its melting point is reached (point A). In this region of the plot, the slope is rather steep because of the low specific heats of solids [e.g., 2.09 J/g·°C for H₂O(s)]. If the solid is heated at its melting point (A), its temperature remains constant until the solid has melted, because the melting process requires energy. The length of this horizontal line is proportional to the heat of fusion of the substance—the higher the heat of fusion, the longer the line. When all of the solid has melted, heating the liquid raises its temperature until its boiling point is reached (point B). The slope of this line is less steep than that for warming the solid, because the specific heat of the liquid phase [e.g., 4.18 J/g·°C for H₂O(l)] is usually greater than that of the corresponding solid. If heat is added to the liquid at its boiling point (B), the added heat energy is absorbed as the liquid boils. This horizontal line is longer than the previous one, because the heat of vaporization of a substance is always higher than its heat of fusion. When all of the liquid has been converted to a gas (vapor), the addition of more heat raises the temperature of the gas. This segment of the plot has a steep slope because of the relatively low specific heat of the gas phase [e.g., 2.03 J/g·°C for H₂O(g)]. Each step in the process can be reversed by removing the same amount of heat.

at the melting point until all of the substance has melted. After melting is complete, the continued addition of heat results in an increase in the temperature of the liquid, until the boiling point is reached. This is illustrated graphically in the first three segments of the heating curve in Figure 13-15.

The **molar heat (or enthalpy) of fusion** (ΔH_{fus} ; kJ/mol) is the amount of heat required to melt one mole of a solid at its melting point. Heats of fusion can also be expressed on a per gram basis. The heat of fusion depends on the *intermolecular* forces of attraction in the solid state. These forces “hold the molecules together” as a solid. Heats of fusion are *usually* higher for substances with higher melting points. Values for some common compounds are shown in Table 13-7. Appendix E has more values.

The **heat (or enthalpy) of solidification** of a liquid is equal in magnitude to the heat of fusion. It represents removal of a sufficient amount of heat from a given amount (1 mol or 1 g) of liquid to solidify the liquid at its freezing point. For water,

Melting is always endothermic. The term “fusion” means “melting.”

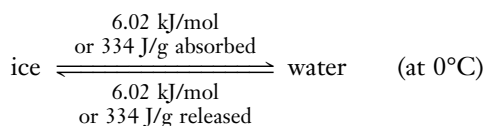


TABLE 13-7 Some Melting Points and Heats of Fusion

Substance	Melting Point (°C)	Heat of Fusion	
		J/g	kJ/mol
methane, CH ₄	-182	58.6	0.92
ethyl alcohol, CH ₃ CH ₂ OH	-117	109	5.02
water, H ₂ O	0	334	6.02
naphthalene, C ₁₀ H ₈	80.2	147	18.8
silver nitrate, AgNO ₃	209	67.8	11.5
aluminum, Al	658	395	10.6
sodium chloride, NaCl	801	519	30.3

EXAMPLE 13-5 Heat of Fusion

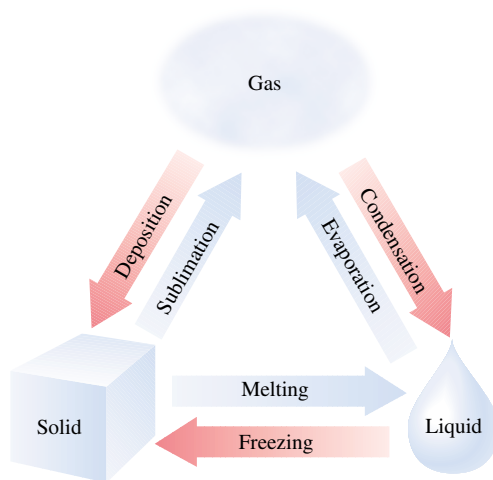
The molar heat of fusion, ΔH_{fus} , of Na is 2.6 kJ/mol at its melting point, 97.5°C. How much heat must be absorbed by 5.0 g of solid Na at 97.5°C to melt it?

Plan

Melting takes place at a constant temperature. The molar heat of fusion tells us that every mole of Na, 23 grams, absorbs 2.6 kJ of heat at 97.5°C during the melting process. We want to know the amount of heat that 5.0 grams would absorb. We use the appropriate unit factors, constructed from the atomic weight and ΔH_{fus} , to find the amount of heat absorbed.

Solution

$$\underline{?} \text{ kJ} = 5.0 \text{ g Na} \times \frac{1 \text{ mol Na}}{23 \text{ g Na}} \times \frac{2.6 \text{ kJ}}{1 \text{ mol Na}} = \boxed{0.57 \text{ kJ}}$$



Transitions among the three states of matter. The transitions shown in blue are endothermic (absorb heat); those shown in red are exothermic (release heat).

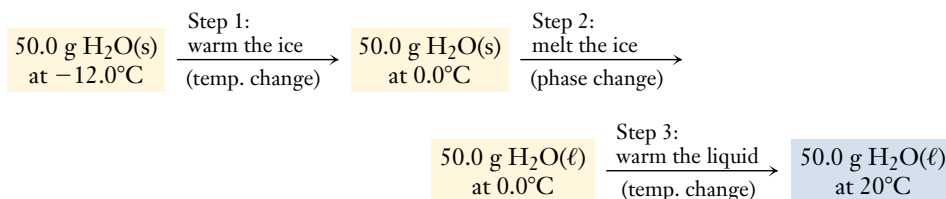
Ice is very efficient for cooling because considerable heat is required to melt a given mass of it. However, ΔH_{vap} is generally much greater than ΔH_{fusion} , so evaporative cooling is preferable when possible.

EXAMPLE 13-6 Heat of Fusion

Calculate the amount of heat that must be absorbed by 50.0 grams of ice at -12.0°C to convert it to water at 20.0°C . Refer to Appendix E.

Plan

We must determine the amount of heat absorbed during three steps: (1) warming 50.0 g of ice from -12.0°C to its melting point, 0.0°C (we use the specific heat of ice, $2.09 \text{ J/g}\cdot^\circ\text{C}$); (2) melting the ice with no change in temperature (we use the heat of fusion of ice at 0.0°C , 334 J/g); and (3) warming the resulting liquid from 0.0°C to 20.0°C (we use the specific heat of water, $4.18 \text{ J/g}\cdot^\circ\text{C}$).



Solution

$$\begin{aligned}
 1. \quad & 50.0 \text{ g} \times \frac{2.09 \text{ J}}{\text{g}\cdot^\circ\text{C}} \times [0.0 - (-12.0)]^\circ\text{C} = 1.25 \times 10^3 \text{ J} = 0.125 \times 10^4 \text{ J} \\
 2. \quad & 50.0 \text{ g} \times \frac{334 \text{ J}}{\text{g}} = 1.67 \times 10^4 \text{ J} \\
 3. \quad & 50.0 \text{ g} \times \frac{4.18 \text{ J}}{\text{g}\cdot^\circ\text{C}} \times (20.0 - 0.0)^\circ\text{C} = 4.18 \times 10^3 \text{ J} = 0.418 \times 10^4 \text{ J}
 \end{aligned}$$

$$\text{Total amount of heat absorbed} = 2.21 \times 10^4 \text{ J} = 22.1 \text{ kJ}$$

Note that most of the heat was absorbed in step 2, melting the ice.

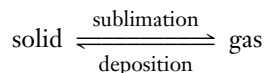
You should now work Exercise 56.



Figure 13-16 Sublimation can be used to purify volatile solids. The high vapor pressure of the solid substance causes it to sublime when heated. Crystals of purified substance are formed when the vapor is deposited to form solid on the cooler (upper) portion of the apparatus. Iodine, I_2 , sublimes readily. I_2 vapor is purple.

13-12 SUBLIMATION AND THE VAPOR PRESSURE OF SOLIDS

Some solids, such as iodine and carbon dioxide, vaporize at atmospheric pressure without passing through the liquid state. This process is known as **sublimation**. Solids exhibit vapor pressures just as liquids do, but they generally have much lower vapor pressures. Solids with high vapor pressures sublime easily. The characteristic odor of a common household solid, *para*-dichlorobenzene (moth repellent), is due to sublimation. The reverse process, by which a vapor solidifies without passing through the liquid phase, is called **deposition**.



Some impure solids can be purified by sublimation and subsequent deposition of the vapor (as a solid) onto a cooler surface. Purification of iodine by sublimation is illustrated in Figure 13-16.

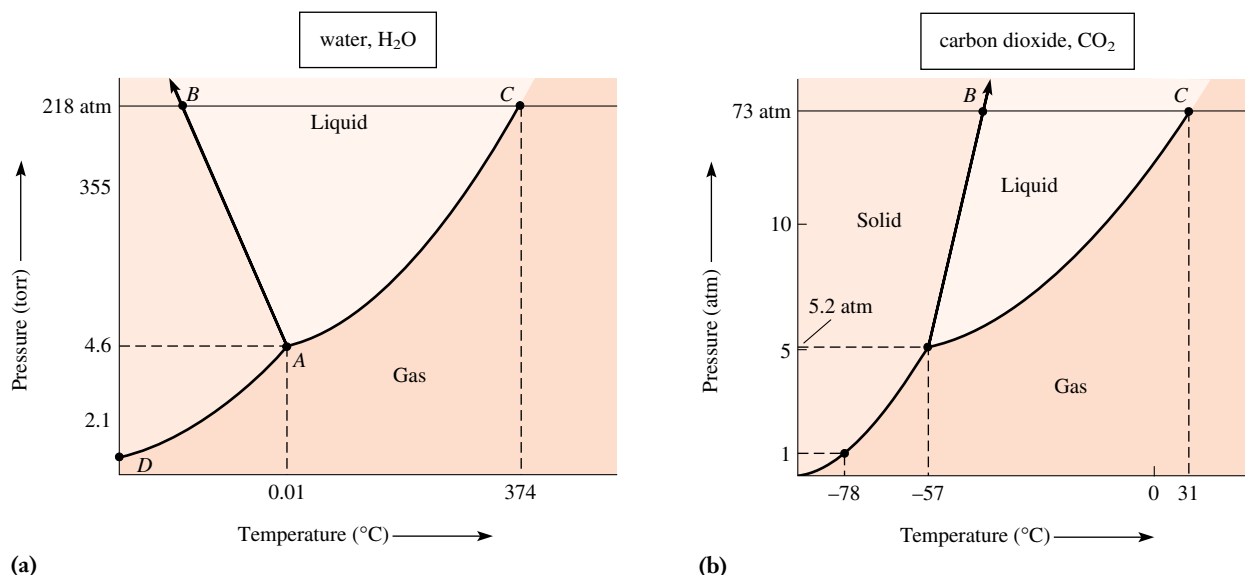


Figure 13-17 Phase diagrams (not to scale). (a) Diagram for water. For water and a few other substances for which the solid is less dense than the liquid, the solid–liquid equilibrium line (AB) has negative slope, that is, up and to the left. (b) Diagram for carbon dioxide, a substance for which the solid is denser than the liquid. Note that the solid–liquid equilibrium line has positive slope, that is, up and to the right. This is true for most substances.

13-13 PHASE DIAGRAMS (P VERSUS T)

We have discussed the general properties of the three phases of matter. Now we can describe **phase diagrams** that show the equilibrium pressure–temperature relationships among the different phases of a given pure substance in a closed system. Our discussion of phase diagrams applies only to *closed systems* (e.g., a sample in a sealed container), in which matter does not escape into the surroundings. This limitation is especially important when the vapor phase is involved. Figure 13-17 shows a portion of the phase diagrams for water and carbon dioxide. The curves are not drawn to scale. The distortion allows us to describe the changes of state over wide ranges of pressure or temperature using one diagram.

The curved line from A to C in Figure 13-17a is a vapor pressure curve obtained experimentally by measuring the vapor pressures of water at various temperatures (Table 13-8). Points along this curve represent the temperature–pressure combinations for which liquid and gas (vapor) coexist in equilibrium. At points above AC , the stable form of water is liquid; below the curve, it is vapor.



 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 13.17, Phase Diagrams.

TABLE 13-8 Points on the Vapor Pressure Curve for Water

temperature ($^{\circ}\text{C}$)	-10	0	20	30	50	70	90	95	100	101
vapor pressure (torr)	2.1	4.6	17.5	31.8	92.5	234	526	634	760	788

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 13.7, The Weird Properties of Water.



Benzene is *denser* as a solid than as a liquid, so the solid sinks in the liquid (*left*). This is the behavior shown by nearly all known substances except water (*right*).

The CO_2 in common fire extinguishers is liquid. As you can see from Figure 13-17b, the liquid must be at some pressure greater than 10 atm for temperatures above 0°C . It is ordinarily at about 65 atm (more than 900 lb/in.²), so these cylinders must be *handled with care*.

Phase diagrams are obtained by combining the results of heating curves measured experimentally at different pressures.



Line AB represents the liquid–solid equilibrium conditions. We see that it has a negative slope. Water is one of the very few substances for which this is the case. The negative slope (up and to the left) indicates that increasing the pressure sufficiently on the surface of ice causes it to melt. This is because ice is *less dense* than liquid water in the vicinity of the liquid–solid equilibrium. The network of hydrogen bonding in ice is more extensive than that in liquid water and requires a greater separation of H_2O molecules. This causes ice to float in liquid water. Almost all other solids are denser than their corresponding liquids; they would have positive slopes associated with line AB . The stable form of water at points to the left of AB is solid (ice). Thus AB is called a *melting curve*.

There is only one point, A , at which all three phases of a substance—solid, liquid, and gas—can coexist at equilibrium. This is called the **triple point**. For water it occurs at 4.6 torr and 0.01°C .

At pressures below the triple-point pressure, the liquid phase does not exist; rather, the substance goes directly from solid to gas (sublimes) or the reverse happens (crystals deposit from the gas). At pressures and temperatures along AD , the *sublimation curve*, solid and vapor are in equilibrium.

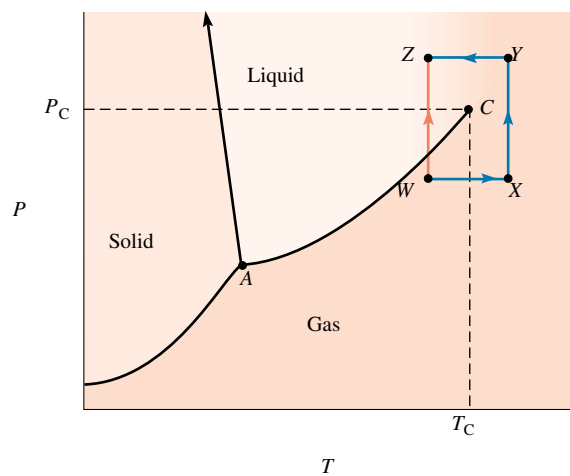
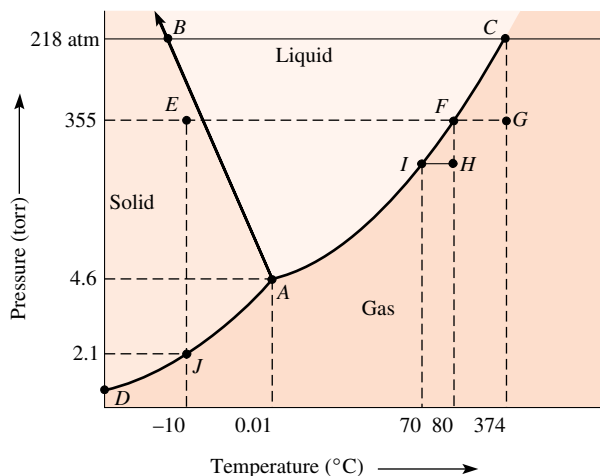
Consider CO_2 (Figure 13-17b). The triple point is at 5.2 atmospheres and -57°C . This pressure is *above* normal atmospheric pressure, so liquid CO_2 cannot exist at atmospheric pressure. Dry ice (solid CO_2) sublimates and does not melt at atmospheric pressure.

The **critical temperature** is the temperature above which a gas cannot be liquefied, that is, the temperature above which the liquid and gas do not exist as distinct phases. A substance at a temperature above its critical temperature is called a *supercritical fluid*. The **critical pressure** is the pressure required to liquefy a gas (vapor) *at* its critical temperature. The combination of critical temperature and critical pressure is called the **critical point** (C in Figure 13-17). For H_2O , the critical point is at 374°C and 218 atmospheres; for CO_2 , it is at 31°C and 73 atmospheres. There is no such upper limit to the solid–liquid line, however, as emphasized by the arrowhead at the top of that line.

To illustrate the use of a phase diagram in determining the physical state or states of a system under different sets of pressures and temperatures, let's consider a sample of water at point E in Figure 13-18a (355 torr and -10°C). At this point all the water is in the form of ice, $\text{H}_2\text{O}(\text{s})$. Suppose that we hold the pressure constant and gradually increase the temperature—in other words, trace a path from left to right along EG . At the temperature at which EG intersects AB , the melting curve, some of the ice melts. If we stopped here, equilibrium between solid and liquid water would eventually be established, and both phases would be present. If we added more heat, all the solid would melt with no temperature change. Remember that all phase changes of pure substances occur at constant temperature.

Once the solid is completely melted, additional heat causes the temperature to rise. Eventually, at point F (355 torr and 80°C), some of the liquid begins to boil; liquid, $\text{H}_2\text{O}(\ell)$, and vapor, $\text{H}_2\text{O}(\text{g})$, are in equilibrium. Adding more heat at constant pressure vaporizes the rest of the water with no temperature change. Adding still more heat warms the vapor (gas) from F to G . Complete vaporization would also occur if, at point F and before all the liquid had vaporized, the temperature were held constant and the pressure were

Camphor, which is used in inhalers, has a high vapor pressure. When stored in a bottle, camphor sublimates and then deposits elsewhere in the bottle.



(a)

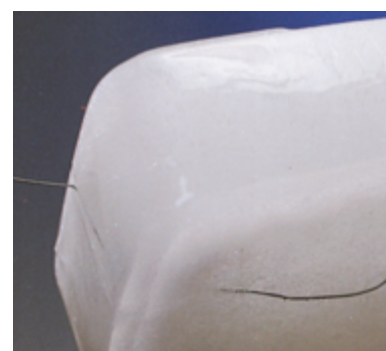
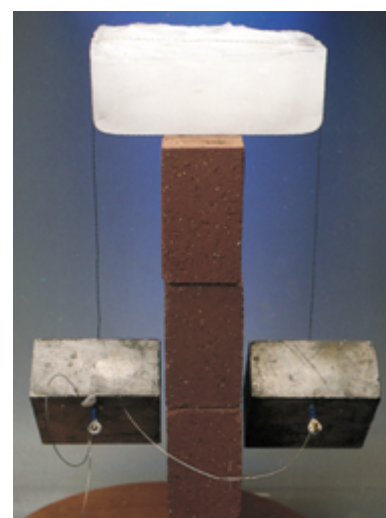
(b)

Figure 13-18 Some interpretations of phase diagrams. (a) The phase diagram of water. Phase relationships at various points in this diagram are described in the text. (b) Two paths by which a gas can be liquefied. (1) Below the critical temperature. Compressing the sample at *constant* temperature is represented by the vertical line WZ . Where this line crosses the vapor pressure curve AC , the gas liquefies; at that set of conditions, *two distinct phases*, gas and liquid, are present in equilibrium with each other. These two phases have different properties, for example, different densities. Raising the pressure further results in a completely liquid sample at point Z . (2) Above the critical temperature. Suppose that we instead first warm the gas at constant pressure from W to X , a temperature above its critical temperature. Then, holding the temperature constant, we increase the pressure to point Y . Along this path, the sample increases *smoothly* in density, with no sharp transition between phases. From Y , we then decrease the temperature to reach final point Z , where the sample is clearly a liquid.

decreased to, say, 234 torr at point H . If we wished to hold the pressure at 234 torr and condense some of the vapor, it would be necessary to cool the vapor to 70°C , point I , which lies on the vapor pressure curve, AC . To state this in another way, the vapor pressure of water at 70°C is 234 torr.

Suppose we move back to solid at point E (355 torr and -10°C). If we now hold the temperature at -10°C and reduce the pressure, we move vertically down along EJ . At a pressure of 2.1 torr we reach the sublimation curve, at which point the solid passes directly into the gas phase (sublimes) until all the ice has sublimed. An important application of this phenomenon is in the freeze-drying of foods. In this process a water-containing food is cooled below the freezing point of water to form ice, which is then removed as a vapor by decreasing the pressure.

Let us clarify the nature of the fluid phases (liquid and gas) and of the critical point by describing two different ways that a gas can be liquefied. A sample at point W in the phase diagram of Figure 13-18b is in the vapor (gas) phase, below its critical temperature. Suppose we compress the sample at constant T from point W to point Z . We can identify a definite pressure (the intersection of line WZ with the vapor pressure curve AC) where the transition from gas to liquid takes place. If we go *around* the critical point by the path $WXYZ$, however, no such clear-cut transition takes place. By this second path, the density and other properties of the sample vary in a continuous manner; there is no definite point at which we can say that the sample changes from gas to liquid.



A weighted wire cuts through a block of ice. The ice melts under the high pressure of the wire, and then refreezes behind the wire.

A fluid *below* its critical temperature may properly be identified as a liquid or as a gas. *Above* the critical temperature, we should use the term “fluid.”



The regular external shape of a crystal is the result of regular internal arrangements of atoms, molecules, or ions. Crystals of the ionic solid sodium chloride, NaCl, from a kitchen saltshaker have the same shape as the large crystal shown here.

See the *Saunders Interactive General Chemistry CD-ROM*, Screen 13.12, Solid Structures (1): Crystalline and Amorphous Solids.

One test for the purity of a crystalline solid is the sharpness of its melting point. Impurities disrupt the intermolecular forces and cause melting to occur over a considerable temperature range.

The lattice planes are planes within the crystal containing ordered arrangements of particles.

13-14 AMORPHOUS SOLIDS AND CRYSTALLINE SOLIDS

We have already seen that solids have definite shapes and volumes, are not very compressible, are dense, and diffuse only very slowly into other solids. They are generally characterized by compact, ordered arrangements of particles that vibrate about fixed positions in their structures.

Some noncrystalline solids, called **amorphous solids**, have no well-defined, ordered structure. Examples include rubber, some kinds of plastics, and amorphous sulfur.

Some amorphous solids are called glasses because, like liquids, they flow, although *very* slowly. The irregular structures of glasses are intermediate between those of freely flowing liquids and those of crystalline solids; there is only short-range order. Crystalline solids such as ice and sodium chloride have well-defined, sharp melting temperatures. Particles in amorphous solids are irregularly arranged, so intermolecular forces among their particles vary in strength within a sample. Melting occurs at different temperatures for various portions of the same sample as the intermolecular forces are overcome. Unlike crystalline solids, glasses and other amorphous solids do not exhibit sharp melting points, but soften over a temperature range.

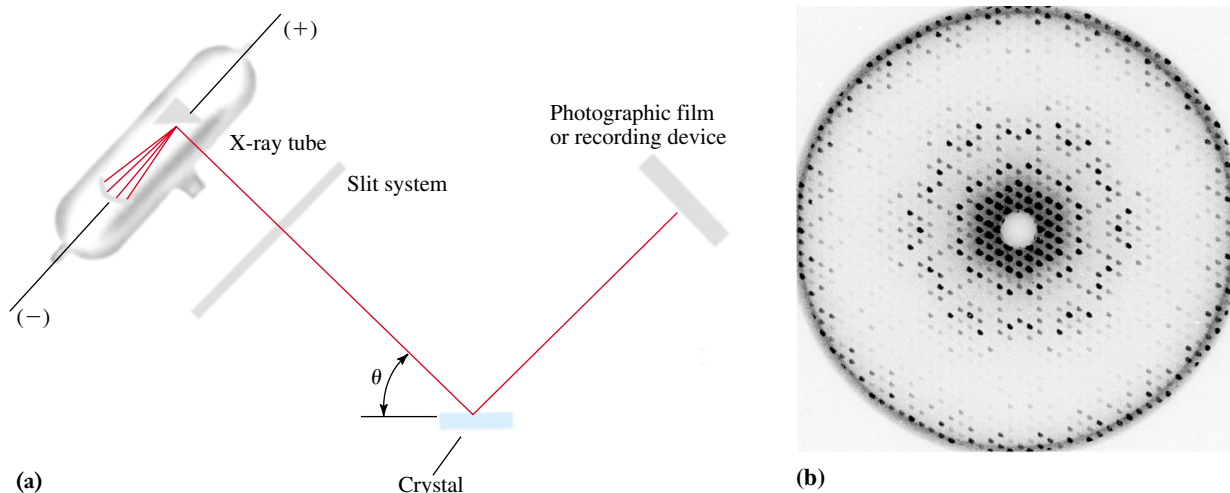
The shattering of a crystalline solid produces fragments having the same (or related) interfacial angles and structural characteristics as the original sample. The shattering of a cube of rock salt produces several smaller cubes of rock salt. This cleaving occurs preferentially along crystal lattice planes between which the interionic or intermolecular forces of attraction are weakest. Amorphous solids with irregular structures, such as glasses, shatter irregularly to yield pieces with curved edges and irregular angles.

Enrichment

X-Ray Diffraction

Atoms, molecules, and ions are much too small to be seen with the eye. The arrangements of particles in crystalline solids are determined indirectly by X-ray diffraction (scattering). In 1912, the German physicist Max von Laue (1879–1960) showed that any crystal could serve as a three-dimensional diffraction grating for incident electromagnetic radiation with wavelengths approximating the internuclear separations of atoms in the crystal. Such radiation is in the X-ray region of the electromagnetic spectrum. Using an apparatus such as that shown in Figure 13-19, a monochromatic (single-wavelength) X-ray beam is defined by a system of slits and directed onto a crystal. The crystal is rotated to vary the angle of incidence θ . At various angles, strong beams of deflected X-rays hit a photographic plate. Upon development, the plate shows a set of symmetrically arranged spots due to deflected X-rays. Different crystals produce different arrangements of spots.

William and Lawrence Bragg are the only father and son to receive the Nobel Prize, which they shared in physics in 1915.



In 1913, the English scientists William (1862–1942) and Lawrence (1890–1971) Bragg found that diffraction photographs are more easily interpreted by considering the crystal as a reflection grating rather than a diffraction grating. The analysis of the spots is somewhat complicated, but an experienced crystallographer can determine the separations between atoms within identical layers and the distances between layers of atoms. The more electrons an atom has, the more strongly it scatters X-rays, so it is also possible to determine the identities of individual atoms using this technique.

Figure 13-20 illustrates the determination of spacings between layers of atoms. The X-ray beam strikes parallel layers of atoms in the crystal at an angle θ . Those rays colliding with atoms in the first layer are reflected at the same angle θ . Those passing through the first layer may be reflected from the second layer, third layer, and so forth. A reflected beam results only if all rays are in phase.

For the waves to be in phase (interact constructively), the difference in path length must be equal to the wavelength, λ , times an integer, n . This leads to the condition known as the **Bragg equation**.

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

It tells us that for X-rays of a given wavelength λ , atoms in planes separated by distances d give rise to reflections at angles of incidence θ . The reflection angles increases with increasing order, $n = 1, 2, 3, \dots$

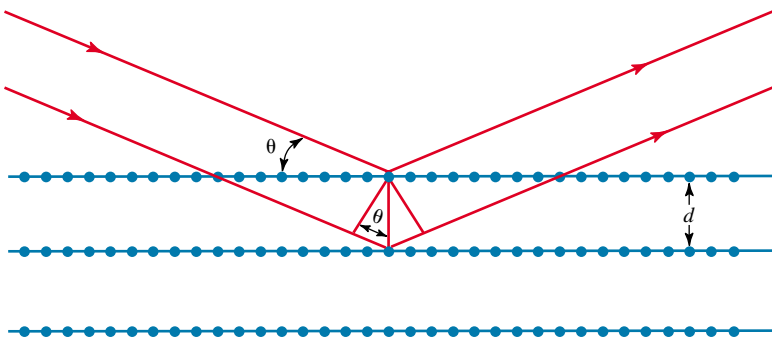
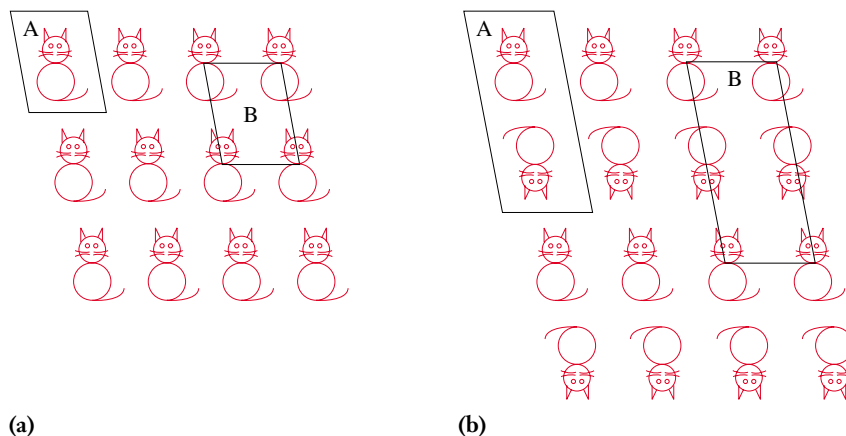


Figure 13-19 (a) X-ray diffraction by crystals (schematic). (b) A photograph of the X-ray diffraction pattern from a crystal of the enzyme histidine decarboxylase (MW \approx 37,000 amu). The crystal was rotated so that many different lattice planes with different spacings were moved in succession into diffracting position (see Figure 13-20).

Figure 13-20 Reflection of a monochromatic beam of X-rays by two lattice planes (layers of atoms) of a crystal.

Figure 13-21 Patterns that repeat in two dimensions. Such patterns might be used to make wallpaper. We must imagine that the pattern extends indefinitely (to the end of the wall). In each pattern two of the many possible choices of unit cells are outlined. Once we identify a unit cell and its contents, repetition by translating this unit generates the entire pattern. In (a) the unit cell contains only one cat. In (b) each cell contains two cats related to one another by a 180° rotation. Any crystal is an analogous pattern in which the contents of the three-dimensional unit cell consist of atoms, molecules, or ions. The pattern extends in *three* dimensions to the boundaries of the crystal, usually including many thousands of unit cells.



13-15 STRUCTURES OF CRYSTALS

All crystals contain regularly repeating arrangements of atoms, molecules, or ions. They are analogous (but in three dimensions) to a wallpaper pattern (Figure 13-21). Once we discover the pattern of a wallpaper, we can repeat it in two dimensions to cover a wall. To describe such a repeating pattern we must specify two things: (1) the size and shape of the repeating unit and (2) the contents of this unit. In the wallpaper pattern of Figure 13-21a, two different choices of the repeating unit are outlined. Repeating unit A contains one complete cat; unit B, with the same area, contains parts of four different cats, but these still add up to one complete cat. From whichever unit we choose, we can obtain the entire pattern by repeatedly translating the contents of that unit in two dimensions.

In a crystal the repeating unit is three-dimensional; its contents consist of atoms, molecules, or ions. The smallest unit of volume of a crystal that shows all the characteristics of the crystal's pattern is a **unit cell**. We note that the unit cell is just the fundamental *box* that describes the arrangement. The unit cell is described by the lengths of its edges— a , b , c (which are related to the spacings between layers, d)—and the angles between the edges— α , β , γ (Figure 13-22). Unit cells are stacked in three dimensions to build a lattice, the three-dimensional *arrangement* corresponding to the crystal. It can be proven that unit cells must fit into one of the seven crystal systems (Table 13-9). Each crystal system is

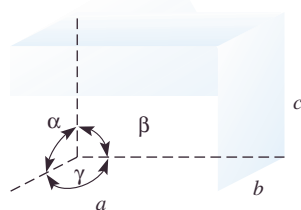


Figure 13-22 A representation of a unit cell.

TABLE 13-9 The Unit Cell Relationships for the Seven Crystal Systems*

System	Unit Cell		Example (common name)
	Lengths	Angles	
cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl (rock salt)
tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	TiO ₂ (rutile)
orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	MgSO ₄ ·7H ₂ O (epsomite)
monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$	CaSO ₄ ·2H ₂ O (gypsum)
triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	K ₂ Cr ₂ O ₇ (potassium dichromate)
hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ; \gamma = 120^\circ$	SiO ₂ (silica)
rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	CaCO ₃ (calcite)

*In these definitions, the sign \neq means "is not necessarily equal to."

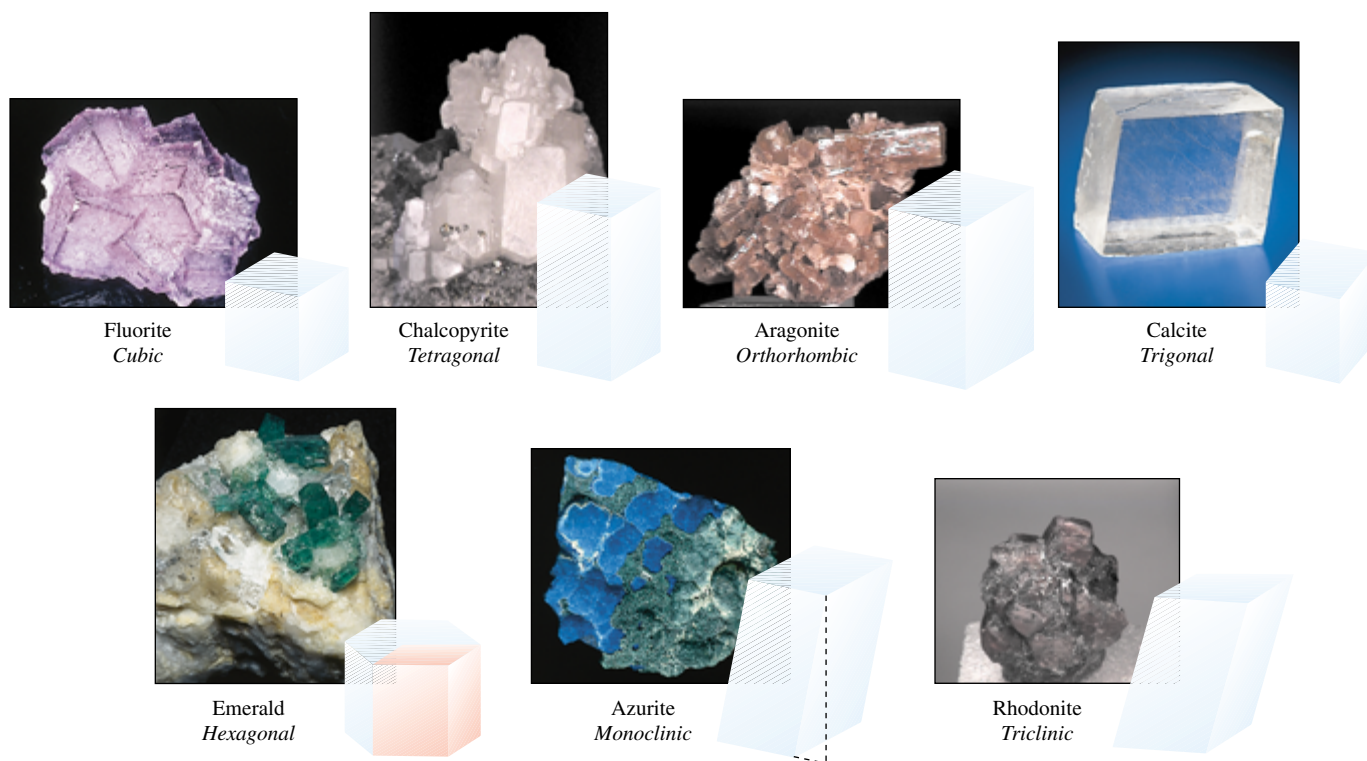


Figure 13-23 Shapes of unit cells for the seven crystal systems and a representative mineral of each system.

distinguished by the relations between the unit cell lengths and angles *and* by the symmetry of the resulting three-dimensional patterns. Crystals have the same symmetry as their constituent unit cells because all crystals are repetitive multiples of such cells.

Let us replace each repeat unit in the crystal by a point (called a *lattice point*) placed at the same place in the unit. All such points have the same environment and are indistinguishable from one another. The resulting three-dimensional array of points is called a **lattice**. It is a simple but complete description of the way in which a crystal structure is built up.

The unit cells shown in Figure 13-23a are the simple, or primitive, unit cells corresponding to the seven crystal systems listed in Table 13-9. Each of these unit cells corresponds to *one* lattice point. As a two-dimensional representation of the reasoning behind this statement, look at the unit cell marked “B” in Figure 13-21a. Each corner of the unit cell is a lattice point, and can be imagined to represent one cat. The cat at each corner is shared among four unit cells (remember—we are working in two dimensions here). The unit cell has four corners, and in the corners of the unit cell are enough pieces to make one complete cat. Thus, unit cell B contains one cat, the same as the alternative unit cell choice marked “A.” Now imagine that each lattice point in a three-dimensional crystal represents an object (a molecule, an atom, and so on). Such an object at a corner (Figure 13-24a) is shared by the eight unit cells that meet at that corner. Each unit cell has eight corners, so it contains eight “pieces” of the object, so it contains $8(\frac{1}{8}) = 1$ object. Similarly, an object on an edge, but not at a corner, is shared by four unit cells (Figure 13-24b), and an object on a face is shared by two unit cells (Figure 13-24c).

Each unit cell contains atoms, molecules, or ions in a definite arrangement. Often the unit cell contents are related by some additional symmetry. (For instance, the unit cell in Figure 13-21b contains *two* cats, related to one another by a rotation of 180° .) Different

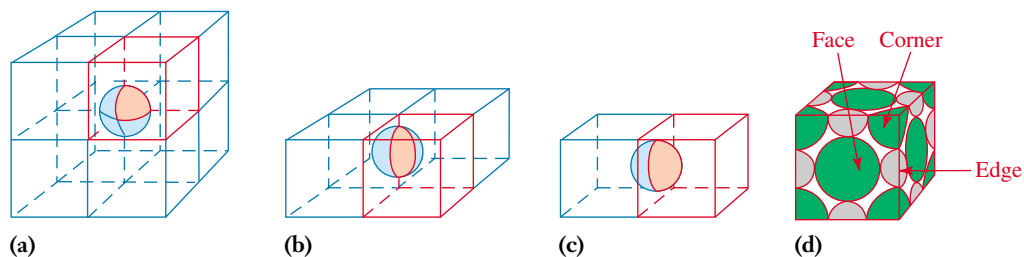


Figure 13-24 Representation of the sharing of an object (an atom, ion, or molecule) among unit cells. The fraction of each sphere that “belongs” to a single unit cell is shown in red. (a) The sharing of an object at a corner by eight unit cells. (b) The sharing of an object on an edge by four unit cells. (c) The sharing of an object in a face by two unit cells. (d) A representation of a unit cell that illustrates the portions of atoms presented in more detail in Figure 13-28. The green ion at each corner is shared by eight unit cells, as in part (a). The gray ion at each edge is shared by four unit cells, as in part (b). The green ion in each face is shared by two unit cells, as in part (c).

substances that crystallize in the same type of lattice with the same atomic arrangement are said to be **isomorphous**. A single substance that can crystallize in more than one arrangement is said to be **polymorphous**.

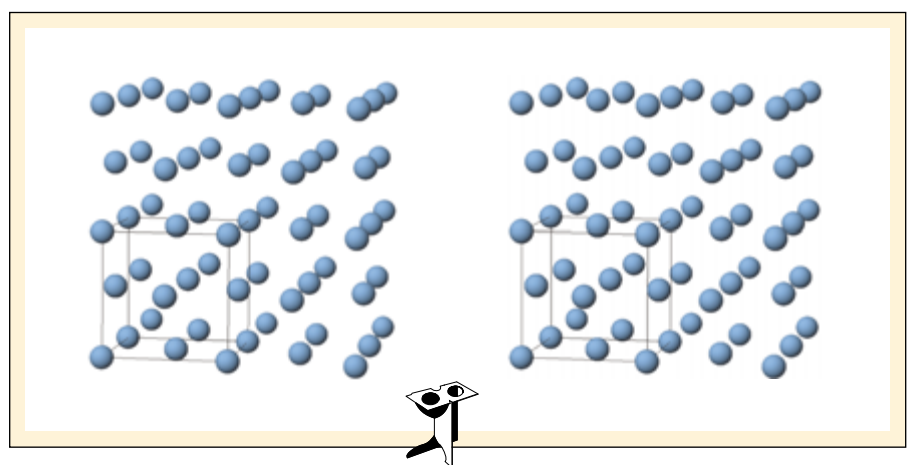
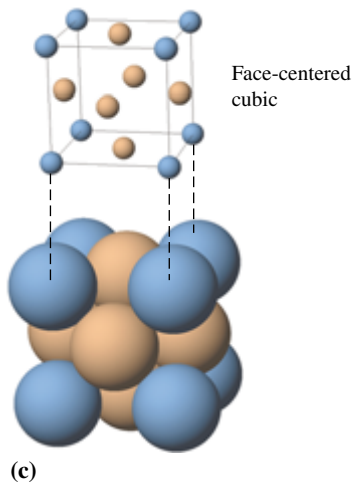
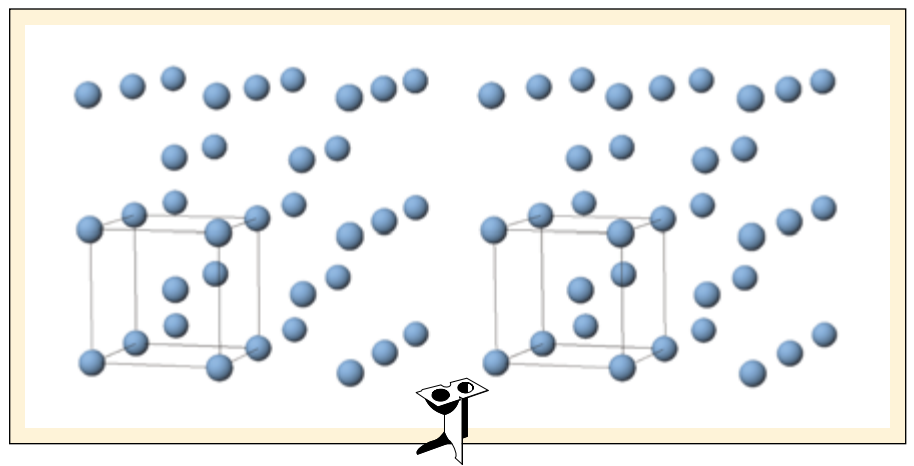
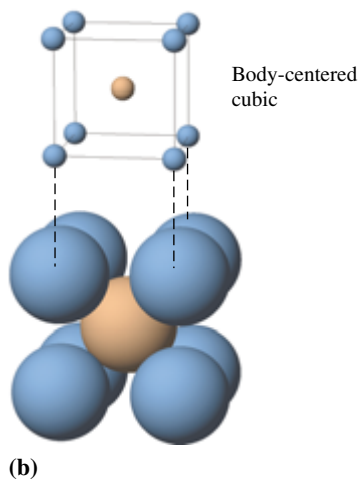
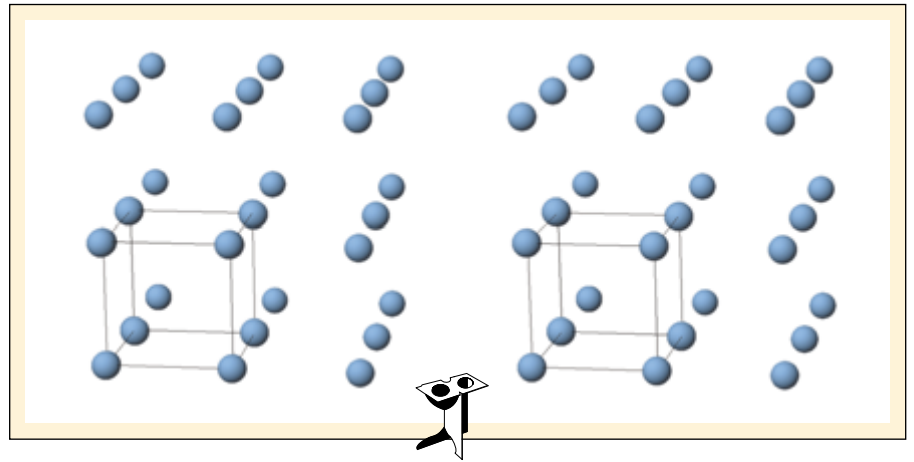
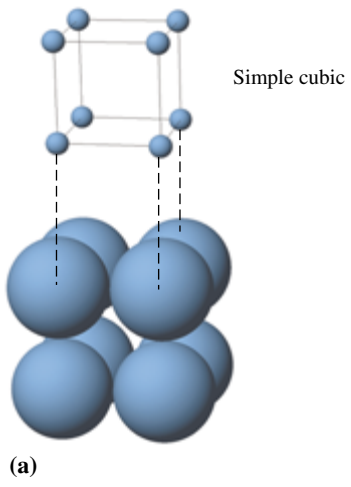
A crystal of one form of manganese metal has Mn atoms at the corners of a simple cubic unit cell that is 6.30° \AA on edge (Example 13-7).

In a *simple*, or *primitive*, lattice, only the eight corners of the unit cell are equivalent. In other types of crystals, objects equivalent to those forming the outline of the unit cell may occupy extra positions within the unit cell. (In this context, “equivalent” means that the same atoms, molecules, or ions appear in *identical environments and orientations* at the eight corners of the cell and, when applicable, at other locations in the unit cell.) This results in additional lattices besides the simple ones in Figure 13-23. Two of these are shown in Figure 13-25b, c. A *body-centered* lattice has equivalent points at the eight unit cell corners *and* at the center of the unit cell (see Figure 13-25). Iron, chromium, and many other metals crystallize in a body-centered cubic (bcc) arrangement. The unit cell of such a metal contains $8(\frac{1}{8}) = 1$ atom at the corners of the cell *plus* one atom at the center of the cell (and therefore entirely in this cell); this makes a total of *two* atoms per unit cell. A *face-centered* structure involves the eight points at the corners and six more equivalent points, one in the middle of each of the six square faces of the cell. A metal (calcium and silver are cubic examples) that crystallizes in this arrangement has $8(\frac{1}{8}) = 1$ atom at the corners *plus* $6(\frac{1}{2}) = 3$ more in the faces, for a total of *four* atoms per unit cell. In more complicated crystals, each lattice site may represent several atoms or an entire molecule.

Each object in a face is shared between two unit cells, so it is counted $\frac{1}{2}$ in each; there are six faces in each unit cell.

We have discussed some simple structures that are easy to visualize. More complex compounds crystallize in structures with unit cells that can be more difficult to describe. Experimental determination of the crystal structures of such solids is correspondingly more complex. Modern computer-controlled instrumentation can collect and analyze the large amounts of X-ray diffraction data used in such studies. This now allows analysis of structures ranging from simple metals to complex biological molecules such as proteins and nucleic acids. Most of our knowledge about the three-dimensional arrangements of atoms depends on crystal structure studies.

► **Figure 13-25** Unit cells for (a) simple cubic, (b) body-centered cubic, and (c) face-centered cubic. The spheres in each figure represent *identical* atoms or ions; different colors are shown *only* to help you visualize the spheres in the center of the cube in body-centered cubic (b) and in face-centered cubic (c) forms.



13-16 BONDING IN SOLIDS

We classify crystalline solids into categories according to the types of particles in the crystal and the bonding or interactions among them. The four categories are (1) metallic solids, (2) ionic solids, (3) molecular solids, and (4) covalent solids. Table 13-10 summarizes these categories of solids and their typical properties.

Metallic Solids

Metals crystallize as solids in which metal ions may be thought to occupy the lattice sites and are embedded in a cloud of delocalized valence electrons. Nearly all metals crystallize in one of three types of lattices: (1) body-centered cubic (bcc), (2) face-centered cubic (fcc; also called cubic close-packed), and (3) hexagonal close-packed. The latter two types are called close-packed structures because the particles (in this case metal atoms) are packed together as closely as possible. The differences between the two close-packed structures are illustrated in Figures 13-26 and 13-27. Let spheres of equal size represent identical metal atoms, or any other particles, that form close-packed structures. Consider a layer of spheres packed in a plane, *A*, as closely as possible (Figure 13-27a). An identical plane of spheres, *B*, is placed in the depressions of plane *A*. If the third plane is placed with its spheres directly above those in plane *A*, the *ABA* arrangement results. This is the hexagonal close-packed structure (Figure 13-27a). The extended pattern of arrangement of planes is *ABABAB* If the third layer is placed in the alternate set of depressions in the second layer so that spheres in the first and third layers are not directly above and below each other, the cubic close-packed structure, *ABCABCABC* . . . , results (Figure 13-27b). In close-packed structures each sphere has a *coordination number* of 12, that is, 12 nearest neighbors. In ideal close-packed structures 74% of a given volume is due to spheres and 26% is empty space. The body-centered cubic structure is less efficient in packing; each sphere has only eight nearest neighbors, and there is more empty space.

The term “coordination number” is used in crystallography in a somewhat different sense from that in coordination chemistry (Section 25-3). Here it refers to the number of nearest neighbors.

	Metallic	Ionic	Molecular	Covalent
Particles of unit cell	Metal ions in “electron cloud”	Anions, cations	Molecules (or atoms)	Atoms
Strongest interparticle forces	Metallic bonds attraction between cations and e^- 's)	Electrostatic	Dispersion, dipole–dipole, and/or hydrogen bonds	Covalent bonds
Properties	Soft to very hard; good thermal and electrical conductors; wide range of melting points (–39 to 3400°C)	Hard; brittle; poor thermal and electrical conductors; high melting points (400 to 3000°C)	Soft; poor thermal and electrical conductors; low melting points (–272 to 400°C)	Very hard; poor thermal and electrical conductors;* high melting points (1200 to 4000°C)
Examples	Li, K, Ca, Cu, Cr, Ni (metals)	NaCl, CaBr ₂ , K ₂ SO ₄ (typical salts)	CH ₄ (methane), P ₄ , O ₂ , Ar, CO ₂ , H ₂ O, S ₈	C (diamond), SiO ₂ (quartz)

*Exceptions: Diamond is a good conductor of heat; graphite is soft and conducts electricity well.

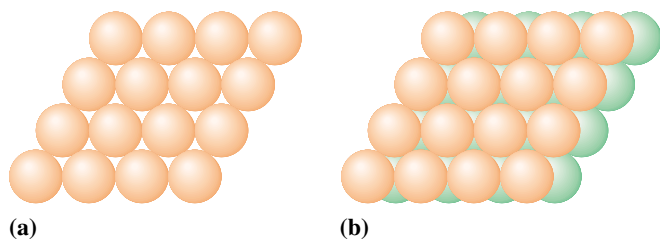


Figure 13-26 (a) Spheres in the same plane, packed as closely as possible. Each sphere touches six others. (b) Spheres in two planes, packed as closely as possible. All spheres represent *identical* atoms or ions; different colors are shown *only* to help you visualize the layers. Real crystals have many more than two planes. Each sphere touches six others in its own layer, three in the layer below it, and three in the layer above it; that is, it contacts a total of 12 other spheres (has a coordination number of 12).

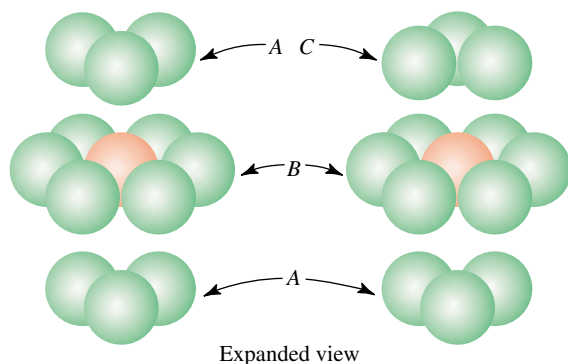
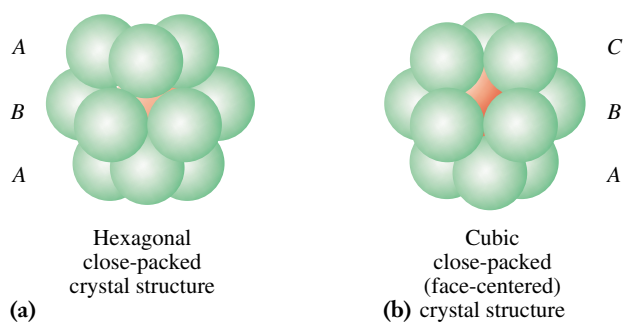


Figure 13-27 There are two crystal structures in which atoms are packed together as compactly as possible. The diagrams show the structures expanded to clarify the difference between them. (a) In the hexagonal close-packed structure, the first and third layers are oriented in the same direction, so that each atom in the third layer (*A*) lies directly above an atom in the first layer (*A*). (b) In the cubic close-packed structure, the first and third layers are oriented in opposite directions, so that no atom in the third layer (*C*) is directly above an atom in either of the first two layers (*A* and *B*). In both cases, every atom is surrounded by 12 other atoms if the structure is extended indefinitely, so each atom has a coordination number of 12. Although it is not obvious from this figure, the cubic close-packed structure is face-centered cubic. To see this, we would have to include additional atoms and tilt the resulting cluster of atoms.



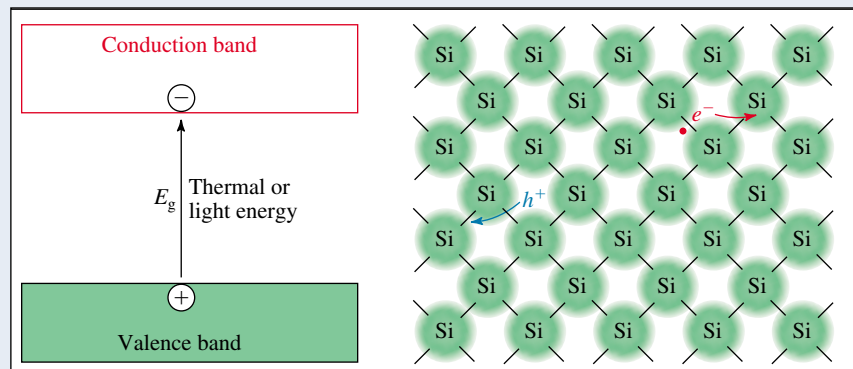
Research & Technology

Semiconductors

A **semiconductor** is an element or a compound with filled bands that are only slightly below, but do not overlap with, empty bands. The difference between an insulator and a semiconductor is only the size of the energy gap, and there is no sharp distinction between them. An **intrinsic** semiconductor (i.e., a semiconductor in its pure form) is a much poorer conductor of electricity than a metal because, for conduction to occur in a semiconductor, electrons must be excited from bonding orbitals in the filled *valence band* into the empty *conduction band*. Figure (a) shows how this happens. An electron that is given an excitation energy greater than or equal to the **band gap** (E_g) enters the conduction band and leaves behind a positively charged **hole** (h^+ , the absence of a bonding electron) in the valence band. Both the electron and the hole reside in *delocalized* orbitals, and both can move in an electric field, much as electrons move in a metal. (Holes migrate when an electron in a nearby orbital moves to fill in the hole, thereby creating a new hole in the nearby orbital.) Electrons and holes move in opposite directions in an electric field.

Silicon, a semiconductor of great importance in electronics, has a band gap of 1.94×10^{-22} kJ, or 1.21 *electron volts* (eV). This is the energy needed to create one electron and one hole or, put another way, the energy needed to break one Si—Si bond. This energy can be supplied either thermally or by using light with a photon energy greater than the band gap. To excite one *mole* of electrons from the valence band to the conduction band, an energy of

$$\frac{6.022 \times 10^{23} \text{ electrons}}{\text{mol}} \times \frac{1.94 \times 10^{-22} \text{ kJ}}{\text{electron}} = 117 \text{ kJ/mol}$$

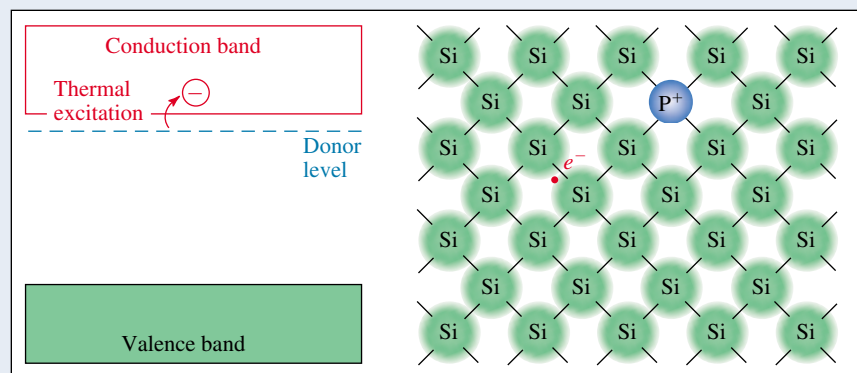


(a) Generation of an electron–hole pair in silicon, an intrinsic semiconductor. The electron (e^-) and hole (h^+) have opposite charges, and so move in opposite directions in an electric field.

is required. For silicon, a large amount of energy is required, so there are very few mobile electrons and holes (about one electron in a trillion—i.e., 1 in 10^{12} —is excited thermally at room temperature); the conductivity of pure silicon is therefore about 10^{11} times lower than that of highly conductive metals such as silver. The number of electrons excited thermally is proportional to $e^{-E_g/2RT}$. Increasing the temperature or decreasing the band gap energy leads to higher conductivity for an intrinsic semiconductor. Insulators such as diamond and silicon dioxide (quartz), which have very large values of E_g , have conductivities 10^{15} to 10^{20} times lower than most metals.

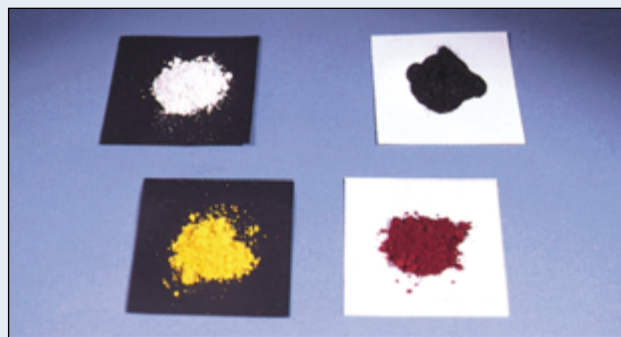
The electrical conductivity of a semiconductor can be greatly increased by **doping** with impurities. For example, silicon, a Group IVA element, can be doped by adding small amounts of a Group VA element, such as phosphorus, or a Group IIIA element, such as boron. Figure (b) shows the effect of substituting phosphorus for silicon in the crystal structure (silicon has the same structure as diamond, Figure 13-31a). There are exactly enough valence band orbitals to accommodate four of the valence electrons from the phosphorus atom. However, a phosphorus atom has one more electron (and one more proton in its nucleus) than does silicon. The fifth electron enters a higher energy orbital that is localized in the lattice near the phosphorus atom; the energy of this orbital, called a **donor level**, is just below the conduction band, within the energy gap. An electron in this orbital can easily become *delocalized* when a small amount of thermal energy promotes it into the conduction band. Because the phosphorus-doped silicon contains mobile, *negatively* charged carriers (electrons), it is said to be doped

***n*-type**. Doping the silicon crystal with boron produces a related, but opposite, effect. Each boron atom contributes only three valence electrons to bonding orbitals in the valence band, and therefore a *hole* is localized near each boron atom. Thermal energy is enough to separate the negatively



(b) *n*-type doping of silicon by phosphorus. The extra valence electron from a phosphorus atom is thermally excited into the conduction band, leaving a fixed positive charge on the phosphorus atom.

charged boron atom from the hole, delocalizing the latter. In this case the charge carriers are the holes, which are *positive*, and the crystal is doped ***p*-type**. In both *p*- and *n*-type doping, an extremely small concentration of dopants (as little as one part per billion) is enough to cause a significant increase in conductivity. For this reason, great pains are taken to purify the semiconductors used in electronic devices.



The colors of semiconductors are determined by the band gap energy E_g . Only photons with energy greater than E_g can be absorbed. From the Planck radiation formula ($E = h\nu$) and $\lambda\nu = c$, we calculate that the wavelength, λ , of an absorbed photon must be less than hc/E_g . Gallium arsenide (GaAs ; $E_g = 1.4 \text{ eV}$) absorbs photons of wavelengths shorter than 890 nm, which is in the near infrared region. Because it absorbs all wavelengths of visible light, gallium arsenide appears black to the eye. Iron oxide (Fe_2O_3 ; $E_g = 2.2 \text{ eV}$) absorbs light of wavelengths shorter than 570 nm; it absorbs both yellow and blue light, and therefore appears red. Cadmium sulfide (CdS ; $E_g = 2.6 \text{ eV}$), which absorbs blue light ($\lambda \leq 470 \text{ nm}$), appears yellow. Strontium titanate (SrTiO_3 ; $E_g = 3.2 \text{ eV}$) absorbs only in the ultraviolet ($\lambda \leq 390 \text{ nm}$). It appears white to the eye because visible light of all colors is reflected by the fine particles.

Even in a doped semiconductor, mobile electrons and holes are both present, although one carrier type is predominant. For example, in a sample of silicon doped with arsenic (*n*-type doping), the concentrations of mobile electrons are slightly less than the concentration of arsenic atoms (usually expressed in terms of atoms/cm³), and the concentrations of mobile holes are extremely low. Interestingly, the concentrations of electrons and holes always follow an equilibrium expression that is entirely analogous to that for the autodissociation of water into H^+ and OH^- ions (Chapter 18); that is,

$$[e^-][h^+] = K_{\text{eq}}$$

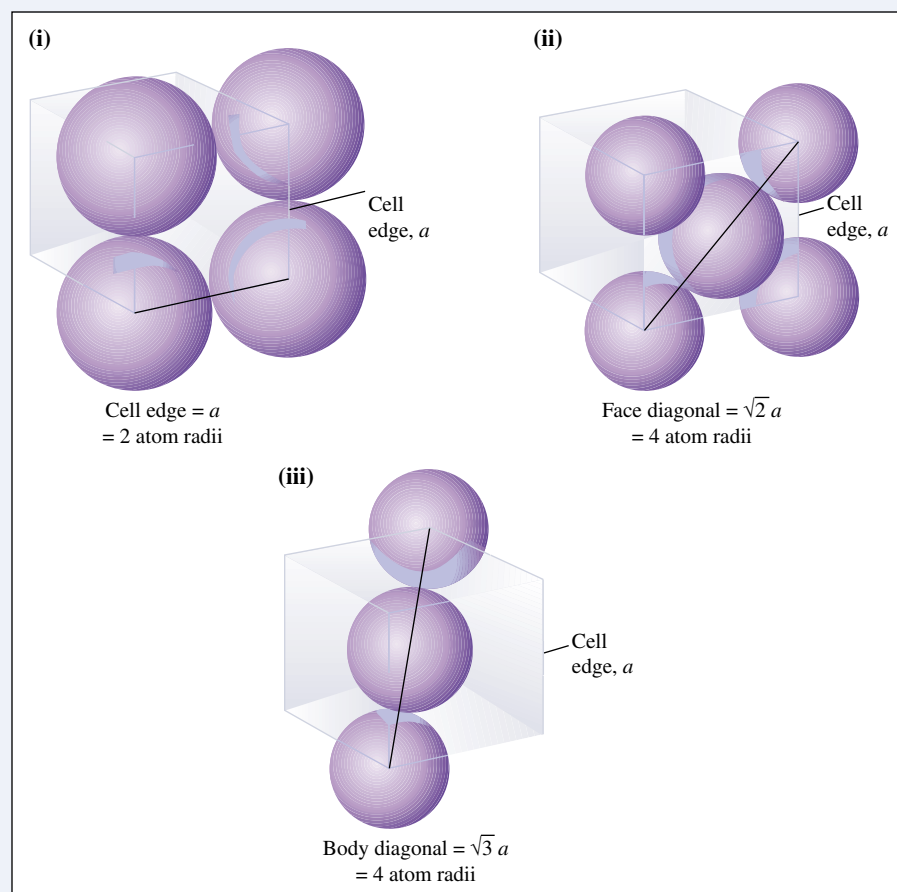
where the equilibrium constant K_{eq} depends only on the identity of the semiconductor and the absolute temperature. For silicon at room temperature, $K_{\text{eq}} = 4.9 \times 10^{19} \text{ carriers}^2/\text{cm}^6$.

Doped semiconductors are extremely important in electronic applications. A ***p*-*n* junction** is formed by joining *p*- and *n*-type semiconductors. At the junction, free electrons and holes combine, annihilating each other and leaving positively and negatively charged dopant atoms on opposite sides. The unequal charge distribution on the two sides of the junction causes an electric field to develop and gives rise to current rectification (electrons can flow, with a small applied voltage, only from the *n* side to the *p* side of the junction; holes flow only in the reverse direction). Devices such as **diodes** and **transistors**, which form the bases of most analog and digital electronic circuits, are composed of *p*-*n* junctions.

Professor Thomas A. Mallouk
Pennsylvania State University

 **Problem-Solving Tip:** *The Locations of the Nearest Neighbors in Cubic Crystals*

The distance from an atom to one of its nearest neighbors in any crystal structure depends on the arrangement of atoms and on the size of the unit cell. For structures (such as metals) that contain only one kind of atom, the nearest neighbors of each atom can be visualized as follows. (Recall that for a cubic structure, the unit cell edge is a). In a simple cubic structure, the nearest neighbors are along the cell edge (i). In a face-centered cubic structure, the nearest neighbors are along the face diagonal (ii). In a body-centered cubic structure, they are along the body diagonal (iii).



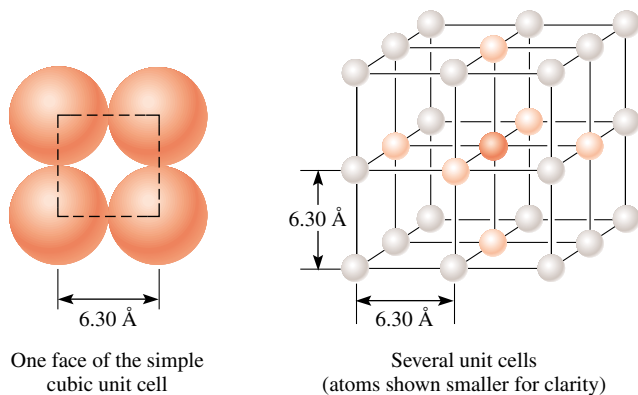
The relationships just described hold only for structures composed of a single kind of atom. For other structures, the relationships are more complex.

EXAMPLE 13-7 *Nearest Neighbors*

In the simple cubic form of manganese there are Mn atoms at the corners of a simple cubic unit cell that is 6.30 \AA on edge. (a) What is the shortest distance between centers of neighboring Mn atoms? (b) How many nearest neighbors does each atom have?

Plan

We visualize the simple cubic cell.

**Solution**

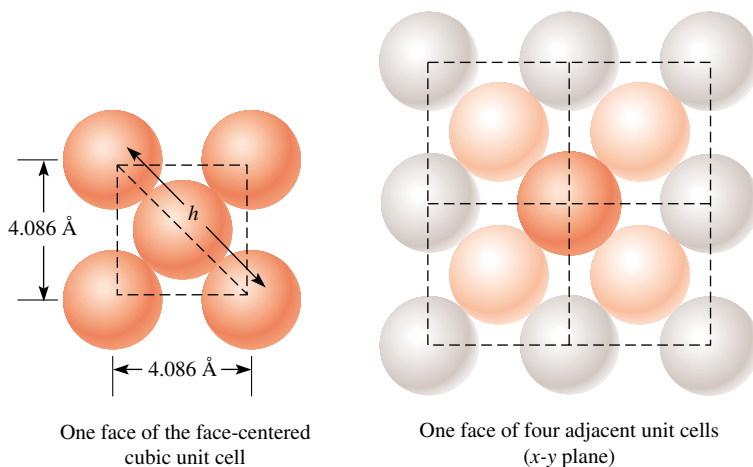
(a) One face of the cubic unit cell is shown in the left-hand drawing, with the atoms touching. The centers of the nearest neighbor atoms are separated by one unit cell edge, at the distance 6.30 \AA . (b) A three-dimensional representation of eight unit cells is also shown. In that drawing the atoms are shown smaller for clarity. Some atoms are represented with different colors to aid in visualizing the arrangement, but *all atoms are identical*. Consider the atom shown in red at the center (at the intersection of the eight unit cells). Its nearest neighbors in all of the unit cell directions are shown as light red atoms. As we can see, there are $\text{six nearest neighbors}$. The same would be true of any atom in the structure.

EXAMPLE 13-8 Nearest Neighbors

Silver crystals are face-centered cubic, with a cell edge of 4.086 \AA . (a) What is the distance between centers of the two closest Ag atoms? (b) What is the atomic radius of silver in this crystal? (c) How many nearest neighbors does each atom have?

Plan

We reason as in Example 13-7, except that now the two atoms closest to each other are those along the face diagonal.



Solution

(a) One face of the face-centered cubic unit cell is shown in the left-hand drawing, with the atoms touching. The nearest neighbor atoms are the ones along the diagonal of the face of the cube. We may visualize the face as consisting of two right isosceles triangles sharing a common hypotenuse, h , and having sides of length $a = 4.086 \text{ \AA}$. The hypotenuse is equal to *twice* the center-to-center distance. The hypotenuse can be calculated from the Pythagorean theorem, $h^2 = a^2 + a^2$. The length of the hypotenuse equals the square root of the sum of the squares of the sides.

$$h = \sqrt{a^2 + a^2} = \sqrt{2a^2} = \sqrt{2(4.086 \text{ \AA})^2} = 5.778 \text{ \AA}$$

The distance between centers of adjacent silver atoms is one half of h , so

$$\text{Distance} = \frac{5.778 \text{ \AA}}{2} = 2.889 \text{ \AA}$$

(b) The hypotenuse of the unit cell face is four times the radius of the silver atom.

$$\text{Atom radius} = \frac{5.778 \text{ \AA}}{4} = 1.444 \text{ \AA}$$

(c) To see the number of nearest neighbors, we expand the left-hand drawing to include several unit cells, as shown in the right-hand drawing. Suppose that this is the x - y plane. The atom shown in red has four nearest neighbors in this plane. There are four more such neighbors in the x - z plane (perpendicular to the x - y plane), and four additional neighbors in the y - z plane (also perpendicular to the x - y plane). This gives a total of 12 nearest neighbors.

EXAMPLE 13-9 *Density and Cell Volume*

From data in Example 13-8, calculate the density of metallic silver.

Plan

We first determine the mass of a unit cell, that is, the mass of four atoms of silver. The density of the unit cell, and therefore of silver, is its mass divided by its volume.

Solution

$$\begin{aligned} \text{? g Ag per unit cell} &= \frac{4 \text{ Ag atoms}}{\text{unit cell}} \times \frac{1 \text{ mol Ag}}{6.022 \times 10^{23} \text{ Ag atoms}} \times \frac{107.87 \text{ g Ag}}{1 \text{ mol Ag}} \\ &= 7.165 \times 10^{-22} \text{ g Ag/unit cell} \end{aligned}$$

$$V_{\text{unit cell}} = (4.086 \text{ \AA})^3 = 68.22 \text{ \AA}^3 \times \left(\frac{10^{-8} \text{ cm}}{\text{\AA}}\right)^3 = 6.822 \times 10^{-23} \text{ cm}^3/\text{unit cell}$$

$$\text{Density} = \frac{7.165 \times 10^{-22} \text{ g Ag/unit cell}}{6.822 \times 10^{-23} \text{ cm}^3/\text{unit cell}} = 10.50 \text{ g/cm}^3$$

A handbook gives the density of silver as 10.5 g/cm^3 at 20°C .

You should now work Exercises 90 and 92.

Data obtained from crystal structures and observed densities give us information from which we can calculate the value of Avogadro's number. The next example illustrates these calculations.

EXAMPLE 13-10 *Density, Cell Volume, and Avogadro's Number*

Titanium crystallizes in a body-centered cubic unit cell with an edge length of 3.306 Å. The density of titanium is 4.401 g/cm³. Use these data to calculate Avogadro's number.

Plan

We relate the density and the volume of the unit cell to find the total mass contained in one unit cell. Knowing the number of atoms per unit cell, we can then find the mass of one atom. Comparing this to the known atomic weight, which is the mass of one mole (Avogadro's number) of atoms, we can evaluate Avogadro's number.

Solution

We first determine the volume of the unit cell.

$$V_{\text{cell}} = (3.306 \text{ \AA})^3 = 36.13 \text{ \AA}^3$$

We now convert Å³ to cm³.

$$\underline{\quad} \text{ cm}^3 = 36.13 \text{ \AA}^3 \times \left(\frac{10^{-8} \text{ cm}}{\text{\AA}} \right)^3 = 3.613 \times 10^{-23} \text{ cm}^3$$

The mass of the unit cell is its volume times the observed density.

$$\text{Mass of unit cell} = 3.613 \times 10^{-23} \text{ cm}^3 \times \frac{4.401 \text{ g}}{\text{cm}^3} = 1.590 \times 10^{-22} \text{ g}$$

The bcc unit cell contains $8\left(\frac{1}{8}\right) + 1 = 2$ Ti atoms, so this represents the mass of two Ti atoms. The mass of a single Ti atom is

$$\text{Mass of atom} = \frac{1.590 \times 10^{-22} \text{ g}}{2 \text{ atoms}} = 7.950 \times 10^{-23} \text{ g/atom}$$

From the known atomic weight of Ti (47.88), we know that the mass of one mole of Ti is 47.88 g/mol. Avogadro's number represents the number of atoms per mole, and can be calculated as

$$N_{\text{Av}} = \frac{47.88 \text{ g}}{\text{mol}} \times \frac{1 \text{ atom}}{7.950 \times 10^{-23} \text{ g}} = 6.023 \times 10^{23} \text{ atoms/mol}$$

You should now work Exercise 96.

Ionic Solids

Most salts crystallize as ionic solids with ions occupying the unit cell. Sodium chloride (Figure 13-28) is an example. Many other salts crystallize in the sodium chloride (face-centered cubic) arrangement. Examples are the halides of Li⁺, K⁺, and Rb⁺, and M²⁺X²⁻ oxides and sulfides such as MgO, CaO, CaS, and MnO. Two other common ionic structures are those of cesium chloride, CsCl (simple cubic lattice), and zincblende, ZnS (face-centered cubic lattice), shown in Figure 13-29. Salts that are isomorphous with the CsCl structure include CsBr, CsI, NH₄Cl, TlCl, TlBr, and TlI. The sulfides of Be²⁺, Cd²⁺, and Hg²⁺, together with CuBr, CuI, AgI, and ZnO, are isomorphous with the zincblende structure (Figure 13-29c).

The ions in an ionic solid can vibrate only about their fixed positions, so ionic solids are poor electrical and thermal conductors. Liquid (molten) ionic compounds are excellent conductors, however, because their ions are freely mobile.



See the *Saunders Interactive General Chemistry CD-ROM*, Screen 13.13, Solid Structures (2): Ionic Solids.

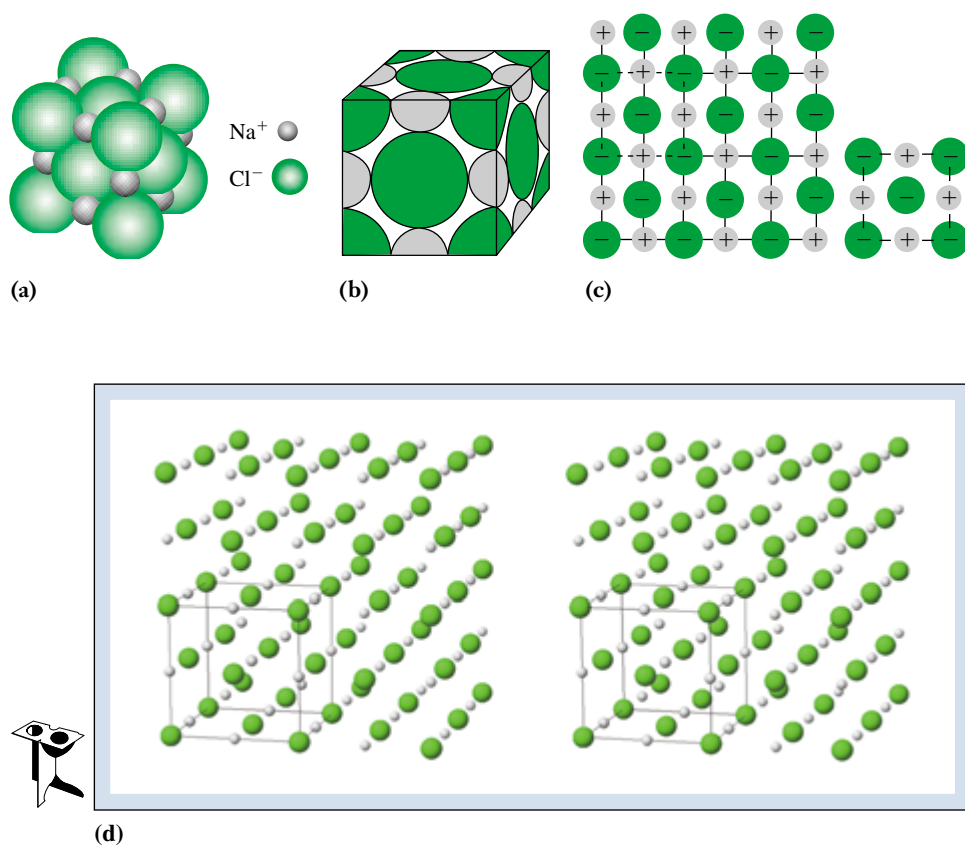


Figure 13-28 Some representations of the crystal structure of sodium chloride, NaCl. Sodium ions are shown in gray and chloride ions are shown in green. (a) One unit cell of the crystal structure of sodium chloride. (b) A representation of the unit cell of sodium chloride that indicates the relative sizes of the Na^+ and Cl^- ions as well as how ions are shared between unit cells. Particles at the corners, edges, and faces of unit cells are shared by other unit cells. Remember that there is an additional Na^+ ion at the center of the cube. (c) A cross-section of the structure of NaCl, showing the repeating pattern of its unit cell at the right. The dashed lines outline an alternative choice of the unit cell. The entire pattern is generated by repeating either unit cell (and its contents) in all three directions. Several such choices of unit cells are usually possible. (d) A stereoview of the sodium chloride structure, extending over several unit cells.

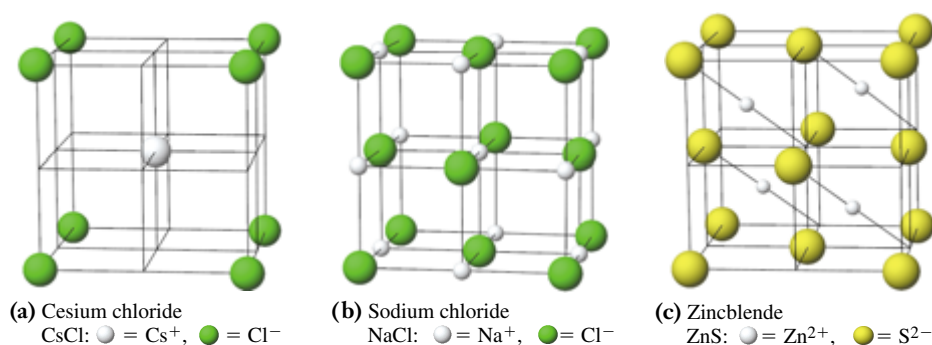


Figure 13-29 Crystal structures of some ionic compounds of the MX type. The gray circles represent cations. One unit cell of each structure is shown. (a) The structure of cesium chloride, CsCl, is simple cubic. It is *not* body-centered, because the point at the center of the cell (Cs^+ , gray) is not the same as the point at a corner of the cell (Cl^- , green). (b) Sodium chloride, NaCl, is face-centered cubic. (c) Zincblende, ZnS, is face-centered cubic, with four Zn^{2+} (gray) and four S^{2-} (yellow) ions per unit cell. The Zn^{2+} ions are related by the same translations as the S^{2-} ions.

Plan


The edge length, $a = 5.501 \text{ \AA}$, is twice the radius of the Br^- ion plus twice the radius of the Li^+ ion. We know from Example 13-11 that the radius for the Br^- ion is 1.945 \AA .

Solution

$$\begin{aligned} 5.501 \text{ \AA} &= 2 r_{\text{Br}^-} + 2 r_{\text{Li}^+} \\ 2 r_{\text{Li}^+} &= 5.501 \text{ \AA} - 2(1.945 \text{ \AA}) = 1.611 \text{ \AA} \\ r_{\text{Li}^+} &= 0.806 \text{ \AA} \end{aligned}$$

You should now work Exercise 88.

The value of 1.945 \AA for the Br^- radius calculated in Example 13-11 is a little different from the value of 1.82 \AA given in Figure 6-1; the Li^+ value of 0.806 \AA from Example 13-12 also differs somewhat from the value of 0.90 \AA given in Figure 6-1. We should remember that the tabulated value in Figure 6-1 is the *average* value obtained from a number of crystal structures of compounds containing the specified ion. Calculations of ionic radii usually assume that anion–anion contact exists, but this assumption is not always true. Calculated radii therefore vary from structure to structure, and we should not place too much emphasis on a value of an ionic radius obtained from any *single* structure determination. We now see that there is some difficulty in determining precise values of ionic radii. Similar difficulties can arise in the determination of atomic radii from molecular and covalent solids or of metallic radii from solid metals.

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 13.14, Solid Structures (3): Molecular Solids.

Dispersion forces are also present among polar molecules.

Molecular Solids

The lattice positions that describe unit cells of molecular solids represent molecules or monatomic elements (sometimes referred to as monatomic molecules). Figure 13-31 shows the unit cells of two simple molecular crystals. Although the bonds *within* molecules are covalent and strong, the forces of attraction *between* molecules are much weaker. They range from hydrogen bonds and weaker dipole–dipole interactions in polar molecules such as H_2O and SO_2 to very weak dispersion forces in symmetrical, nonpolar molecules such as CH_4 , CO_2 , and O_2 and monatomic elements, such as the noble gases. Because of the relatively weak intermolecular forces of attraction, molecules can be easily displaced. Thus, molecular solids are usually soft substances with low melting points. Because electrons do not move from one molecule to another under ordinary conditions, molecular solids are poor electrical conductors and good insulators.

Covalent Solids

Covalent solids (or “network solids”) can be considered giant molecules that consist of covalently bonded atoms in an extended, rigid crystalline network. Diamond (one crystalline form of carbon) and quartz are examples of covalent solids (Figure 13-32). Because of their rigid, strongly bonded structures, *most* covalent solids are very hard and melt at high temperatures. Because electrons are localized in covalent bonds, they are not freely


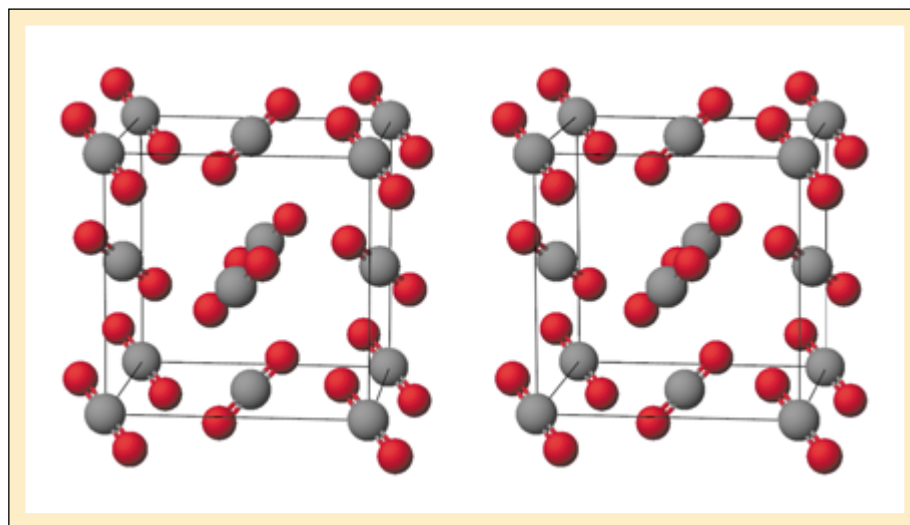
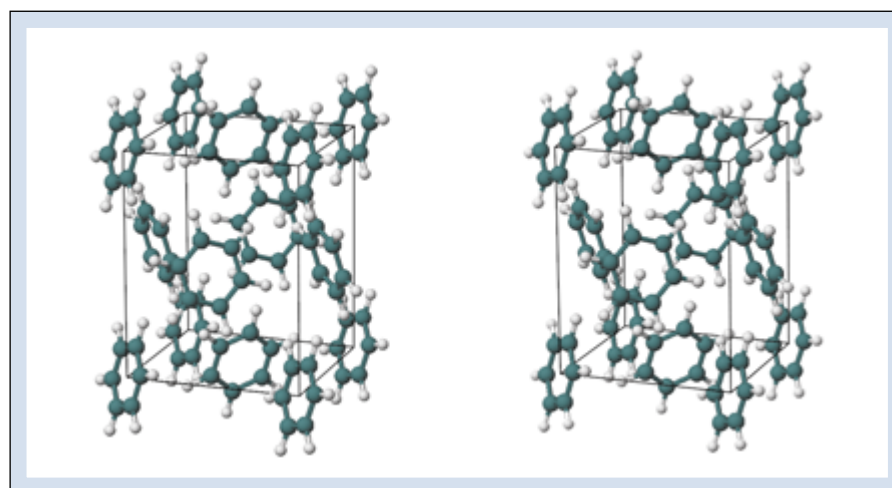
 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 13.15, Solid Structures (4): Network Solids.

Figure 13-31 The packing arrangement in a molecular crystal depends on the shape of the molecule as well as on the electrostatic interactions of any regions of excess positive and negative charge in the molecules. The arrangements in some molecular crystals are shown here: (a) carbon dioxide, CO_2 ; (b) benzene, C_6H_6 .



(a)



(b)



mobile. As a result, covalent solids are *usually* poor thermal and electrical conductors at ordinary temperatures. (Diamond, however, is a good conductor of heat; jewelers use this property to distinguish diamonds from imitations.)

An important exception to these generalizations about properties is *graphite*, an allotropic form of carbon. It has the layer structure shown in Figure 13-32c. The overlap of an extended π -electron network in each plane makes graphite an excellent conductor. The very weak attraction between layers allows these layers to slide over one another easily. Graphite is used as a lubricant, as an additive for motor oil, and in pencil “lead” (combined with clay and other fillers to control hardness).

It is interesting to note that the allotropes of carbon include one very hard substance and one very soft substance. They differ only in the arrangement and bonding of the C atoms.

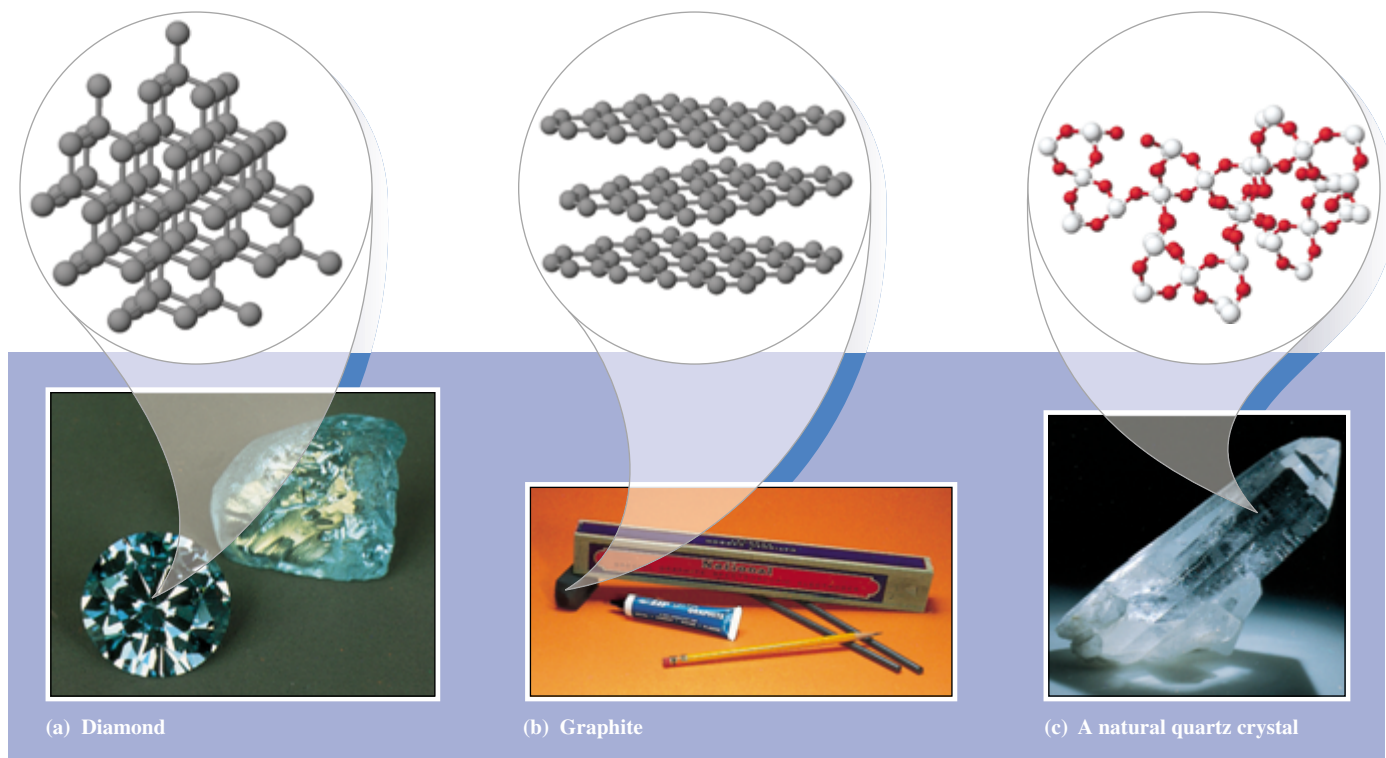


Figure 13-32 Portions of the atomic arrangements in three covalent solids. (a) Diamond. Each C is bonded tetrahedrally to four others through sp^3 - sp^3 σ -bonds. (1.54 Å). (b) Graphite. C atoms are linked in planes by sp^2 - sp^2 σ -bonds (1.42 Å). The crystal is soft, owing to the weakness of the attractions between planes (3.40 Å). Electrons move freely through the π -bonding network in these planes, but they do not jump between planes easily. (c) Quartz (SiO_2). Each Si atom (gray) is bonded tetrahedrally to four O atoms (red).

13-17 BAND THEORY OF METALS



Metals can be formed into many shapes because of their malleability and ductility.

As described in the previous section, most metals crystallize in close-packed structures. The ability of metals to conduct electricity and heat must result from strong electronic interactions of an atom with its 8 to 12 nearest neighbors. This might be surprising at first if we recall that each Group IA and Group IIA metal atom has only one or two valence electrons available for bonding. This is too few to participate in bonds localized between it and each of its nearest neighbors.

Bonding in metals is called **metallic bonding**. It results from the electrical attractions among positively charged metal ions and mobile, delocalized electrons belonging to the crystal as a whole. The properties associated with metals—metallic luster, high thermal and electrical conductivity, and so on—can be explained by the **band theory** of metals, which we now describe.

The overlap interaction of two atomic orbitals, say the $3s$ orbitals of two sodium atoms, produces two molecular orbitals, one bonding orbital and one antibonding orbital (Chapter 9). If N atomic orbitals interact, N molecular orbitals are formed. In a single metallic

crystal containing one mole of sodium atoms, for example, the interaction (overlap) of 6.022×10^{23} $3s$ atomic orbitals produces 6.022×10^{23} molecular orbitals. Atoms interact more strongly with nearby atoms than with those farther away. The energy that separates bonding and antibonding molecular orbitals resulting from two given atomic orbitals decreases as the overlap between the atomic orbitals decreases (Chapter 9). The interactions among the mole of Na atoms result in a series of very closely spaced molecular orbitals (formally σ_{3s} and σ_{3s}^*). These constitute a nearly continuous **band** of orbitals that belongs to the crystal as a whole. One mole of Na atoms contributes 6.022×10^{23} valence electrons (Figure 13-33a), so the 6.022×10^{23} orbitals in the band are half-filled.

The ability of metallic Na to conduct electricity is due to the ability of any of the highest energy electrons in the “ $3s$ ” band to jump to a slightly higher-energy vacant orbital in the same band when an electric field is applied. The resulting net flow of electrons through the crystal is in the direction of the applied field.

The empty $3p$ atomic orbitals of the Na atoms also interact to form a wide band of $3 \times 6.022 \times 10^{23}$ orbitals. The $3s$ and $3p$ atomic orbitals are quite close in energy, so the fanned-out bands of molecular orbitals overlap, as shown in Figure 13-33b. The two overlapping bands contain $4 \times 6.022 \times 10^{23}$ orbitals and only 6.022×10^{23} electrons. Because each orbital can hold two electrons, the resulting combination of bands is only one-eighth full.

Overlap of “ $3s$ ” and “ $3p$ ” bands is not necessary to explain the ability of Na or of any other Group IA metal to conduct electricity. It can do so utilizing only the half-filled “ $3s$ ” band. In the Group IIA metals, however, such overlap is important. Consider a crystal of magnesium as an example. The $3s$ atomic orbital of an isolated Mg atom is filled with two electrons. Thus, without this overlap, the “ $3s$ ” band in a crystal of Mg is also filled. Mg is a good conductor at room temperature because the highest energy electrons are able to move readily into vacant orbitals in the “ $3p$ ” band (Figure 13-34).

According to band theory, the highest energy electrons of metallic crystals occupy either a partially filled band or a filled band that overlaps an empty band. A band within which

The alkali metals are those of Group IA; the alkaline earth metals are those of Group IIA.

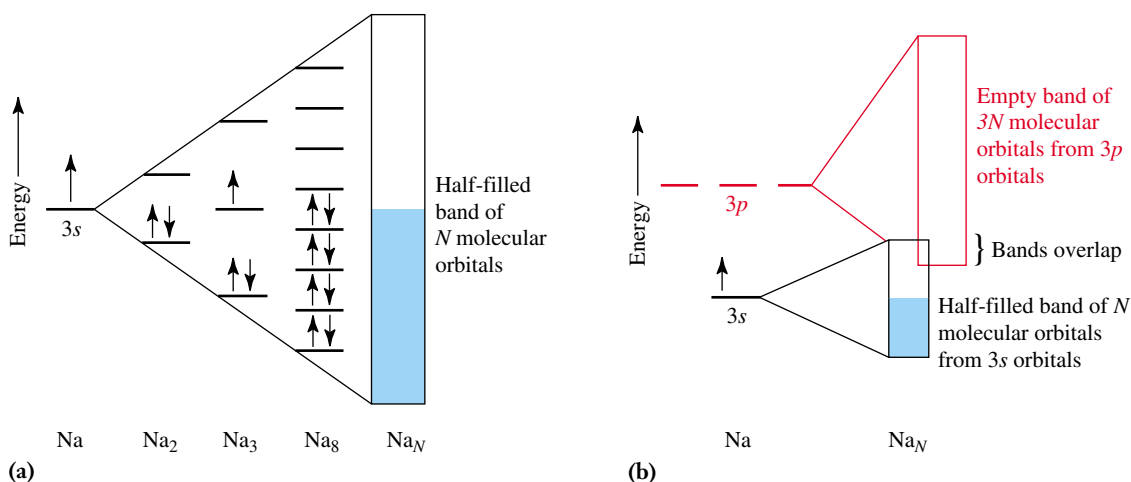


Figure 13-33 (a) The band of orbitals resulting from interaction of the $3s$ orbitals in a crystal of sodium. (b) Overlapping of a half-filled “ $3s$ ” band (black) with an empty “ $3p$ ” band (red) of Na_N crystal.

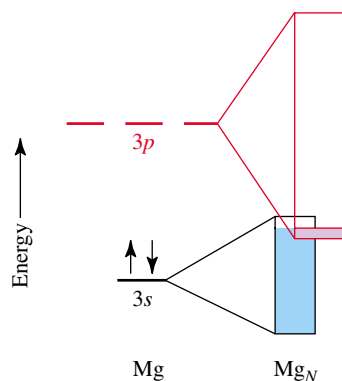


Figure 13-34 Overlapping of a filled “3s” band (blue) with an empty “3p” band of Mg_N crystal. The higher-energy electrons are able to move into the “3p” band (red) as a result of this overlap.

(or into which) electrons move to allow electrical conduction is called a **conduction band**. The electrical conductivity of a metal decreases as temperature increases. The increase in temperature causes thermal agitation of the metal ions. This impedes the flow of electrons when an electric field is applied.

Crystalline nonmetals, such as diamond and phosphorus, are **insulators**—they do not conduct electricity. The reason for this is that their highest energy electrons occupy filled bands of molecular orbitals that are separated from the lowest empty band (conduction band) by an energy difference called the **band gap**. In an insulator, this band gap is an energy difference that is too large for electrons to jump to get to the conduction band (Figure 13-35).

Elements that are **semiconductors** have filled bands that are only slightly below, but do not overlap with, empty bands. They do not conduct electricity at low temperatures, but a small increase in temperature is sufficient to excite some of the highest energy electrons into the empty conduction band.

Let us now summarize some of the physical properties of metals in terms of the band theory of metallic bonding.

1. We have just accounted for the *ability of metals to conduct electricity*.
2. Metals are also *conductors of heat*. They can absorb heat as electrons become thermally excited to low-lying vacant orbitals in a conduction band. The reverse process accompanies the release of heat.
3. Metals have a *lustrous appearance* because the mobile electrons can absorb a wide range of wavelengths of radiant energy as they jump to higher energy levels. Then they emit photons of visible light and fall back to lower levels within the conduction band.



Various samples of elemental silicon. The circle at the lower right is a disk of ultrapure silicon on which many electronic circuits have been etched.

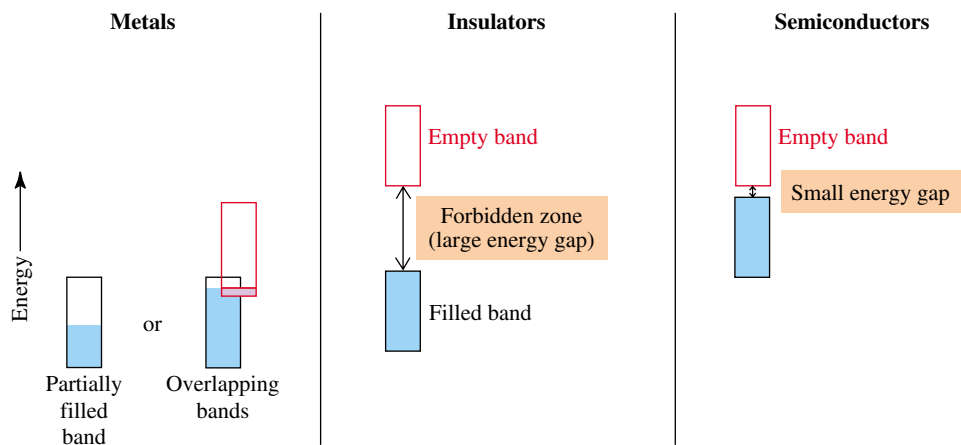
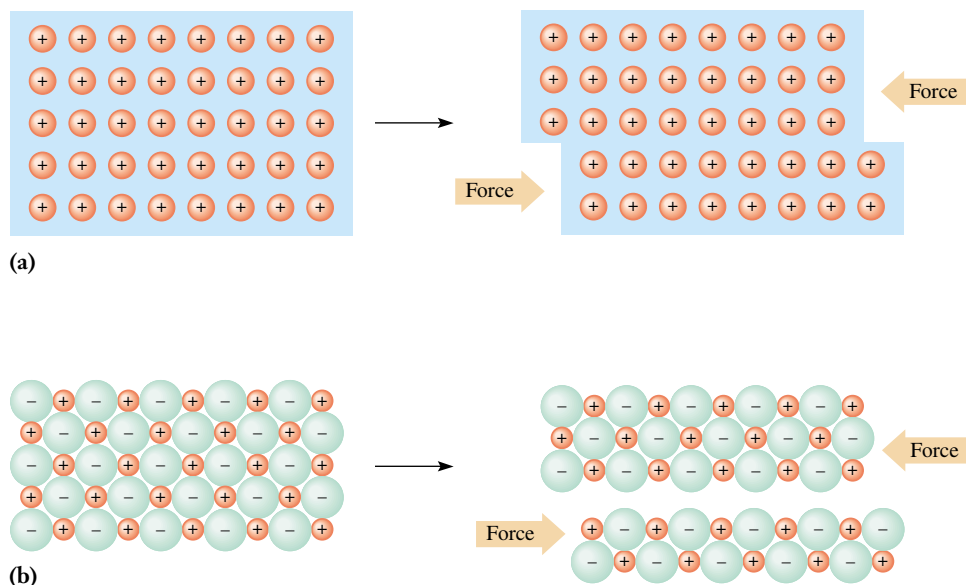


Figure 13-35 Distinction among metals, insulators, and semiconductors. In each case an unshaded area represents a conduction band.



A crystal can be cleaved into smaller crystals that have the same appearance as the larger crystal. Here a worker is cleaving a large crystal of sodium chloride.

Figure 13-36 (a) In a metal, the positively charged metal ions are immersed in a delocalized “cloud of electrons.” When the metal is distorted (e.g., rolled into sheets or drawn into wires), the environment around the metal atoms is essentially unchanged, and no new repulsive forces occur. This explains why metal sheets and wires remain intact. (b) By contrast, when an ionic crystal is subjected to a force that causes it to slip along a plane, the increased repulsive forces between like-charged ions cause the crystal to break.

4. Metals are *malleable* or *ductile* (or both). A crystal of a metal is easily deformed when a mechanical stress is applied to it. All of the metal ions are identical, and they are imbedded in a “sea of electrons.” As bonds are broken, new ones are readily formed with adjacent metal ions. The features of the arrangement remain unchanged, and the environment of each metal ion is the same as before the deformation occurred (Figure 13-36). The breakage of bonds involves the promotion of electrons to higher-energy levels. The formation of bonds is accompanied by the return of the electrons to the original energy levels.

A **malleable** substance can be rolled or pounded into sheets. A **ductile** substance can be drawn into wires.

Key Terms

Adhesive force Force of attraction between a liquid and another surface.

Allotropes Different forms of the same element in the same physical state.

Amorphous solid A noncrystalline solid with no well-defined, ordered structure.

Band A series of very closely spaced, nearly continuous molecular orbitals that belong to the crystal as a whole.

Band gap An energy separation between an insulator’s highest filled electron energy band and the next higher-energy vacant band.

Band theory of metals A theory that accounts for the bonding and properties of metallic solids.

Boiling point The temperature at which the vapor pressure of a liquid is equal to the external pressure; also the condensation point.

Capillary action The drawing of a liquid up the inside of a small-bore tube when adhesive forces exceed cohesive forces, or the depression of the surface of the liquid when cohesive forces exceed adhesive forces.

Cohesive forces All the forces of attraction among particles of a liquid.

Condensation Liquefaction of vapor.

Condensed phases The liquid and solid phases; phases in which particles interact strongly.

Conduction band A partially filled band or a band of vacant energy levels just higher in energy than a filled band; a band within which, or into which, electrons must be promoted to allow electrical conduction to occur in a solid.

Coordination number In describing crystals, the number of nearest neighbors of an atom or ion.

Critical point The combination of critical temperature and critical pressure of a substance.

Critical pressure The pressure required to liquefy a gas (vapor) at its critical temperature.

Critical temperature The temperature above which a gas cannot be liquefied; the temperature above which a substance cannot exhibit distinct gas and liquid phases.

Crystal lattice The pattern of arrangement of particles in a crystal.

Crystalline solid A solid characterized by a regular, ordered arrangement of particles.

Deposition The direct solidification of a vapor by cooling; the reverse of sublimation.

Dipole–dipole interactions Interactions between polar molecules, that is, between molecules with permanent dipoles.

Dipole-induced dipole interaction See *Dispersion forces*.

Dispersion forces Very weak and very short-range attractive forces between short-lived temporary (induced) dipoles; also called London forces.

Distillation The separation of a liquid mixture into its components on the basis of differences in boiling points.

Dynamic equilibrium A situation in which two (or more) processes occur at the same rate so that no net change occurs.

Evaporation Vaporization of a liquid below its boiling point.

Heat of condensation The amount of heat that must be removed from a specific amount of a vapor at its condensation point to condense the vapor with no change in temperature; usually expressed in J/g or kJ/mol; in the latter case it is called the *molar heat of condensation*.

Heat of fusion The amount of heat required to melt a specific amount of a solid at its melting point with no change in temperature; usually expressed in J/g or kJ/mol; in the latter case it is called the *molar heat of fusion*.

Heat of solidification The amount of heat that must be removed from a specific amount of a liquid at its freezing point to freeze it with no change in temperature; usually expressed in J/g or kJ/mol; in the latter case it is called the *molar heat of solidification*.

Heat of vaporization The amount of heat required to vaporize a specific amount of a liquid at its boiling point with no change in temperature; usually expressed in J/g or kJ/mol; in the latter case it is called the *molar heat of vaporization*.

Hydrogen bond A fairly strong dipole–dipole interaction (but still considerably weaker than covalent or ionic bonds) between

molecules containing hydrogen directly bonded to a small, highly electronegative atom, such as N, O, or F.

Insulator A poor conductor of electricity and heat.

Intermolecular forces Forces *between* individual particles (atoms, molecules, ions) of a substance.

Intramolecular forces Forces between atoms (or ions) *within* molecules (or formula units).

Isomorphous Refers to crystals having the same atomic arrangement.

LeChatelier's Principle A system at equilibrium, or striving to attain equilibrium, responds in such a way as to counteract any stress placed upon it.

London forces See *Dispersion forces*.

Melting point The temperature at which liquid and solid coexist in equilibrium; also the freezing point.

Meniscus The upper surface of a liquid in a cylindrical container.

Metallic bonding Bonding within metals due to the electrical attraction of positively charged metal ions for mobile electrons that belong to the crystal as a whole.

Molar heat capacity The amount of heat necessary to raise the temperature of one mole of a substance one degree Celsius with no change in state; usually expressed in kJ/mol·°C. See *Specific heat*.

Molar heat of condensation The amount of heat that must be removed from one mole of a vapor at its condensation point to condense the vapor with no change in temperature; usually expressed in kJ/mol. See *Heat of condensation*.

Molar heat of fusion The amount of heat required to melt one mole of a solid at its melting point with no change in temperature; usually expressed in kJ/mol. See *Heat of fusion*.

Molar heat of vaporization The amount of heat required to vaporize one mole of a liquid at its boiling point with no change in temperature; usually expressed in kJ/mol. See *Heat of vaporization*.

Normal boiling point The temperature at which the vapor pressure of a liquid is equal to one atmosphere pressure.

Normal melting point The melting (freezing) point at one atmosphere pressure.

Phase diagram A diagram that shows equilibrium temperature–pressure relationships for different phases of a substance.

Polymorphous Refers to substances that crystallize in more than one crystalline arrangement.

Semiconductor A substance that does not conduct electricity well at low temperatures but that does at higher temperatures.

Specific heat The amount of heat necessary to raise the temperature of a specific amount of a substance one degree Celsius with no change in state; usually expressed in J/g·°C. See *Molar heat capacity*.

Sublimation The direct vaporization of a solid by heating without passing through the liquid state.

Supercritical fluid A substance at a temperature above its critical temperature.

Surface tension The result of inward intermolecular forces of attraction among liquid particles that must be overcome to expand the surface area.

Triple point The point on a phase diagram that corresponds to the only pressure and temperature at which three phases (usually solid, liquid, and gas) of a substance can coexist at equilibrium.

Unit cell The smallest repeating unit showing all the structural characteristics of a crystal.

Vapor pressure The partial pressure of a vapor in equilibrium with its parent liquid or solid.

Viscosity The tendency of a liquid to resist flow; the inverse of its fluidity.

Volatility The ease with which a liquid vaporizes.

Exercises

General Concepts

1. What causes dispersion forces? What factors determine the strengths of dispersion forces between molecules?
2. What is hydrogen bonding? Under what conditions can strong hydrogen bonds be formed?
3. Which of the following substances have permanent dipole–dipole forces? (a) SiH_4 , (b) molecular MgCl_2 , (c) NBr_3 , (d) F_2O .
4. Which of the following substances have permanent dipole–dipole forces? (a) Molecular AlCl_3 , (b) PCl_5 , (c) NO , (d) SeF_4 .
5. For which of the substances in Exercise 3 are dispersion forces the only important forces in determining boiling points?
6. For which of the substances in Exercise 4 are dispersion forces the only important forces in determining boiling points?
7. For each of the following pairs of compounds, predict which compound would exhibit stronger hydrogen bonding. Justify your prediction. It may help to write a Lewis formula for each. (a) water, H_2O , or hydrogen sulfide, H_2S ; (b) dichloromethane, CH_2Cl_2 or fluoroamine, NH_2F ; (c) acetone, $\text{C}_3\text{H}_6\text{O}$ (contains a $\text{C}=\text{O}$ double bond) or ethyl alcohol, $\text{C}_2\text{H}_6\text{O}$ (contains one $\text{C}-\text{O}$ single bond).
8. Hydrogen bonding is a very strong dipole–dipole interaction. Why is hydrogen bonding so strong in comparison with other dipole–dipole interactions?
9. What is the effect of pressure on sublimation?
10. Which of the following substances exhibit strong hydrogen bonding in the liquid and solid states? (a) CH_3OH (methyl alcohol), (b) PH_3 , (c) CH_4 , (d) CH_2Cl_2 , (e) CH_3NH_2 .
11. Which of the following substances exhibit strong hydrogen bonding in the liquid and solid states? (a) H_2S , (b) NH_3 , (c) SiH_4 , (d) HF , (e) HCl .
12. The molecular weights of SiH_4 and PH_3 are nearly the same. Account for the fact that the melting and boiling points of PH_3 (-133°C and -88°C) are higher than those of SiH_4 (-185°C and -112°C).
- *13. Imagine replacing one H atom of a methane molecule, CH_4 , with another atom or group of atoms. Account for the order in the normal boiling points of the resulting compounds: CH_4 (-161°C), CH_3Br (3.59°C), CH_3F (-78°C), CH_3OH (65°C).
14. For each of the following pairs of compounds, predict which would exhibit stronger hydrogen bonding. Justify your prediction. It may help to write a Lewis formula for each. (a) ammonia, NH_3 , or phosphine, PH_3 ; (b) ethylene, C_2H_4 , or hydrazine, N_2H_4 ; (c) hydrogen fluoride, HF , or hydrogen chloride, HCl .
15. Describe the intermolecular forces that are present in each of the following compounds. Which kind of force would have the greatest influence on the properties of each compound? (a) bromine pentafluoride, BrF_5 , (b) acetone, $\text{C}_3\text{H}_6\text{O}$ (contains a central $\text{C}=\text{O}$ double bond); (c) formaldehyde, H_2CO .
16. Describe the intermolecular forces that are present in each of the following compounds. Which kind of force would have the greatest influence on the properties of each compound? (a) ethyl alcohol, $\text{C}_2\text{H}_6\text{O}$ (contains one $\text{C}-\text{O}$ single bond); (b) phosphine, PH_3 ; (c) sulfur hexafluoride, SF_6 .
17. Give the correct names for these changes in state: (a) Crystals of *para*-dichlorobenzene, used as a moth repellent, gradually become vapor without passing through the liquid phase. (b) As you enter a warm room from the outdoors on a cold winter day, your eyeglasses become fogged with a film of moisture. (c) On the same (windy) winter day, a pan of water is left outdoors. Some of it turns to vapor, the rest to ice.
18. The normal boiling point of trichlorofluoromethane, CCl_3F , is 24°C , and its freezing point is -111°C . Complete these sentences by supplying the proper terms that describe a state of matter or a change in state. (a) At standard temperature and pressure, CCl_3F is a _____. (b) In an arctic winter at -40°C and 1 atm pressure, CCl_3F is a _____. If it is cooled to -120°C , the molecules arrange themselves in an orderly lattice, the CCl_3F _____ and becomes a _____. (c) If

- (a) Convert the latter value to standard molar heat of vaporization, $\Delta H_{\text{vap}}^{\circ}$, at 37°C.
 (b) Why is the heat of vaporization greater at 37°C than at 100°C?
41. Plot a vapor pressure curve for $\text{C}_2\text{Cl}_2\text{F}_4$ from the following vapor pressures. Determine the boiling point of $\text{C}_2\text{Cl}_2\text{F}_4$ under a pressure of 300 torr from the plot:

t (°C)	-95.4	-72.3	-53.7	-39.1	-12.0	3.5
vp (torr)	1	10	40	100	400	760

42. Plot a vapor pressure curve for $\text{C}_2\text{H}_4\text{F}_2$ from the following vapor pressures. From the plot, determine the boiling point of $\text{C}_2\text{H}_4\text{F}_2$ under a pressure of 200 torr.

t (°C)	-77.2	-51.2	-31.1	-15.0	14.8	31.7
vp (torr)	1	10	40	100	400	760

Phase Changes and Associated Heat Transfer

The following values will be useful in some exercises in this section:

Specific heat of ice	2.09 J/g·°C
Heat of fusion of ice at 0°C	334 J/g
Specific heat of liquid H_2O	4.18 J/g·°C
Heat of vaporization of liquid H_2O at 100°C	2.26×10^3 J/g
Specific heat of steam	2.03 J/g·°C

43. What amount of heat energy, in joules, must be removed to condense 23.2 g of water vapor at 125.0°C to liquid at 22.8°C?
44. Is the equilibrium that is established between two physical states of matter an example of static or dynamic equilibrium? Explain your answer.
45. Which of the following changes of state are exothermic? (a) fusion, (b) liquefaction, (c) sublimation, (d) deposition. Explain.
46. Suppose that heat was added to a 21.8-g sample of solid zinc at the rate of 9.84 J/s. After the temperature reached the normal melting point of zinc, 420°C, it remained constant for 3.60 minutes. Calculate $\Delta H_{\text{fusion}}^{\circ}$ at 420°C, in J/mol, for zinc.
47. The specific heat of silver is 0.237 J/g·°C. Its melting point is 961°C. Its heat of fusion is 11 J/g. How much heat is needed to change 8.72 g of silver from solid at 25°C to liquid at 961°C?
48. The heat of fusion of thallium is 21 J/g, and its heat of vaporization is 795 J/g. The melting and boiling points are 304°C and 1457°C. The specific heat of liquid thallium is 0.13 J/g·°C. How much heat is needed to change 243 g of solid thallium at 304°C to vapor at 1457°C and 1 atm?

49. Calculate the amount of heat required to convert 75.0 g of ice at 0°C to liquid water at 100.°C.
50. Calculate the amount of heat required to convert 75.0 g of ice at -15.0°C to steam at 125.0°C.
51. Use data in Appendix E to calculate the amount of heat required to warm 175 g of mercury from 25°C to its boiling point and then to vaporize it.
52. If 275 g of liquid water at 100.°C and 475 g of water at 30.0°C are mixed in an insulated container, what is the final temperature?
53. If 25.0 g of ice at -10.0°C and 25.0 g of liquid water at 100.°C are mixed in an insulated container, what will the final temperature be?
54. If 175 g of liquid water at 0°C and 17.5 g of steam at 110.°C are mixed in an insulated container, what will the final temperature be?
55. Water can be cooled in hot climates by the evaporation of water from the surfaces of canvas bags. What mass of water can be cooled from 35.0°C to 20.0°C by the evaporation of one gram of water? Assume that ΔH_{vap} does not change with temperature.
56. (a) How much heat must be removed to prepare 15.0 g of ice at 0.0°C from 15.0 g of water at 25.0°C? (b) Calculate the mass of water at 100.0°C that could be cooled to 23.5°C by the same amount of heat as that calculated in part (a).

Clausius–Clapeyron Equation

57. Toluene, $\text{C}_6\text{H}_5\text{CH}_3$, is a liquid used in the manufacture of TNT. Its normal boiling point is 111.0°C, and its molar heat of vaporization is 35.9 kJ/mol. What would be the vapor pressure (torr) of toluene at 75.00°C?
58. At their normal boiling points, the heat of vaporization of water (100°C) is 40,656 J/mol and that of heavy water (101.41°C) is 41,606 J/mol. Use these data to calculate the vapor pressure of each liquid at 80.00°C.
59. (a) Use the Clausius–Clapeyron equation to calculate the temperature (°C) at which pure water would boil at a pressure of 400.0 torr. (b) Compare this result with the temperature read from Figure 13-13. (c) Compare the results of (a) and (b) with a value obtained from Appendix E.
- *60. Show that the Clausius–Clapeyron equation can be written as

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

where B is a constant that has different values for different substances. This is an equation for a straight line.
 (a) What is the expression for the slope of this line?

(b) Using the following vapor pressure data, plot $\ln P$ vs. $1/T$ for ethyl acetate, $\text{CH}_3\text{COOC}_2\text{H}_5$, a common organic solvent used in nail polish removers.

t ($^\circ\text{C}$)	-43.4	-23.5	-13.5	-3.0	+9.1
vp (torr)	1	5	10.	20.	40.
t ($^\circ\text{C}$)	16.6	27.0	42.0	59.3	
vp (torr)	60.	100.	200.	400.	

(c) From the plot, estimate ΔH_{vap} for ethyl acetate.
 (d) From the plot, estimate the normal boiling point of ethyl acetate.

- *61. Repeat Exercise 60(b) and 60(c) for mercury, using the following data for liquid mercury. Then compare this value with the one in Appendix E.

t ($^\circ\text{C}$)	126.2	184.0	228.8	261.7	323.0
vp (torr)	1	10.	40.	100.	400.

62. Isopropyl alcohol, $\text{C}_3\text{H}_8\text{O}$, is marketed as “rubbing alcohol.” Its vapor pressure is 100. torr at 39.5°C and 400. torr at 67.8°C . Estimate the molar heat of vaporization of isopropyl alcohol.
63. Using data from Exercise 62, predict the normal boiling point of isopropyl alcohol.
64. Boiling mercury is often used in diffusion pumps to attain a very high vacuum; pressures down to 10^{-10} atm can be readily attained with such a system. Mercury vapor is very toxic to inhale, however. The normal boiling point of liquid mercury is 357°C . What would be the vapor pressure of mercury at 25°C ?

Phase Diagrams

65. How many phases exist at a triple point? Describe what would happen if a small amount of heat were added under constant-volume conditions to a sample of water at the triple point. Assume a negligible volume change during fusion.
66. What is the critical point? Will a substance always be a liquid below the critical temperature? Why or why not?

Refer to the phase diagram of CO_2 in Figure 13-17b to answer Exercises 67–70.

67. What phase of CO_2 exists at 2 atm pressure and a temperature of -90°C ? -60°C ? 0°C ?
68. What phases of CO_2 are present (a) at a temperature of -78°C and a pressure of 1 atm? (b) at -57°C and a pressure of 5.2 atm?
69. List the phases that would be observed if a sample of CO_2 at 8 atm pressure were heated from -80°C to 40°C .
70. How does the melting point of CO_2 change with pressure? What does this indicate about the relative density of solid CO_2 versus liquid CO_2 ?

- *71. You are given the following data for ethanol, $\text{C}_2\text{H}_5\text{OH}$.

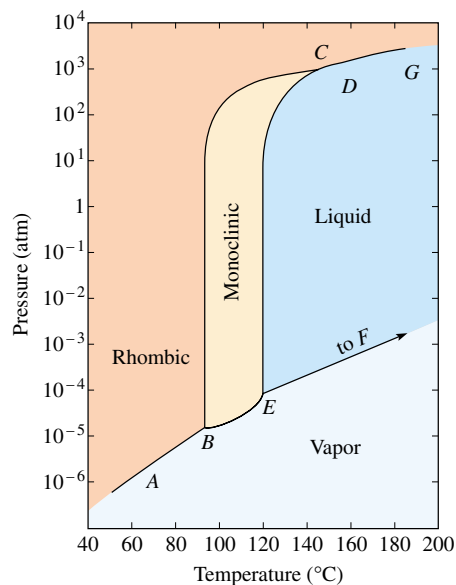
Normal melting point	-117°C
Normal boiling point	78.0°C
Critical temperature	243°C
Critical pressure	63.0 atm

Assume that the triple point is slightly lower in temperature than the melting point and that the vapor pressure at the triple point is about 10^{-5} torr. (a) Sketch a phase diagram for ethanol. (b) Ethanol at 1 atm and $140.^\circ\text{C}$ is compressed to 70. atm. Are two phases present at any time during this process? (c) Ethanol at 1 atm and $270.^\circ\text{C}$ is compressed to 70. atm. Are two phases present at any time during this process?

- *72. You are given the following data for butane, C_4H_{10} .

Normal melting point	-138°C
Normal boiling point	0°C
Critical temperature	152°C
Critical pressure	38 atm

Assume that the triple point is slightly lower in temperature than the melting point and that the vapor pressure at the triple point is 3×10^{-5} torr. (a) Sketch a phase diagram for butane. (b) Butane at 1 atm and 140°C is compressed to 40 atm. Are two phases present at any time during this process? (c) Butane at 1 atm and 200°C is compressed to 40 atm. Are two phases present at any time during this process?



Phase Diagram for Sulfur

Exercises 73 and 74 refer to the phase diagram for sulfur on page 536. (The vertical axis is on a logarithmic scale.) Sulfur has two *solid* forms, monoclinic and rhombic.

- *73. (a) How many triple points are there for sulfur? (b) Indicate the approximate pressure and temperature at each triple point. (c) Which phases are in equilibrium at each triple point?
- *74. Which physical states should be present at equilibrium under the following conditions? (a) 10^{-1} atm and 110°C , (b) 10^{-5} atm and 80°C , (c) 5×10^3 atm and 160°C , (d) 10^{-1} atm and 80°C , (e) 10^{-5} atm and 140°C , (f) 1 atm and 140°C .

The Solid State

75. Comment on the following statement: "The only perfectly ordered state of matter is the crystalline state."
76. Ice floats in water. Why? Would you expect solid mercury to float in liquid mercury at its freezing point? Explain.
77. Distinguish among and compare the characteristics of molecular, covalent, ionic, and metallic solids. Give two examples of each kind of solid.
78. Classify each of the following substances, in the solid state, as molecular, ionic, covalent (network), or metallic solids:

	Melting Point ($^\circ\text{C}$)	Boiling Point ($^\circ\text{C}$)	Electrical Conductor	
			Solid	Liquid
MoF ₆	17.5 (at 406 torr)	35	no	no
BN	3000 (sublimes)	—	no	no
Se ₈	217	684	poor	poor
Pt	1769	3827	yes	yes
RbI	642	1300	no	yes

79. Classify each of the following substances, in the solid state, as molecular, ionic, covalent (network), or metallic solids:

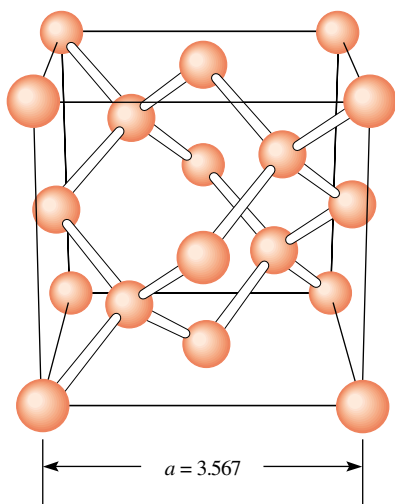
	Melting Point ($^\circ\text{C}$)	Boiling Point ($^\circ\text{C}$)	Electrical Conductor	
			Solid	Liquid
CeCl ₃	848	1727	no	yes
Ti	1675	3260	yes	yes
TiCl ₄	-25	136	no	no
NO ₃ F	-175	-45.9	no	no
B	2300	2550	no	no

80. Based only on their formulas, classify each of the following in the solid state as a molecular, ionic, covalent (network), or metallic solid: (a) SO₂F, (b) MgF₂, (c) W, (d) Pb, (e) PF₅.
81. Based only on their formulas, classify each of the following in the solid state as a molecular, ionic, covalent (network), or metallic solid: (a) Au, (b) NO₂, (c) CaF₂, (d) SF₄, (e) C_{diamond}.
82. Arrange the following solids in order of increasing melting points and account for the order: NaF, MgF₂, AlF₃.
83. Arrange the following solids in order of increasing melting points and account for the order: MgO, CaO, SrO, BaO.
84. Distinguish among and sketch simple cubic, body-centered cubic (bcc), and face-centered cubic (fcc) lattices. Use CsCl, sodium, and nickel as examples of solids existing in simple cubic, bcc, and fcc lattices, respectively.
85. Describe a unit cell as precisely as you can.

Unit Cell Data: Atomic and Ionic Sizes

86. Determine the number of ions of each type present in each unit cell shown in Figure 13-29.
87. Refer to Figure 13-29(a). (a) If the unit cell edge is represented as a , what is the distance (center to center) from Cs⁺ to its nearest neighbor? (b) How many equidistant nearest neighbors does each Cs⁺ ion have? What are the identities of these nearest neighbors? (c) What is the distance (center to center), in terms of a , from a Cs⁺ ion to the nearest Cs⁺ ion? (d) How many equidistant nearest neighbors does each Cl⁻ ion have? What are their identities?
88. Refer to Figure 13-28. (a) If the unit cell edge is represented as a , what is the distance (center to center) from Na⁺ to its nearest neighbor? (b) How many equidistant nearest neighbors does each Na⁺ ion have? What are the identities of these nearest neighbors? (c) What is the distance (center to center), in terms of a , from an Na⁺ ion to the nearest Na⁺ ion? (d) How many equidistant nearest neighbors does each Cl⁻ ion have? What are their identities?
89. Polonium crystallizes in a simple cubic unit cell with an edge length of 3.36 Å. (a) What is the mass of the unit cell? (b) What is the volume of the unit cell? (c) What is the theoretical density of Po?
90. Calculate the density of Na metal. The length of the body-centered cubic unit cell is 4.24 Å.
91. Tungsten has a density of 19.3 g/cm³ and crystallizes in a cubic lattice whose unit cell edge length is 3.16 Å. Which type of cubic unit cell is it?
92. The atomic radius of iridium is 1.36 Å. The unit cell of iridium is a face-centered cube. Calculate the density of iridium.

93. A certain metal has a specific gravity of 10.200 at 25°C. It crystallizes in a body-centered cubic arrangement with a unit cell edge length of 3.147 Å. Determine the atomic weight and identify the metal.
94. The structure of diamond is shown below, with each sphere representing a carbon atom. (a) How many carbon atoms are there per unit cell in the diamond structure? (b) Verify, by extending the drawing if necessary, that each carbon atom has four nearest neighbors. What is the arrangement of these nearest neighbors? (c) What is the distance (center to center) from any carbon atom to its nearest neighbor, expressed in terms of a , the unit cell edge? (d) The observed unit cell edge length in diamond is 3.567 Å. What is the C—C single bond length in diamond? (e) Calculate the density of diamond.



95. The crystal structure of CO_2 is cubic, with a cell edge length of 5.540 Å. A diagram of the cell is shown in Figure 13-31a. (a) What is the number of molecules of CO_2 per unit cell? (b) Is this structure face-centered cubic? How can you tell? (c) What is the density of solid CO_2 at this temperature?
96. A Group IVA element with a density of 11.35 g/cm³ crystallizes in a face-centered cubic lattice whose unit cell edge length is 4.95 Å. Calculate its atomic weight. What is the element?
97. Crystalline silicon has the same structure as diamond, with a unit cell edge length of 5.430 Å. (a) What is the Si—Si distance in this crystal? (b) Calculate the density of crystalline silicon.
- *98. (a) What types of electromagnetic radiation are suitable for diffraction studies of crystals? (b) Describe the X-ray diffraction experiment. (c) What must be the relationship between the wavelength of incident radiation and the spacing of the particles in a crystal for diffraction to occur?

- *99. (a) Write the Bragg equation. Identify each symbol. (b) X-rays from a palladium source ($\lambda = 0.576$ Å) were reflected by a sample of copper at an angle of 9.40°. This reflection corresponds to the unit cell length ($d = a$) with $n = 2$ in the Bragg equation. Calculate the length of the copper unit cell.
100. The spacing between successive planes of platinum atoms parallel to the cubic unit cell face is 2.256 Å. When X-radiation emitted by copper strikes a crystal of platinum metal, the minimum diffraction angle of X-rays is 19.98°. What is the wavelength of the Cu radiation?
101. Gold crystallizes in an fcc structure. When X-radiation of 0.70926 Å wavelength from molybdenum is used to determine the structure of metallic gold, the minimum diffraction angle of X-rays by the gold is 8.683°. Calculate the spacing between parallel layers of gold atoms.

Metallic Bonding and Semiconductors

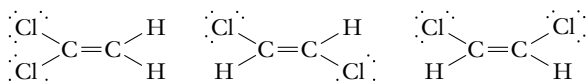
102. In general, metallic solids are ductile and malleable, whereas ionic salts are brittle and shatter readily (although they are hard). Explain this observation.
103. What single factor accounts for the ability of metals to conduct both heat and electricity in the solid state? Why are ionic solids poor conductors of heat and electricity even though they are composed of charged particles?
104. Compare the temperature dependence of electrical conductivity of a metal with that of a typical metalloid. Explain the difference.

Mixed Exercises

105. Benzene, C_6H_6 , boils at 80.1°C. How much energy, in joules, would be required to change 500.0 g of liquid benzene at 21.5°C to a vapor at its boiling point? (The specific heat of liquid benzene is 1.74 J/g·°C and its heat of vaporization is 395 J/g.)
106. The three major components of air are N_2 (bp -196°C), O_2 (bp -183°C), and Ar (bp -186°C). Suppose we have a sample of liquid air at -200°C . In what order will these gases evaporate as the temperature is raised?
- *107. A 10.0-g sample of liquid ethanol, $\text{C}_2\text{H}_5\text{OH}$, absorbs 3.42×10^3 J of heat at its normal boiling point, 78.0°C. The molar enthalpy of vaporization of ethanol, ΔH_{vap} , is 39.3 kJ/mol. (a) What volume of $\text{C}_2\text{H}_5\text{OH}$ vapor is produced? The volume is measured at 78.0°C and 1.00 atm pressure. (b) What mass of $\text{C}_2\text{H}_5\text{OH}$ remains in the liquid state?
- *108. What is the pressure predicted by the ideal gas law for one mole of steam in 31.0 L at 100°C? What is the pressure predicted by the van der Waals equation (Section 12-15) given that $a = 5.464$ L²·atm/mol² and $b = 0.03049$ L/mol? What is the percent difference between these values? Does steam deviate from ideality significantly at 100°C? Why?

*109. The boiling points of HCl, HBr, and HI increase with increasing molecular weight. Yet the melting and boiling points of the sodium halides, NaCl, NaBr, and NaI, decrease with increasing formula weight. Explain why the trends are opposite.

110. The structures for three molecules having the formula $C_2H_2Cl_2$ are



Describe the intermolecular forces present in each of these compounds and predict which has the lowest boiling point.

111. Are the following statements true or false? Indicate why if a statement is false.

(a) The vapor pressure of a liquid will decrease if the volume of liquid decreases.

(b) The normal boiling point of a liquid is the temperature at which the external pressure equals the vapor pressure of the liquid.

(c) The vapor pressures of liquids in a similar series tend to increase with increasing molecular weight.

112. Are the following statements true or false? Indicate why if a statement is false.

(a) The equilibrium vapor pressure of a liquid is independent of the volume occupied by the vapor above the liquid.

(b) The normal boiling point of a liquid changes with changing atmospheric pressure.

(c) The vapor pressure of a liquid will increase if the mass of liquid is increased.

113. The following are vapor pressures at 20°C . Predict the order of increasing normal boiling points of the liquids, acetone, 185 torr; ethanol, 44 torr; carbon disulfide, CS_2 , 309 torr.

114. Refer to Exercise 113. What is the expected order of increasing molar heats of vaporization, ΔH_{vap} , of these liquids at their boiling points? Account for the orders.

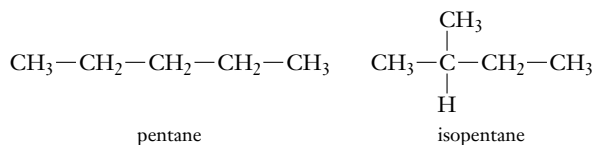
115. Refer to the sulfur phase diagram on page 536. (a) Can rhombic sulfur be sublimed? If so, under what conditions?

(b) Can monoclinic sulfur be sublimed? If so, under what conditions? (c) Describe what happens if rhombic sulfur is slowly heated from 80°C to 140°C at constant 1-atm pressure. (d) What happens if rhombic sulfur is heated from 80°C to 140°C under constant pressure of 5×10^{-6} atm?

116. The normal boiling point of ammonia, NH_3 , is -33°C , and its freezing point is -78°C . Fill in the blanks. (a) At STP (0°C , 1 atm pressure), NH_3 is a _____. (b) If the temperature drops to -40°C , the ammonia will _____ and become a _____. (c) If the temperature drops further to -80°C and the molecules arrange themselves in an orderly pattern, the ammonia will _____ and become a _____. (d) If crystals of ammonia are left on

the planet Mars at a temperature of -100°C , they will gradually disappear by the process of _____ and form a _____.

117. The van der Waals constants (Section 12-15) are $a = 19.01 \text{ L}^2\cdot\text{atm}/\text{mol}^2$, $b = 0.1460 \text{ L}/\text{mol}$ for pentane, and $a = 18.05 \text{ L}^2\cdot\text{atm}/\text{mol}^2$, $b = 0.1417 \text{ L}/\text{mol}$ for isopentane.



(a) Basing your reasoning on intermolecular forces, why would you expect a for pentane to be greater? (b) Basing your reasoning on molecular size, why would you expect b for pentane to be greater?

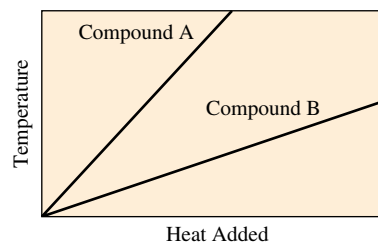
CONCEPTUAL EXERCISES

*118. Iodine sublimates at room temperature and pressure; water does not. Explain the differences you would expect to observe at room temperature if 5.0 grams of iodine crystals were sealed in a 10.-mL container and 5.0 mL of water were sealed in a similar container.

119. Referring to the phase diagram for carbon dioxide shown in Figure 13-17b for approximate values, draw a heating curve similar to that in Figure 13-15 for carbon dioxide at 1 atmosphere pressure. Draw a second heating curve for carbon dioxide at 5 atm pressure. Estimate the transition temperatures.

120. A popular misconception is that “hot water freezes more quickly than cold water.” In an experiment two 100.-mL samples of water, in identical containers, were placed far apart in a freezer at -25°C . One sample had an initial temperature of 78°C , while the other was at 24°C . The second sample took 151 minutes to freeze, and the warmer sample took 166 minutes. The warmer sample took more time but not much. How can you explain their taking about the same length of time to freeze?

121. Consider the portions of the heating curves shown here. Which compound has the highest specific heat capacity?



BUILDING YOUR KNOWLEDGE

122. More than 150 years ago Pierre Dulong and A. T. Petit discovered a *rule of thumb* that the heat capacity of one mole of a pure solid element is about 6.0 calories per °C (i.e., about 25 J/°C). A 100.2-g sample of an unknown metal at 99.9°C is placed in 50.6 g of water at 24.8°C. The temperature is 36.6°C when the system comes to equilibrium. Assume all heat lost by the metal is absorbed by the water. What is the likely identity of this metal?
123. In a flask containing dry air and some *liquid* silicon tetrachloride, SiCl₄, the total pressure was 988 torr at 225°C. Halving the volume of the flask increased the pressure to 1742 torr at constant temperature. What is the vapor pressure of SiCl₄ in this flask at 225°C?
124. A friend comes to you with this problem: “I looked up the vapor pressure of water in a table; it is 26.7 torr at 300 K and 92,826 torr at 600 K. That means that the vapor pressure increases by a factor of 3477 when the absolute temperature doubles over this temperature range. But I thought the pressure was proportional to the absolute temperature, $P = nRT/V$. The pressure doesn't just double. Why?” How would you help the friend?
125. Using as many as six drawings (frames) for each, depict the changes that occur at the molecular level during each of the following physical changes: (a) melting an ice cube, (b) sublimation of an ice cube below 4.6°C and 4.6 torr, and (c) evaporation of a droplet of water at room temperature and pressure.
126. Write the Lewis formula of each member of each of the following pairs. Then use VSEPR theory to predict the geometry about each central atom, and describe any features that lead you to decide which member of each pair would have the lower boiling point. (a) CH₃COOH and HCOOCH₃, (b) NHF₂ and BH₂Cl, (c) CH₃CH₂OH and CH₃OCH₃.
127. At its normal melting point of 271.3°C, solid bismuth has a density of 9.73 g/cm³ and liquid bismuth has a density of 10.05 g/cm³. A mixture of liquid and solid bismuth is in equilibrium at 271.3°C. If the pressure were increased from 1 atm to 10 atm, would more solid bismuth melt or would more liquid bismuth freeze? What unusual property does bismuth share with water?
128. The doping of silicon with boron to an atomic concentration of 0.0010% boron atoms vs. silicon atoms increases its conductivity by a factor of 10³ at room temperature. How many atoms of boron would be needed to dope 12.5 g of silicon? What mass of boron is this?