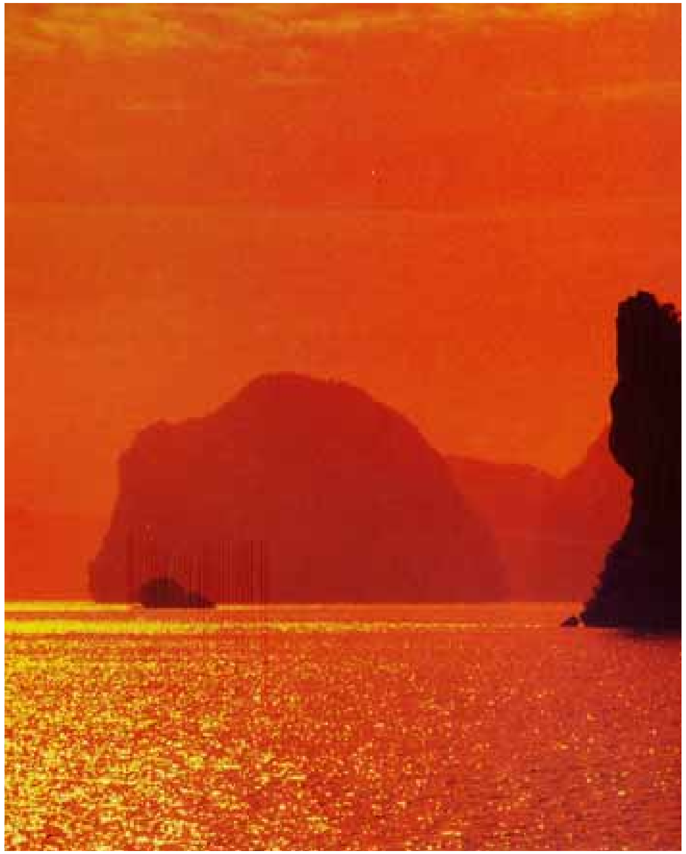
Chemistry

Zumdahl, 7th edition

歐亞書局

CH10 Liquids and Solids



Karst formation in Phang Nga Bay, Thailand at sunset. The Karst is limestone that has eroded into these formations rising out of the sea

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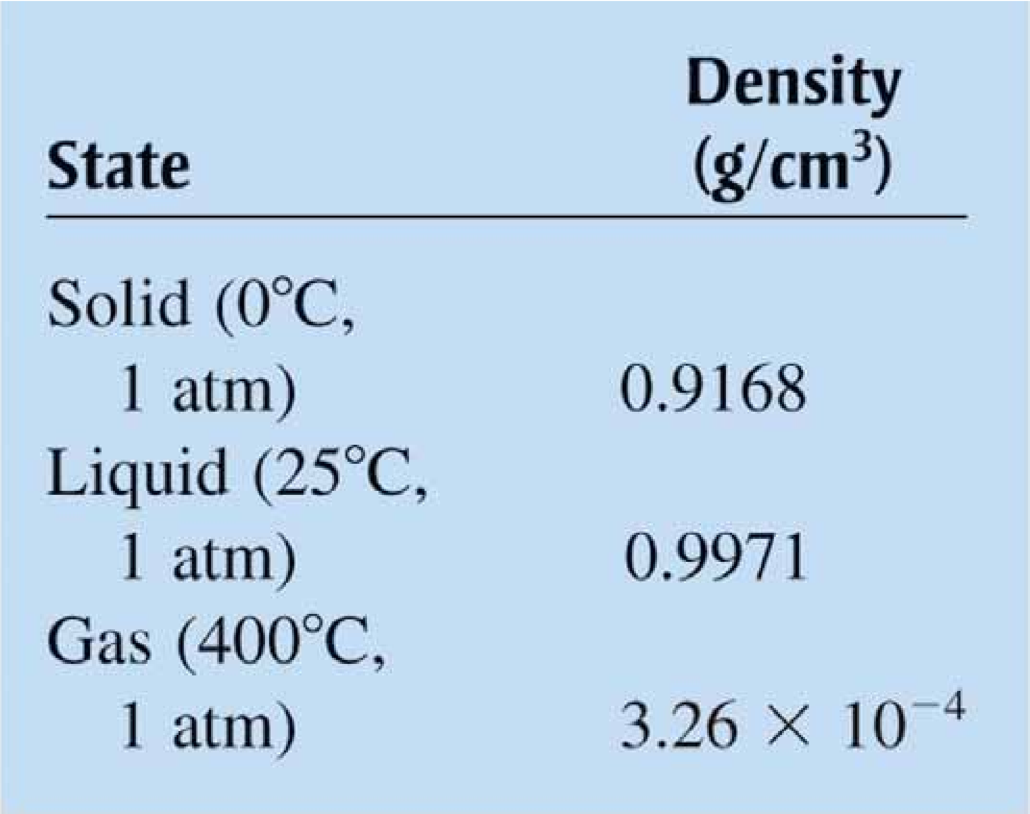
Introduction

- Solids are obviously very different from gases. A gas has low density and high compressibility and completely fills its container.
- Solids have much greater densities, are compressible only to a very slight extent, and are rigid—a solid maintains its shape irrespective of its container.
- As shown in Table 10.1, the densities for liquid and solid water are quite close.

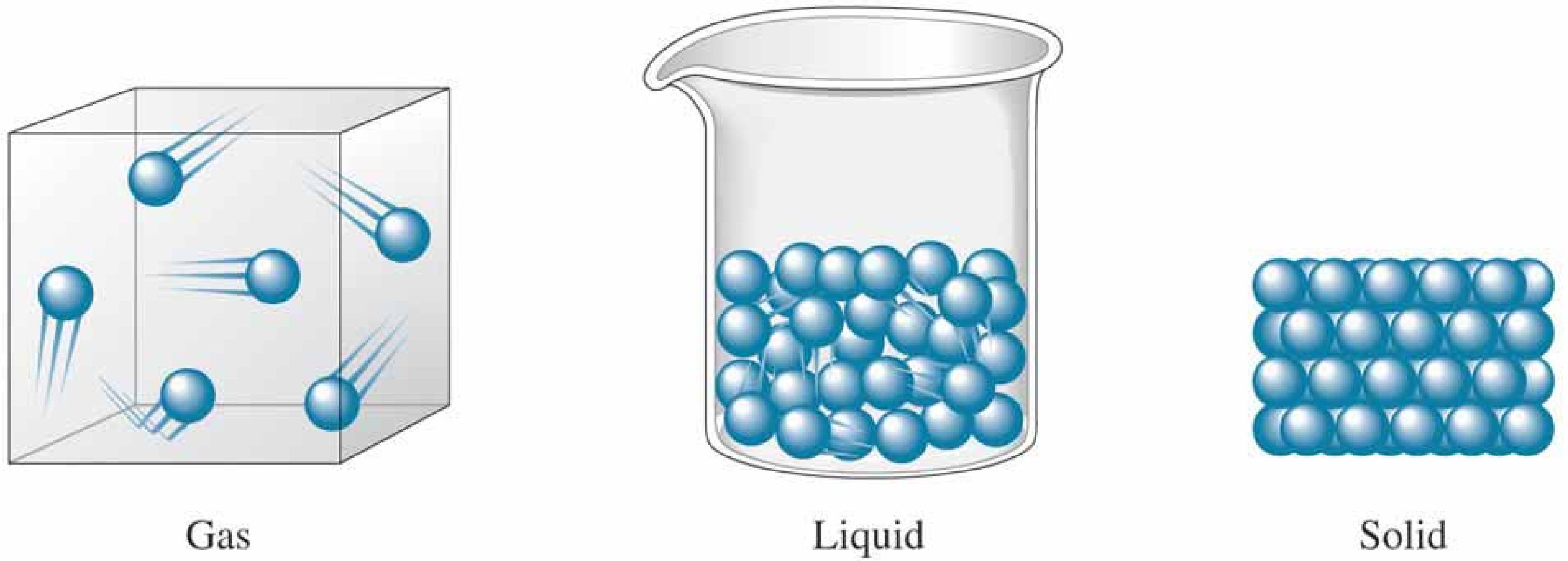
TABLE 10.1 Densities of the Three States of Water



State	Density (g/cm^3)
Solid (0°C, 1 atm)	0.9168
Liquid (25°C, 1 atm)	0.9971
Gas (400°C, 1 atm)	3.26×10^{-4}

- The liquid and solid states show many similarities and are strikingly different from the gaseous state, as shown schematically in Fig. 10.1.

Figure 10.1



Schematic representations of the three states of matter.

10.1 Intermolecular Forces

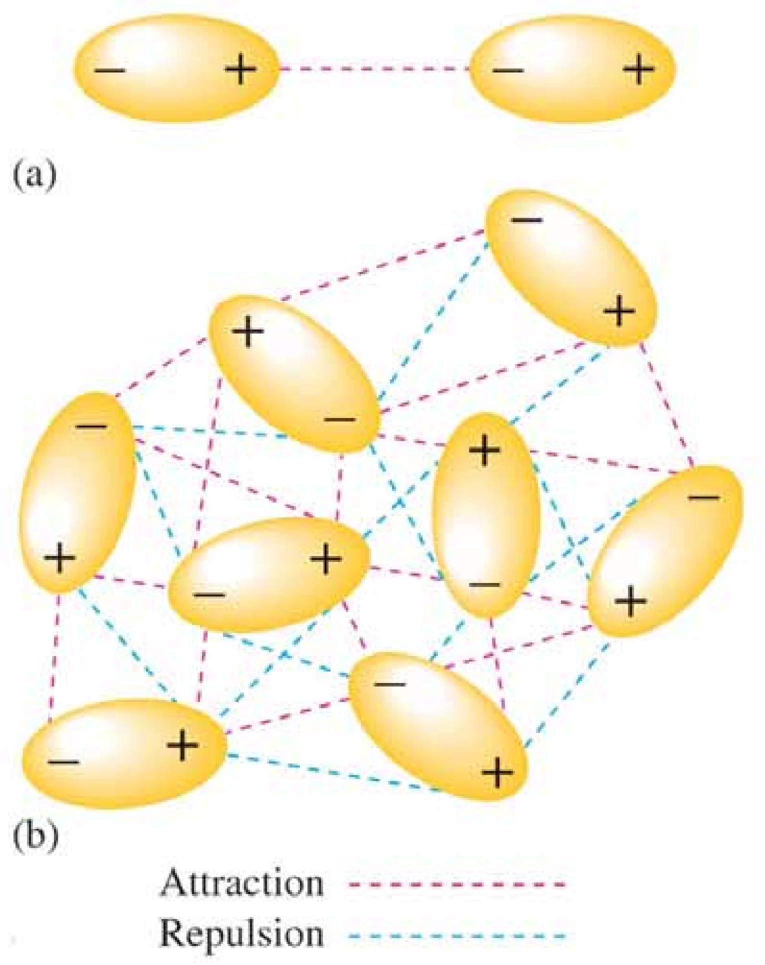
- atoms can form stable units called *molecules* by sharing electrons.
- This is called *intramolecular* (within the molecule) *bonding*.
- These forces may involve covalent or ionic bonding, or they may involve weaker interactions usually called **intermolecular forces**.

- It is important to recognize that when a substance such as water changes from solid to liquid to gas, *the molecules remain intact*.
- The changes in states are due to changes in the forces *among* the molecules rather than in those within the molecules.

Dipole-Dipole Forces

- Molecules with dipole moments can attract each other electrostatically by lining up so that the positive and negative ends are close to each other, as shown in Fig. 10.2(a).
- This is called a **dipole-dipole attraction**.
- The molecules orient themselves to maximize the ⊕… Θ interactions and to minimize ⊕…⊕ and Θ … Θ interactions, as represented in Fig. 10.2(b).

Figure 10.2

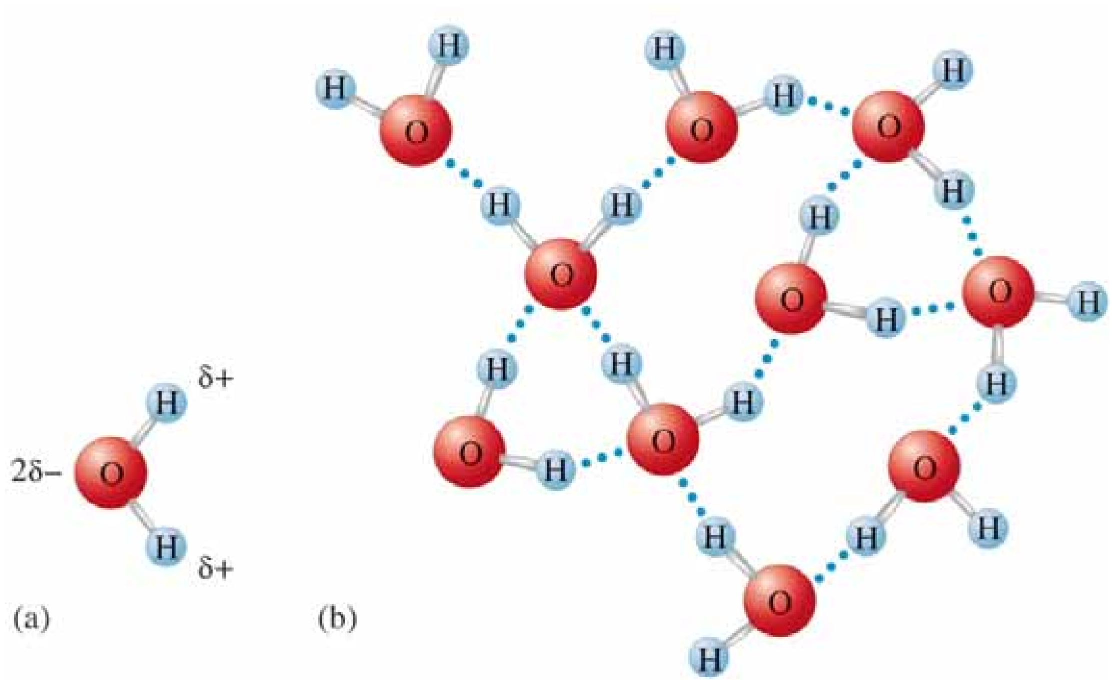


(a) The electrostatic interaction of two polar molecules. (b) The interaction of many dipoles in a condensed state.

- Two factors account for the strengths of these interactions: the great polarity of the bond and the close approach of the dipoles, allowed by the very small size of the hydrogen atom.
- Because dipole-dipole attractions of this type are so unusually strong, they are given a special name—**hydrogen bonding**.

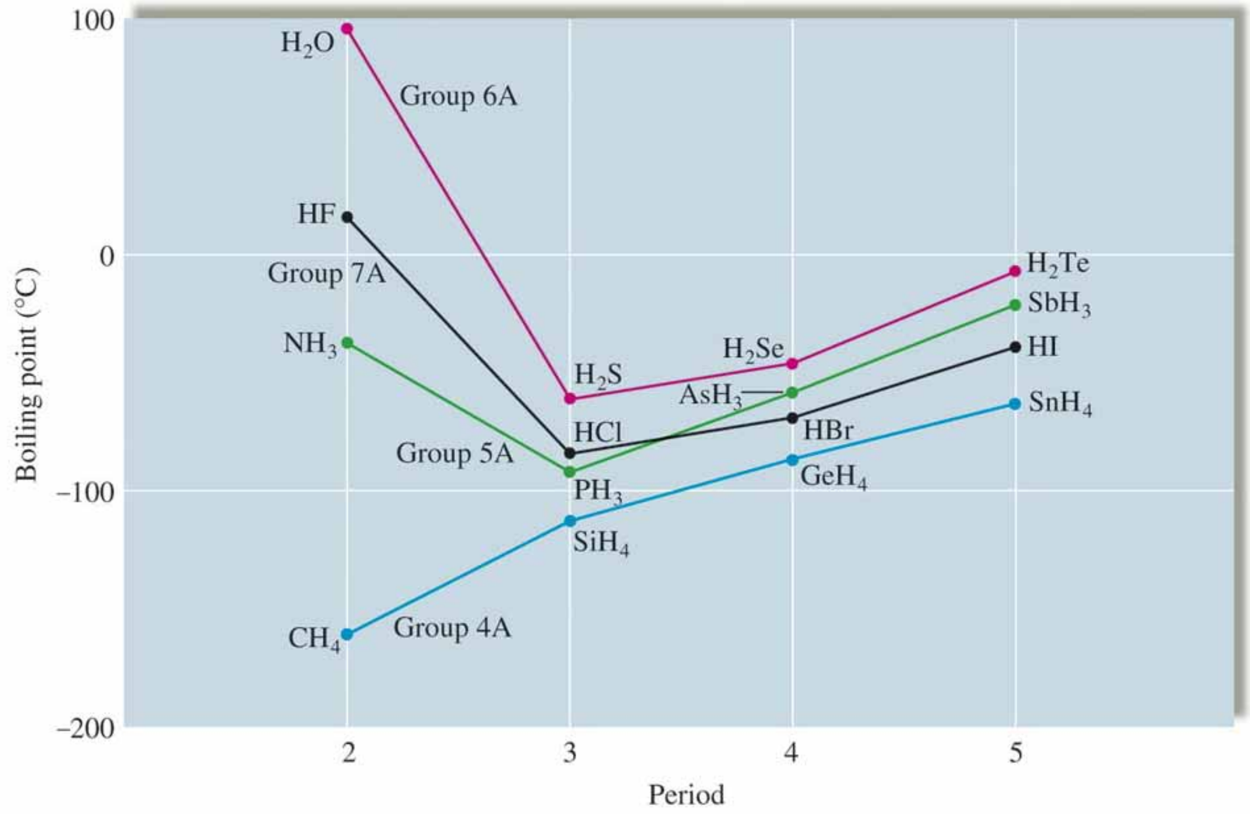
- Figure 10.3 shows hydrogen bonding among water molecules, which occurs between the partially positive H atoms and the lone pairs on adjacent water molecules.
- Hydrogen bonding has a very important effect on physical properties.
- The boiling points for the covalent hydrides of the elements in Groups 4A, 5A, 6A, and 7A are given in Fig. 10.4.

Figure 10.3



(a) The polar water molecule. (b) Hydrogen bonding among water molecules. Note that the small size of the hydrogen atom allows for close interactions.

Figure 10.4



The boiling points of the covalent hydrides of the elements in Groups 4A, 5A, 6A, and 7A.

- These unusually strong hydrogen bonding forces are due primarily to two factors.

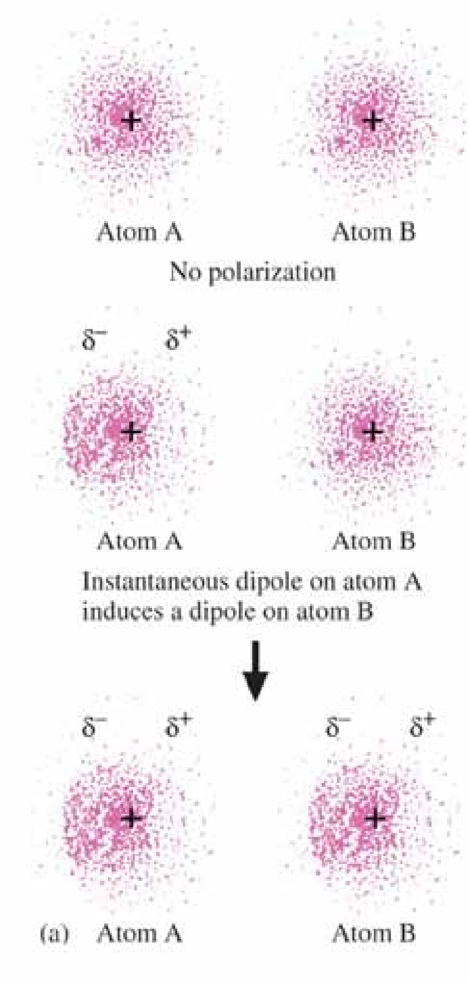
1. One factor is the relatively large electronegativity values of the lightest elements in each group, which leads to especially polar X-H bonds.
2. The second factors is the small size of the first element of each group, which allows for the close approach of the dipoles, further strengthening the intermolecular forces.

London Dispersion Forces

- The forces that exist among noble gas atoms and nonpolar molecules are called **London dispersion forces**.
- This instantaneous dipole that occurs accidentally in a given atom can then *induce* a similar dipole in a neighboring atom, as represented in Fig, 10.5(a).
- This phenomenon leads to an interatomic attraction that is relatively weak and short-lived but that can be very significant especially for large atoms.

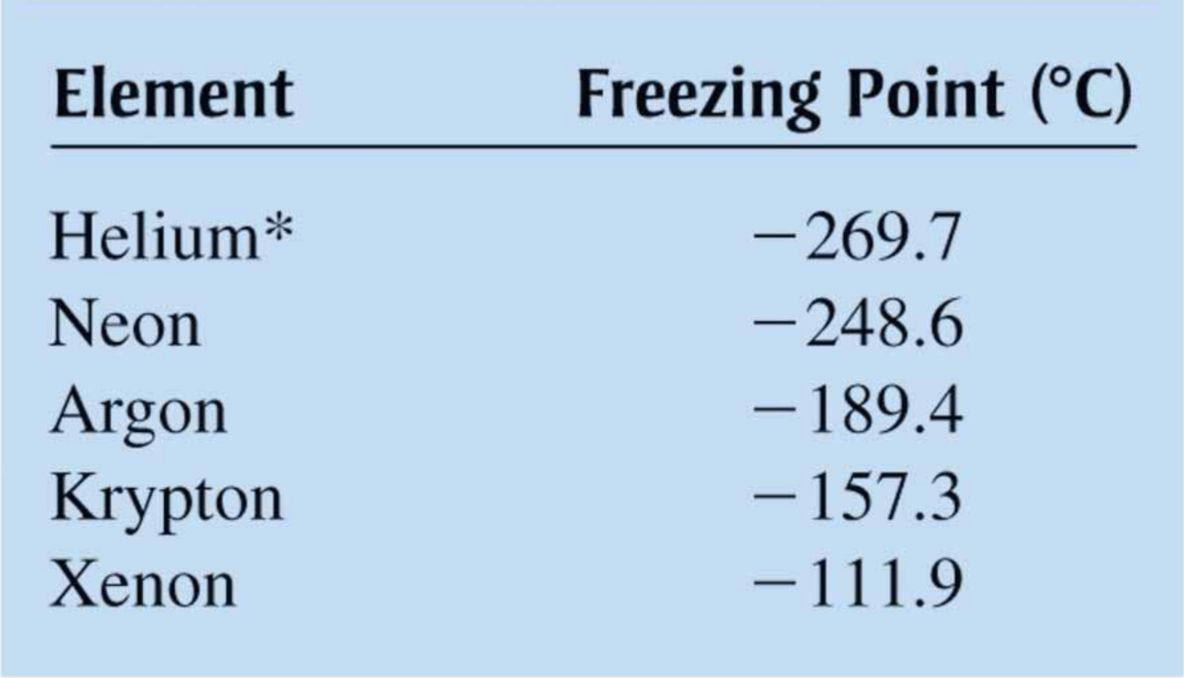
- For these interactions to become strong enough to produce a solid, the motions of the atoms must be greatly showed down.
- This explains, for instance, why the noble gas elements have such low freezing points (see Table 10.2).
- Note from Table 10.2 that the freezing point rises going down the group.

Figure 10.5



(a) An instantaneous polarization can occur on atom A, creating an instantaneous dipole. This dipole creates an induced dipole on neighboring atom B.

TABLE 10.2 The Freezing Points of the Group 8A Elements

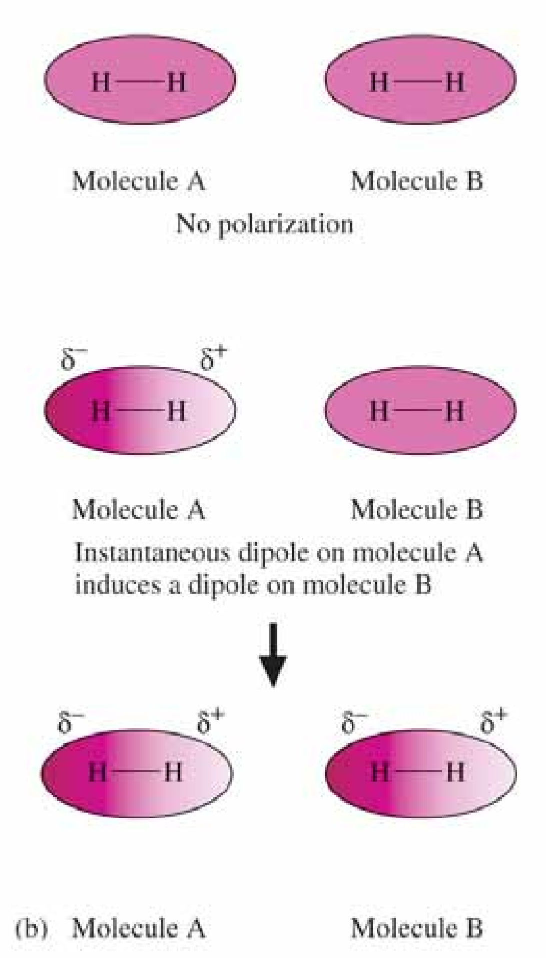


Element	Freezing Point (°C)
Helium*	−269.7
Neon	−248.6
Argon	−189.4
Krypton	−157.3
Xenon	−111.9

- Large atoms with many electrons exhibit a higher polariz-ability than small atoms.
- This means that the importance of London dispersion forces increase greatly as the size of the atom increase.
- These same ideas also apply to nonpolar molecules such as H_2, CH_4, CCl_4, and CO_2 [see Fig. 10.5(b)].

Figure 10.5

(b) Nonpolar molecules such as H_2 also can develop instantaneous and induced dipoles.

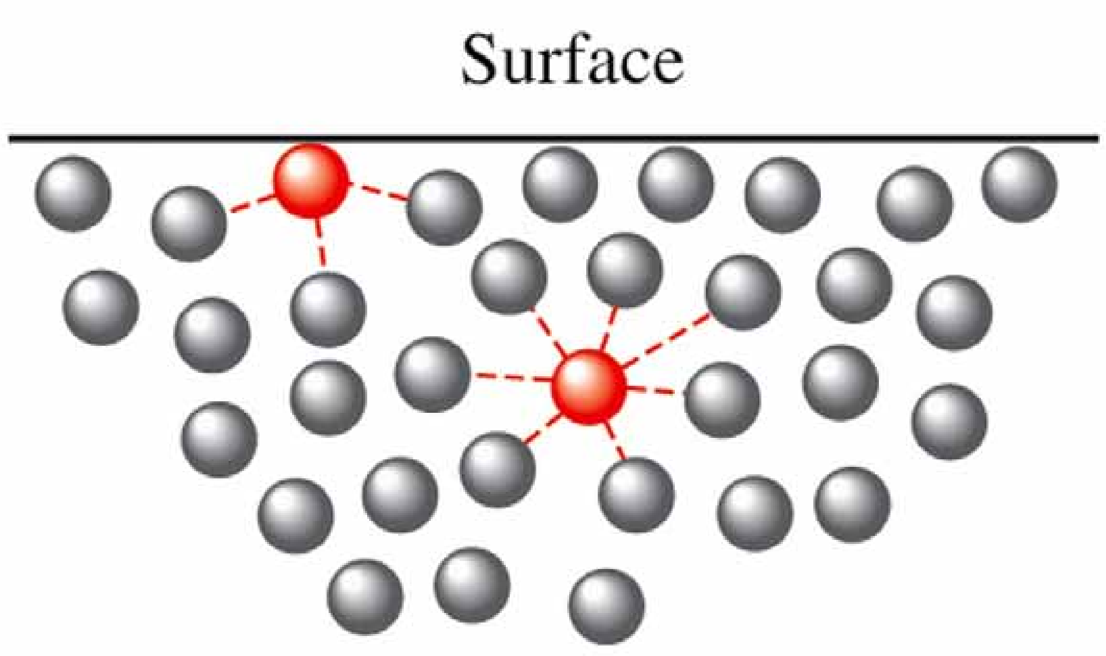


10.2 The Liquid State

- Liquids and liquid solutions are vital to our lives.
- Water is the most important liquid.
- Liquids exhibit many characteristics.
- Many of the properties of liquids give us direct information about the forces that exist among the particles.
- When a liquid is poured onto a solid surface, it tends to bead as droplets, a phenomenon that depends on the intermolecular forces.

- Although molecules in the interior of the liquid are completely surrounded by other molecules, those at the liquid surface are subject to attractions only from the side and from below (Fig. 10.6).
- The resistance of a liquid to an increase in its **surface area** is called the surface tension of the liquid.
- Polar liquids typically exhibit **capillary action**, the spontaneous rising of a liquid in a narrow tube.

Figure 10.6



A molecule in the interior of a liquid is attracted by the molecules surrounding it, whereas a molecule at the surface of a liquid is attracted only by molecules below it and on each side.

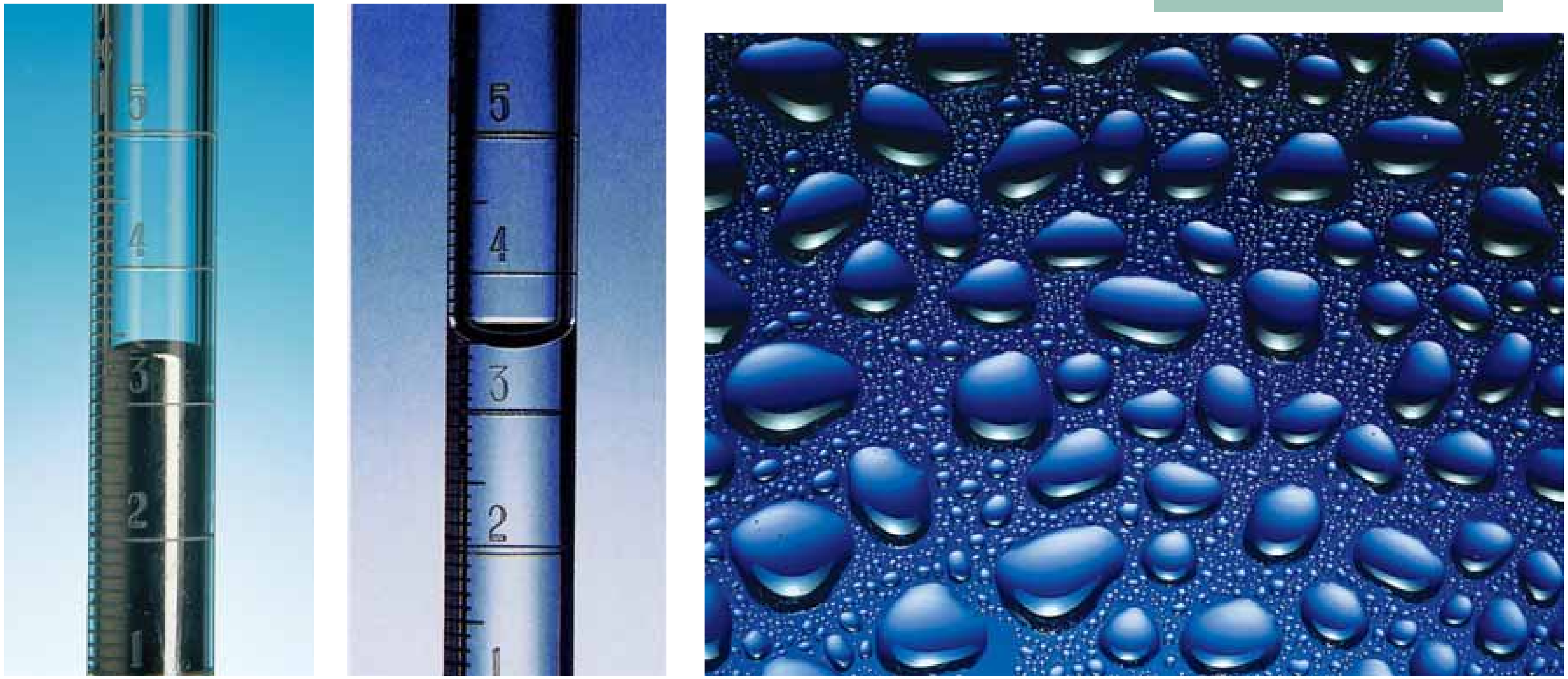
- Two different types of forces are responsible for this property:

1. *cohesive forces*, the intermolecular forces among the molecules of the liquid.
2. *adhesive forces*, the forces between the liquid molecules and their container.

- The concave shape of the meniscus (see Fig. 10.7) shows that water’s adhesive forces toward the glass are stronger than its cohesive forces.

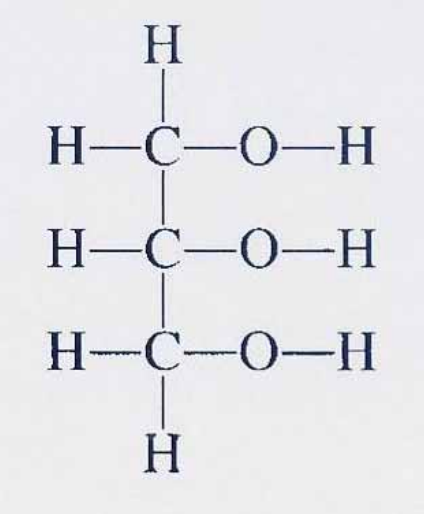
- A nonpolar liquid such as mercury (see Fig. 10.7) shows a convex meniscus.
- This behavior is characteristic of a liquid in which the cohesive forces are stronger than the adhesive forces toward glass.
- Another property of liquids strongly dependent on intermolecular forces is **viscosity**, a measure of a liquid’s resistance to flow.

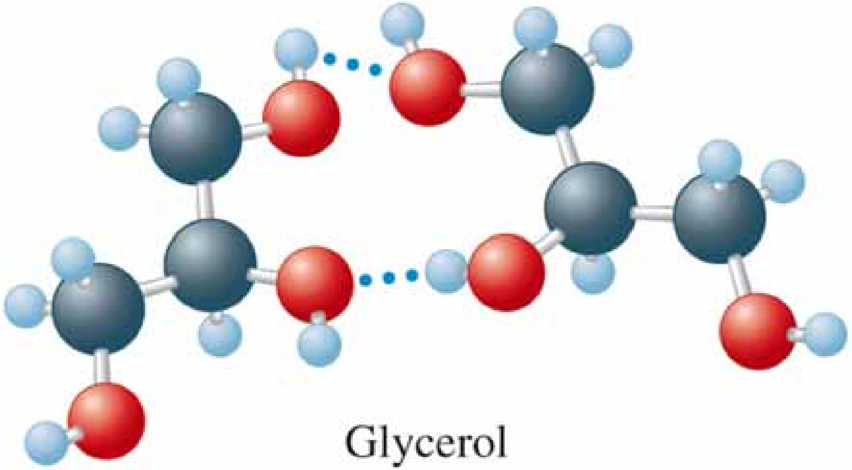
Figure 10.7



Nonpolar liquid mercury forms a convex meniscus in a glass tube, whereas polar water forms a concave meniscus.

- Another property of liquids strongly dependent on intermolecular forces is **viscosity**, a measure of a liquid’s resistance to flow.
- As glycerol,





Structural Model for Liquids

- The liquid state, has both strong intermolecular forces and significant molecular motions.
- Such a situation precludes the use of really simple models for liquids.
- Recent advances in spectroscopy, the study of the manner in which substances interact with electromagnetic radiation, make it possible to follow the very rapid changes that occur in liquids.

10.3 An Introduction to Structures and Types of Solids

- There are many ways to classify solids, but the broadest categories are **crystalline solids**, those with a highly regular arrangement of their components, and **amorphous solids**, those with considerable disorder in their structures.
- The regular arrangement of the components of a crystalline solid at the microscopic level produces the beautiful, characteristic shapes of crystals, such as those shown in Fig. 10.8.

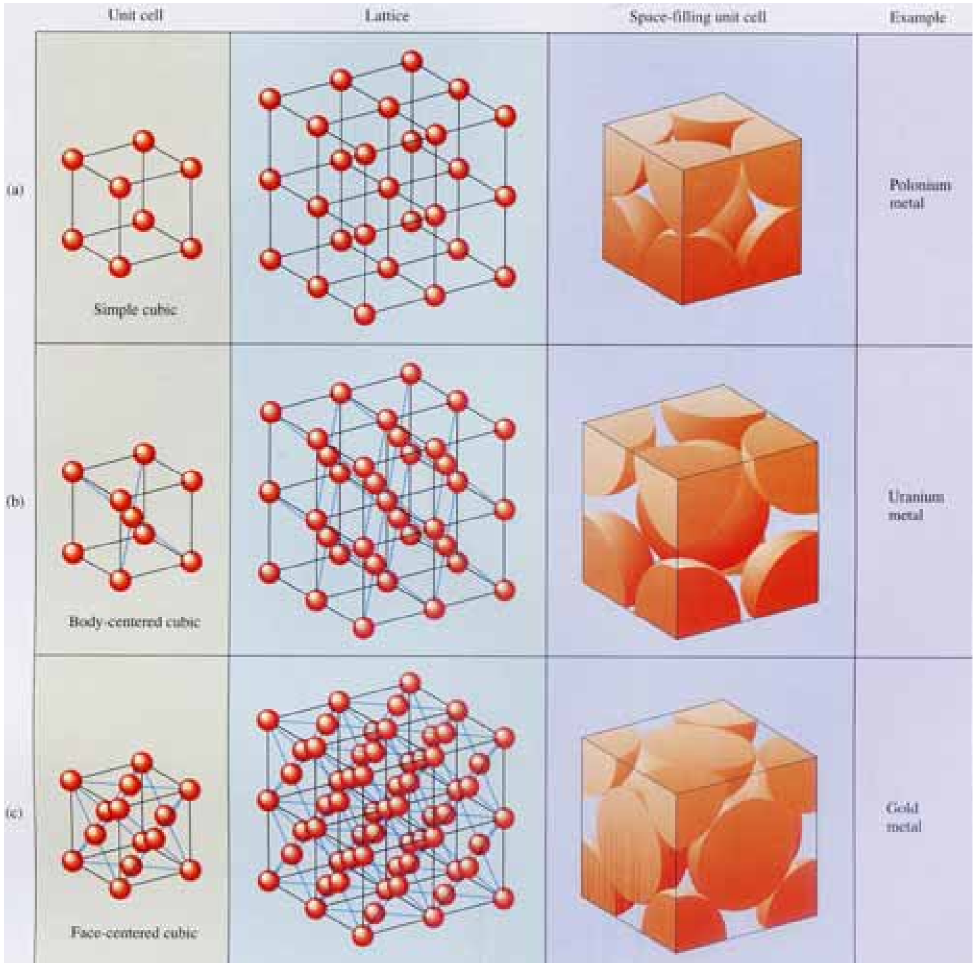
Figure 10.8

Two crystalline solids: pyrite (left), amethyst (right).

- The positions of the components in a crystalline solid are usually represented by a lattice,
- *The smallest repeating unit* of the lattice is called the **unit cell**.
- Three common unit cells and their lattices are shown in Fig. 10.9.

Figure 10.9

Three cubic unit cells and the corresponding lattices. Note that only parts of spheres on the corners and faces of the unit cells reside inside the unit cell, as shown by the "cutoff" versions.



X-Ray Analysis of Solids

- The structures of crystalline solids are most commonly determined by X-ray diffraction.
- When X ray of a single wavelength are directed at a crystal, a diffraction pattern is obtained, as we saw in Fig. 7.5.
- The light and dark areas on the photographic plate occur because the waves scattered from various atoms may reinforce or cancel each other (see Fig. 10.10).

Figure 10.10

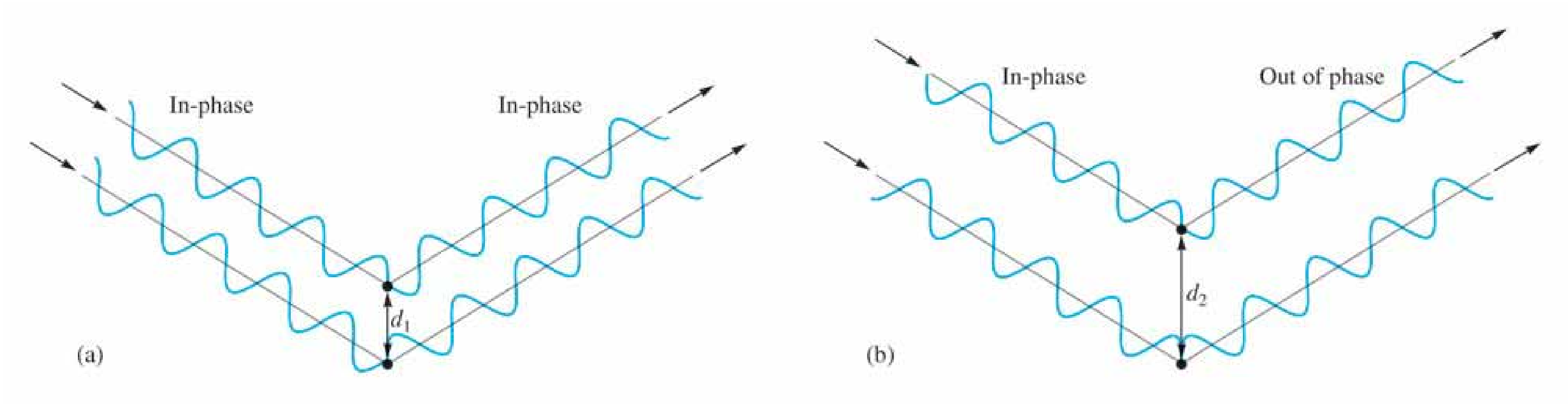
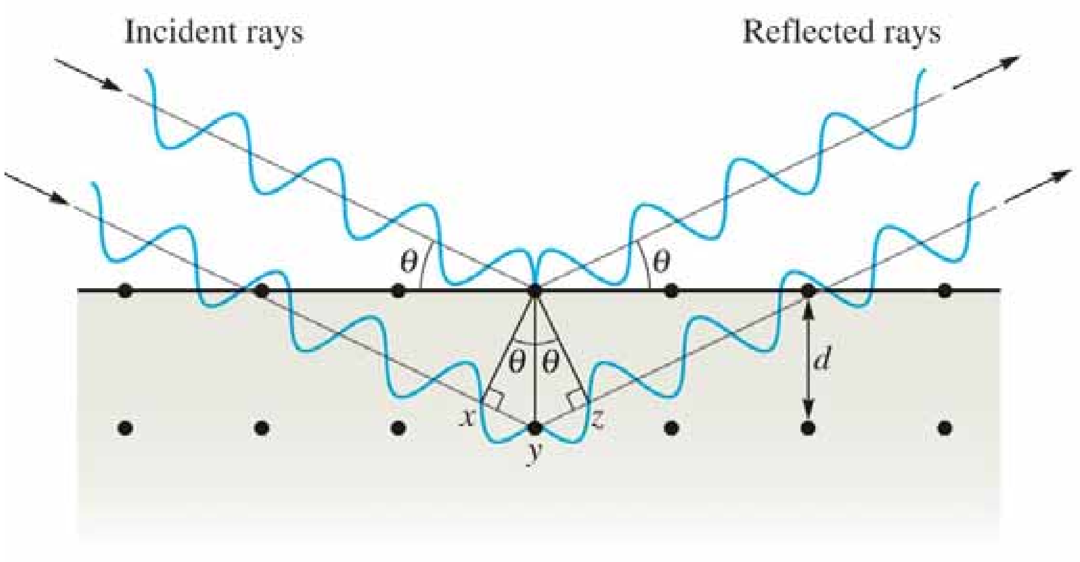


Figure 10.10

X rays scattered from two different atoms may reinforce (constructive interference) or cancel (destructive interference) one another. (a) Both the incident rays and the reflected rays are also in phase. In this case, d_1 is such that the difference in the distances traveled by the two rays is a whole number of wavelengths. (b) The incident rays are in phase but the reflected rays are exactly out of phase. In this case d_2 is such that the difference in distances traveled by the two rays is an odd number of half wavelengths.

- Since the distance traveled depends on the distance between the atoms, the diffraction pattern can be used to determine the interatomic spacings.
- The exact relationship can be worked out using the diagram in Fig. 10.11, which shows two in-phase waves being reflected by atoms in two different layers in a crystal.

Figure 10.11



Reflection of X rays of wavelength λ from a pair of atoms in two different layers of a crystal. The lower wave travels an extra distance equal to the sum of *xy* and *yz*. If this distance is an integral number of wavelengths (*n*=1, 2, 3…), the waves will reinforce each other when they exit the crystal.

- The extra distance traveled by the lower wave is the sum of the distances xy and yz,

$$xy + yz \longrightarrow n\lambda \qquad (10.1)$$

$$xy + yz \longrightarrow 2d\sin\theta \qquad (10.2)$$

$$n\lambda = 2d\sin\theta \qquad (10.3)$$

- Equation (10.3) is called the Bragg equation after William Henry Bragg (1862-1942) and his son William Lawrence Bragg (1890-1972), who shared the Nobel Prize in physics in 1915 for their pioneering work in x-ray crystallography.

Sample Exercise 10.1

Using the Bragg Equation

X rays of wavelength 1.54Å were used to analyze an aluminum crystal. A reflcetion was produced at $\theta = 19.3$ degrees. Assuming $n = 1$, calculate the distance d between the planes of atoms producing this reflection.

Solution

To determine the distance between the planes, we use Equation (10.3) with $n = 1$, $\lambda = 1.54$Å, and $\theta = 19.3$ degrees. Since $2d \sin\theta = n\lambda$,

Sample Exercise 10.1

$$d = \frac{n\lambda}{2 \sin \theta} = \frac{(1)(1.54 \text{ Å})}{(2)(0.3305)} = 2.33 \text{ Å} = 233 \text{ pm}$$

Graduate student Maria Zhuravlera operating an X-ray diffractometer at Michigan State University.

See Exercises 10.41 through 10.44.

Types of Crystalline Solids

- There are many different types of crystalline solids.
- Two important types of solids:

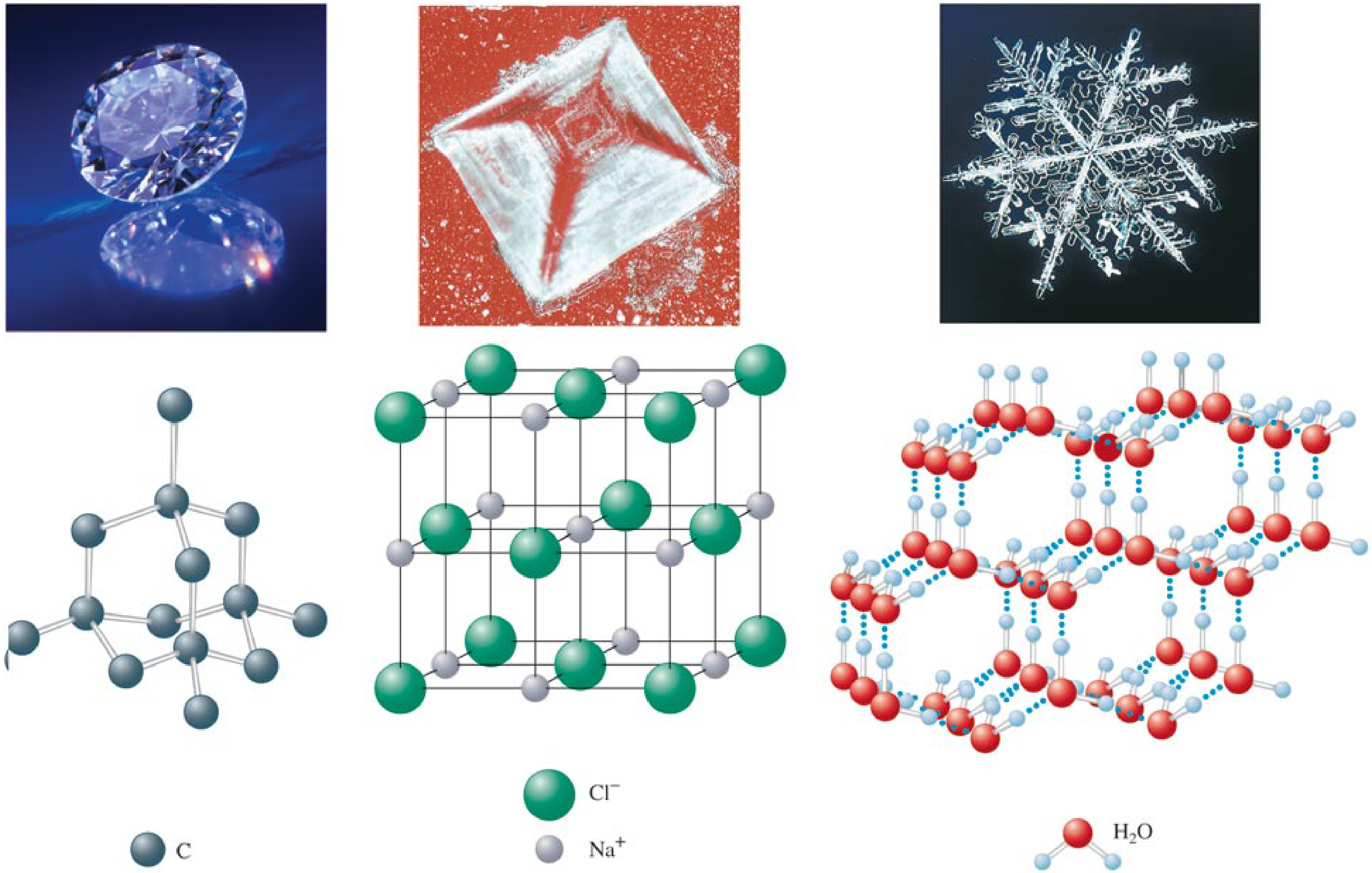
1. **ionic solids**, represented by sodium chloride (NaCl),
2. and **molecular solids**, represented by sucrose.

- Ionic solids have ions at the points of the lattice that describes the structure of the solid.
- A molecular solid, has discrete covalently bonded molecules at each of its lattice points.

- Ice is a molecular solid that has an H_2O molecule at each point (see Fig. 10.12).
- A third type of solid is represented by elements such as carbon (which exists in the forms graphite, diamond, and the fullerenes), boron, silicon, and all metals.
- These substances all have atoms at the lattice points that describe the structure of the solid.
- We call solids of this type **atomic solids**.

- Examples of these three types of solids are shown in Fig. 10.12.
- The classification of solids is summarized in Table 10.3.

Figure 10.12

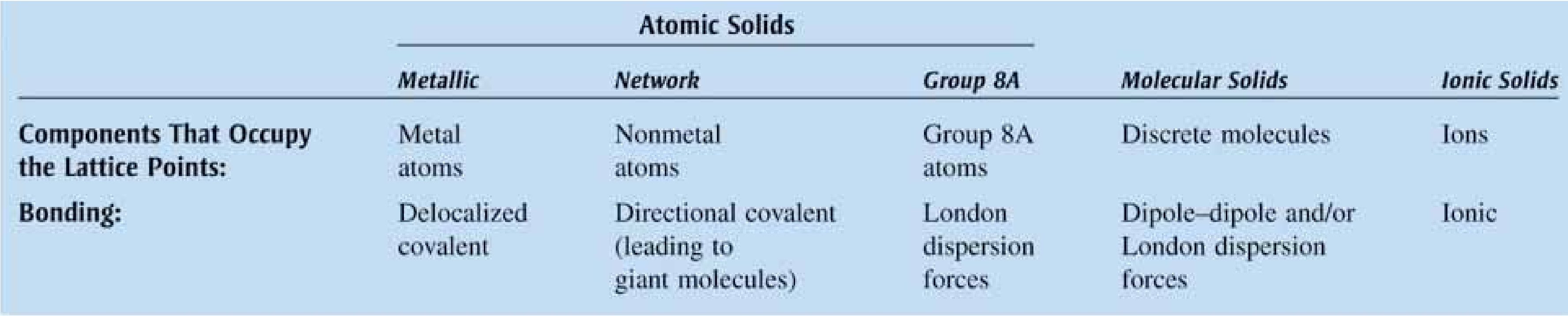


(a) Diamond (b) Sodium chloride (c) Ice

Figure 10.12

Examples of three types of crystalline solids. Only part of the structure is shown in each case. (a) An atomic solid. (b) An ionic solid. (c) A molecular solid. The dotted lines show the hydrogen bonding interactions among the polar water molecules.

TABLE 10.3 Classification of Solids

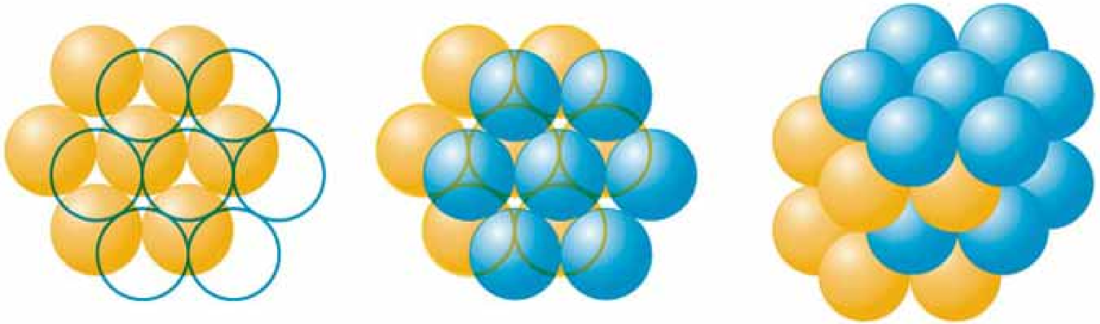


	Atomic Solids				
	Metallic	*Network*	*Group 8A*	*Molecular Solids*	*Ionic Solids*
Components That Occupy the Lattice Points:	Metal atoms	Nonmetal atoms	Group 8A atoms	Discrete molecules	Ions
Bonding:	Delocalized covalent	Directional covalent (leading to giant molecules)	London dispersion forces	Dipole–dipole and/or London dispersion forces	Ionic

10.4 Structure and Bonding in Metals

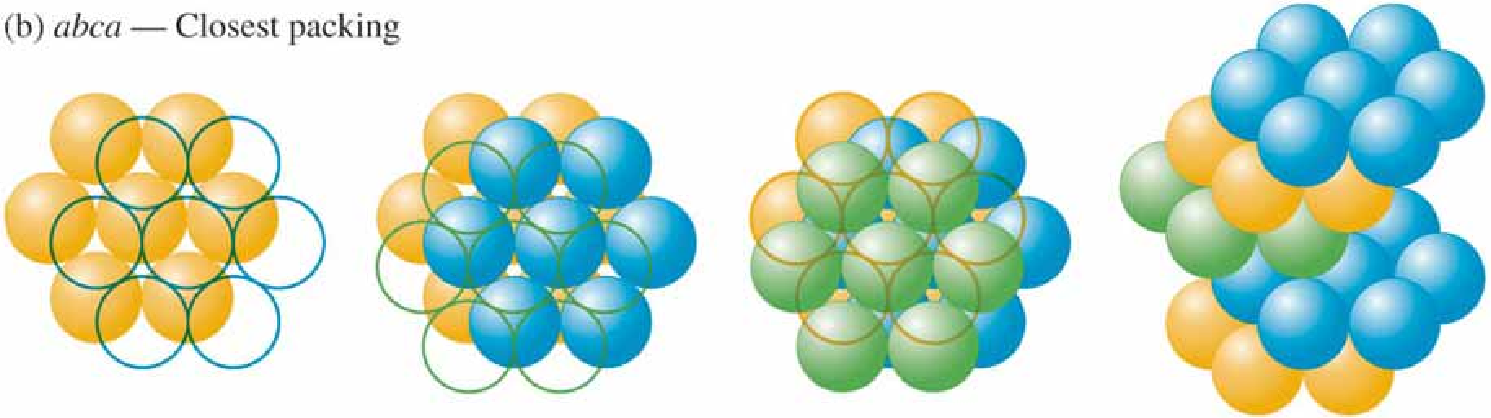
- A metallic crystal can be pictured as containing spherical atoms packed together and bonded to each other equally in all directions.
- Such an arrangement is called **closest packing**.
- The spheres are packed in layers, as shown in Fig. 10.13, in which each sphere is surrounded by six others.

Figure 10.13



Top view Top view Side view

(b) *abca* — Closest packing



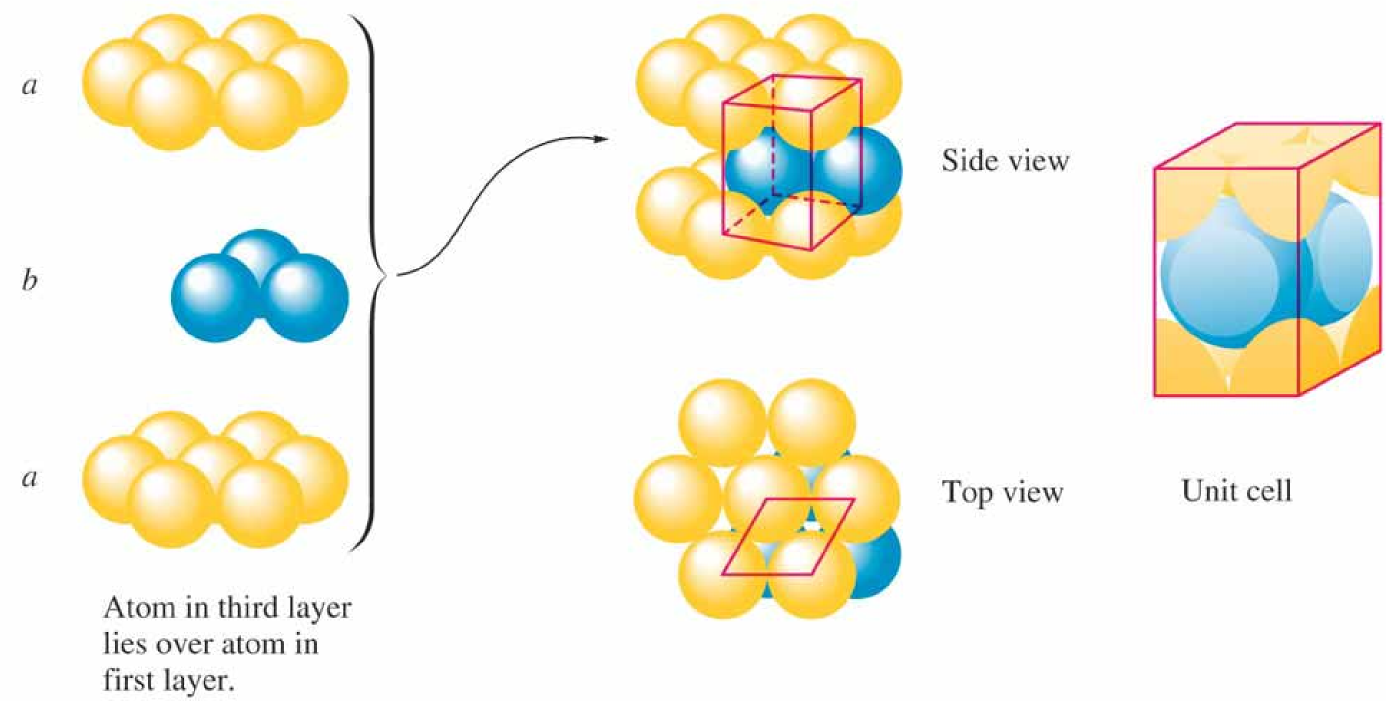
Top view Top view Top view Side view

Figure 10.13

The closest packing arrangement of uniform spheres. In each layer a given sphere is surrounded by six others, creating six dimples, only three of which can be occupied in the next layer. (a) aba packing: The second layer is like the first, but it is displaced so that each sphere in the second layer occupies a dimple in the first layer. The spheres in the third layer occupy dimples in the second layer lie directly over those in the first layer (aba). (b) abc packing: The spheres in the third layer occupy dimples in the second layer so that no spheres in the third layer lie above any in the first layer (abc). The fourth layer is like the first.

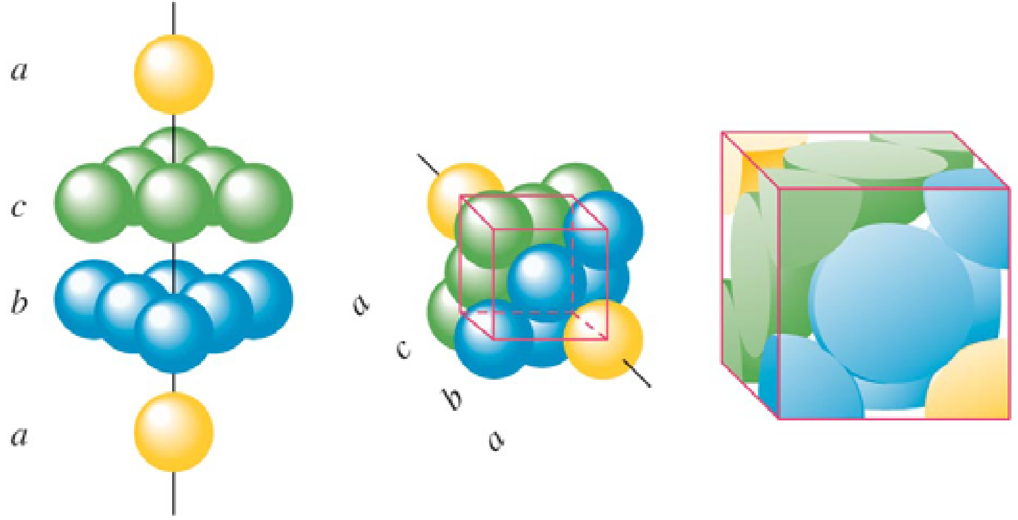
- The *aba* arrangement has the *hexagonal* unit cell shown in Fig. 10.14, and the resulting structure is called the **hexagonal closest packed (hcp) structure**.
- The *abc* arrangement has a face-centered cubic unit cell, as shown in Fig. 10.15, and the resulting structure is called the **cubic closest packed (ccp) structure**.

Figure 10.14



When spheres are closest packed so that the spheres in the third layer are directly over those in the first layer (*aba*), the unit cell is the hexagonal prism illustrated here in red.

Figure 10.15



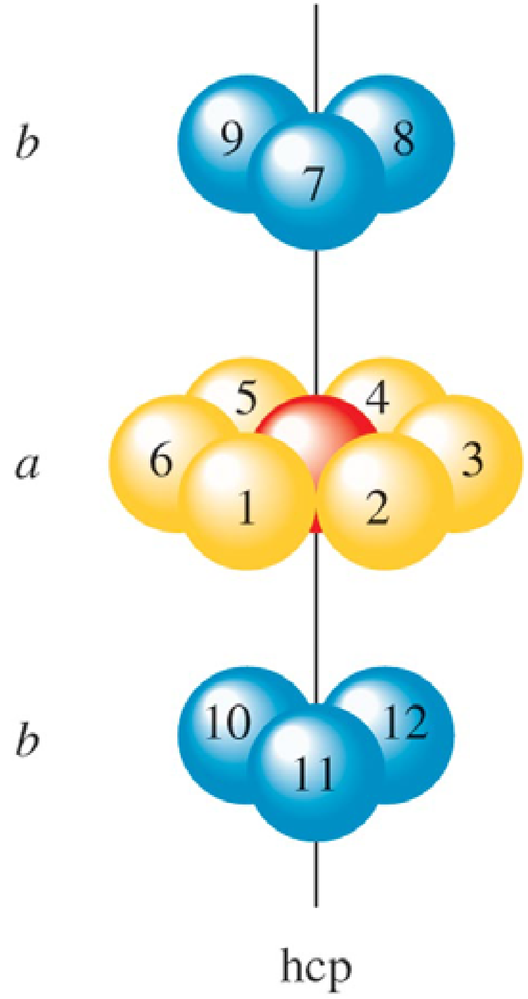
An atom in every fourth layer lies over an atom in the first layer.

Unit cell

When spheres are packed in the *abc* arrangement, the unit cell is face-centered cubic. To make the cubic arrangement easier to see, the vertical axis has been tilted as shown.

- Note that in the hcp structure the spheres in every other layer occupy the same vertical position (*ababab*…), where in the ccp structure the spheres in every fourth layer occupy the same vertical position (*abcabca*…).
- A characteristic of both structures is that each sphere has 12 equivalent nearest neighbors: 6 in the same layer, 3 in the layer above, and 3 in the layer below (that form the dimples).
- This is illustrated for the hcp structure in Fig. 10.16.

Figure 10.16



The indicated sphere has 12 nearest neighbors.

- Face-centered cubic unit cell (Fig. 10.17): this unit cell is defined by the *centers* of the sphere on the cube’s corners.
- Thus 8 cubes share a given sphere, so 1/8 of this sphere lies inside each unit cell.
- The net number of spheres in a face-centered cubic unit cell is

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

Figure 10.17

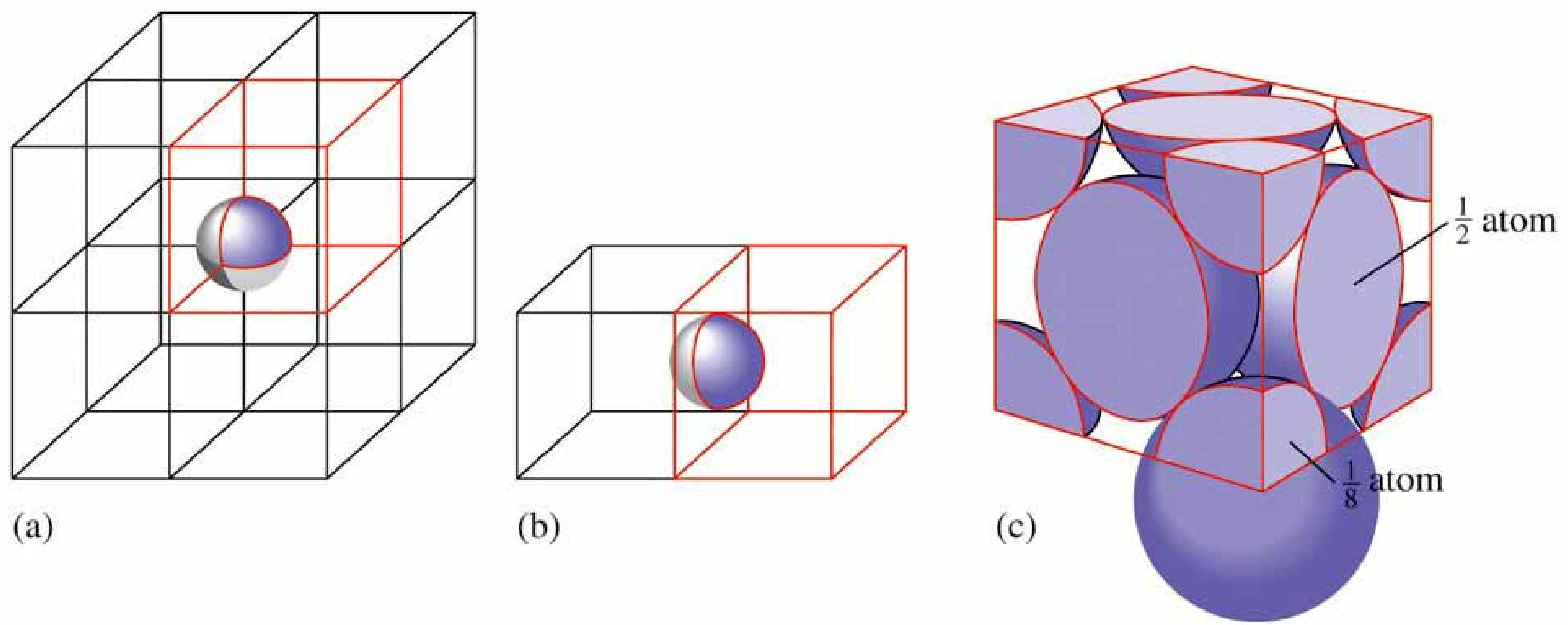


Figure 10.17

The net number of spheres in a face-centered cubic unit cell. (a) Note that the sphere on a corner of the colored cell is shared with 7 order unit cells (a total of 8). Thus 1/8 of such a sphere lies within a given unit cell. Since there are 8 corners in a cube, there are 8 of these 1/8 pieces, or 1 net sphere. (b) The sphere on the center of each face is shared by 2 unit cells, and thus each unit cell has ½ of each of these types of spheres. There are 6 of these ½ spheres to give 3 net spheres. (c) Thus the face-centered cubic unit cell contains 4 net spheres (all of the pieces can be assembled to give 4 spheres.)

Sample Exercise 10.2

Calculating the Density of a Closest Packed Solid

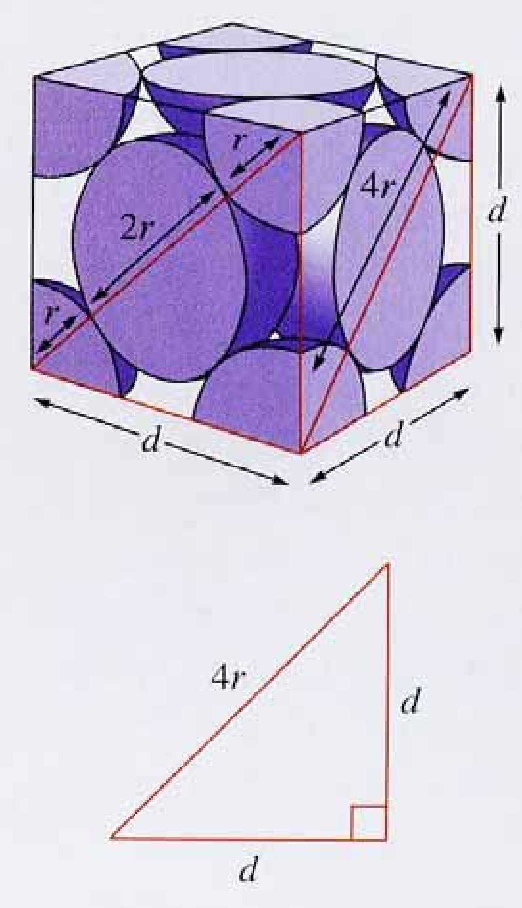
Sliver crystallizes in a cubic closest packed structure. The radius of a silver atom is 144 pm. Calculate the density of solid silver.

Solution

Density is mass per unit volume. Thus we need to know how many silver atoms occupy a given volume in the crystal. The structure is cubic closest packed, which means the unit cell is face0centered cubic, as shoen in the accompanying figure.

Sample Exercise 10.2

We must find the volume of this unit cell for silver and the net number of atoms it contains. Note that in this structure the atoms touch along the diagonals for each face and not along the edges of the cube. Thus the length of the diagonal is $r + 2r + r$, or $4r$. We use this fact to find the length of the edge of the cube by the Pythagorean theorem:



Sample Exercise 10.2

$$
\begin{aligned}
d^2 + d^2 &= (4r)^2 \\
2d^2 &= 16r^2 \\
d^2 &= 8r^2 \\
d &= \sqrt{8r^2} = r\sqrt{8}
\end{aligned}
$$

Since r ＝144 pm for a silver atom,

$$d = (144\ \text{pm})(\sqrt{8}) = 407\ \text{pm}$$

The volume of the unit cell is d^3, which is (407 pm)^3, or 6.74×10^7 pm^3. We convert this to cubic centimeters as follows:

Sample Exercise 10.2

$$6.74 \times 10^{7}\ \text{pm}^3 \times \left(\frac{1.00 \times 10^{-10}\ \text{cm}}{\text{pm}}\right)^3 = 6.74 \times 10^{-23}\ \text{cm}^3$$

Since we know that the net number of atoms in the face-centered cubic until cell is 4, we have 4 silver atoms contained in a volume of 6.74×10^{-23} cm^3. The density is therefore

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{(4\ \text{atoms})(107.9\ \text{g/mol})(1\ \text{mol}/6.022 \times 10^{23}\ \text{atoms})}{6.74 \times 10^{-23}\ \text{cm}^3}$$
$$= 10.6\ \text{g/cm}^3$$

Sample Exercise 10.2

Crystalline silver contains cubic closest packed silver atoms.

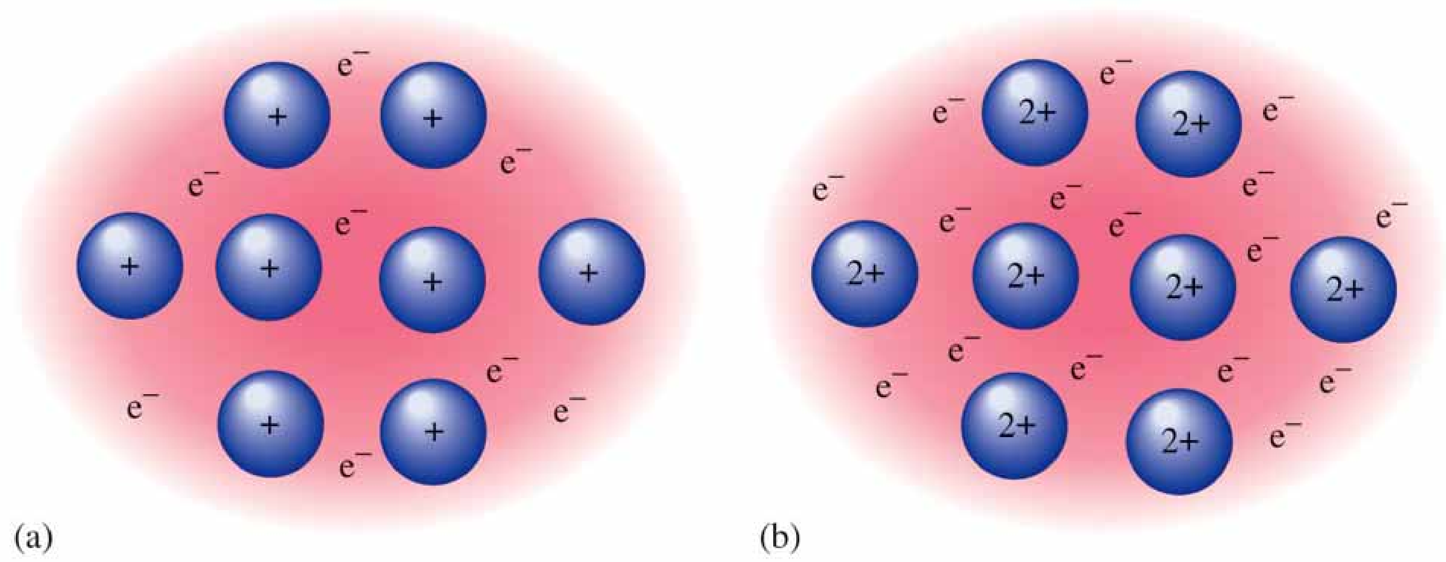
See Exercises 10.45 through 10.48.

- Examples of metals that form cubic closest packed solids are aluminum, iron, copper, cobalt, and nickel.
- Magnesium and zinc are hexagonal closest packed.
- Calcium and certain other metals can crystallize in either of these structures.
- The alkali metals have structures characterized by a *body-centered cubic (bcc) unit cell* (see Fig. 10.9),

Bonding Models for Metals

- The bonding in most metals is both *strong and nondirectional*.
- The simplest pictures that explains these observations is the *electron sea model*, which envisions a regular array of metal cations in a “sea” of valence electrons (see Fig. 10.18).

Figure 10.18



The electron sea model for metals postulates a regular array of cations in a “sea” of valence electrons. (a) Representation of an alkali metal (Group 1A) with one valence electron. (b) Representation of an alkaline earth metal (Group 2A) with two valence electrons.

- A related model that gives a more detailed view of the electron energies and motions is the **band model**, or **molecular orbital (MO) model**, for metals.
- In this model, the electrons are assumed to travel around the metal crystal in molecular orbitals formed from the valence atomic orbitals of the metal atoms (Fig. 10.19).

- When many metal atoms interact, as in a metal crystal, the large number of resulting molecular orbitals become more closely spaced and finally form a virtual continuum of levels, called bands, as shown in Fig. 10.19.

Figure 10.19

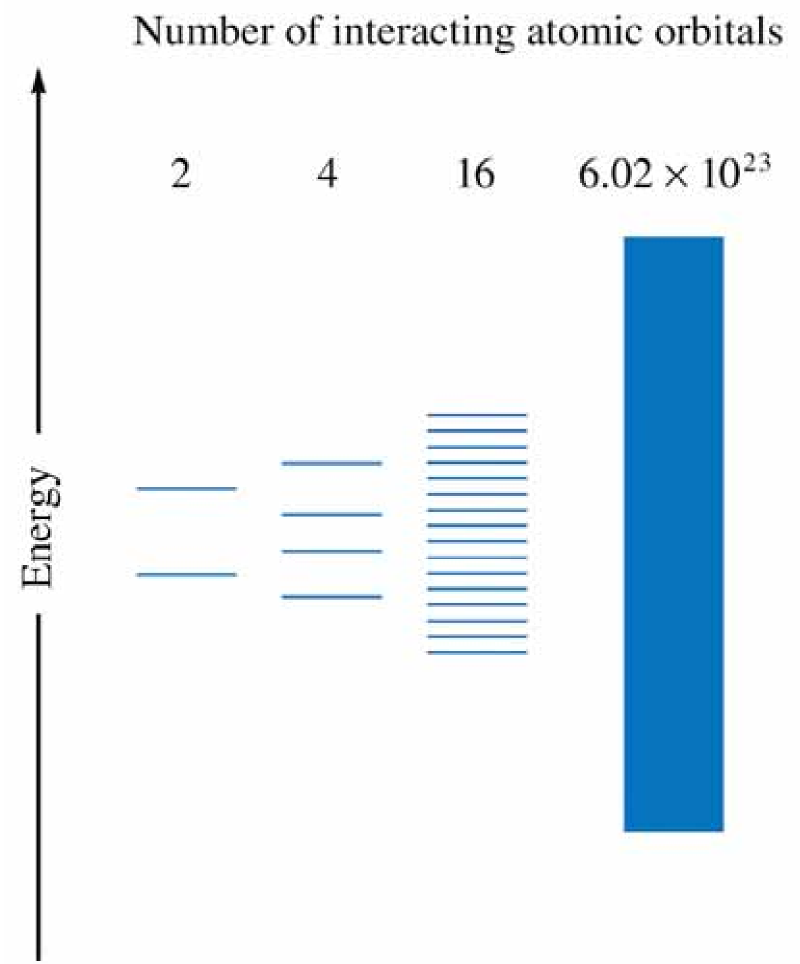

Number of interacting atomic orbitals
Energy
2
4
16
6.02 × 10²³

Figure 10.19

The molecular orbital energy levels produced when various numbers of atomic orbitals interact. Note that for two atomic orbitals two rather widely spaced energy levels result. (Recall the description of H_2 in Section 9.2.) As more atomic orbitals are available to form molecular orbitals, the resulting energy levels are more closely spaced, finally producing a band of very closely spaced orbitals.

- Since each magnesium atom has one 3*s* and three 3*p* valence atomic orbitals, a crystal with n magnesium atoms has available *n*(3*s*) and 3*n*(3*p*) orbitals to form the molecular orbitals, as illustrated in Fig. 10.20.
- The molecular orbitals occupied by these conducting electrons are called *conduction bands*.

Figure 10.20

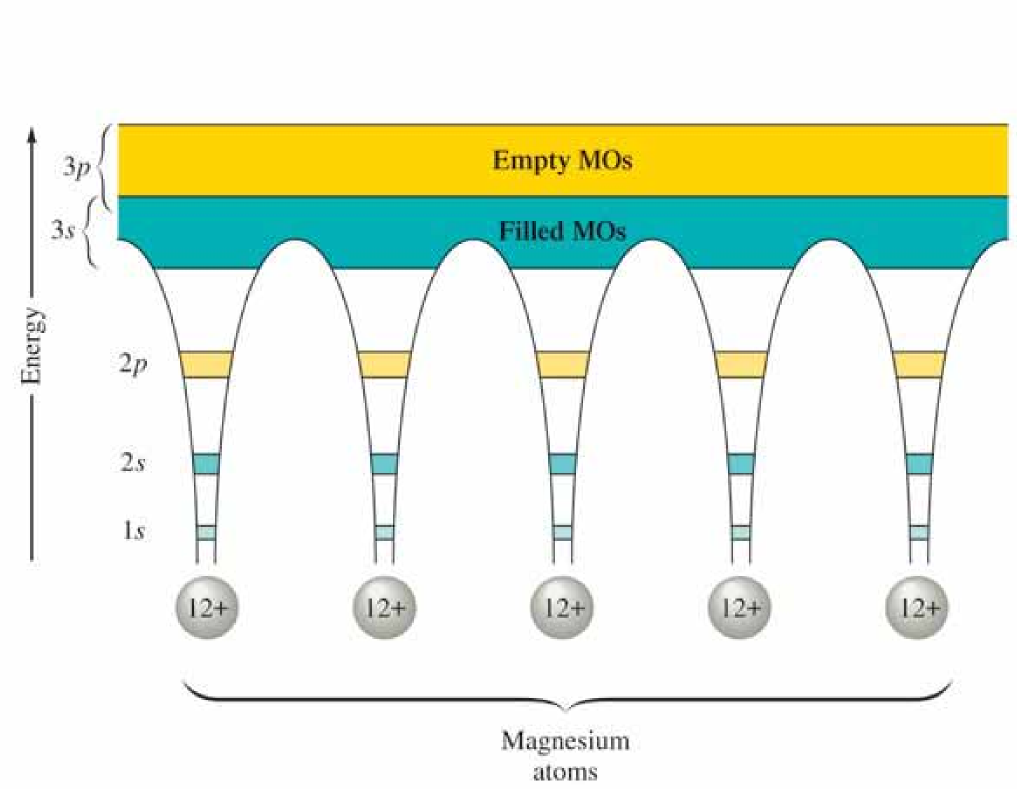

Empty MOs
Filled MOs
3p
3s
Energy
2p
2s
1s
12+
12+
12+
12+
12+
Magnesium atoms

Figure 10.20

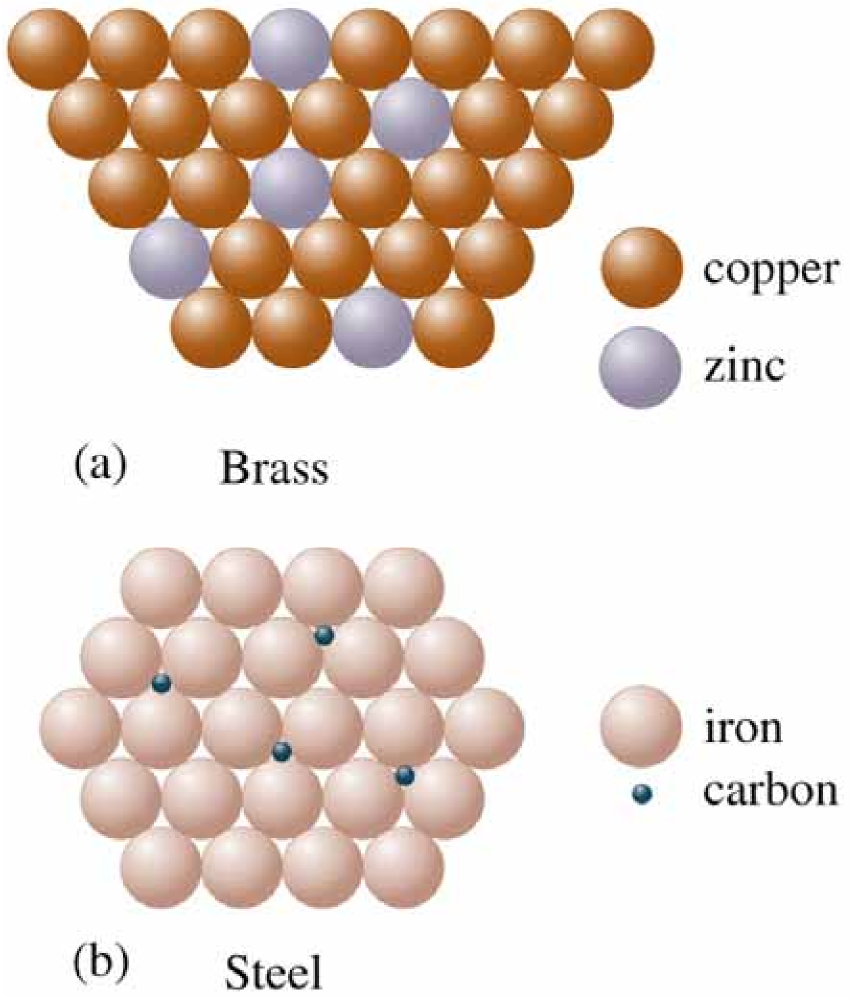
(left) A representation of the energy levels (bands) in a magnesium crystal. The electrons in the 1*s*, 2*s*, and 2*p* orbitals are close to the nuclei and thus are localized on each magnesium atom as shown. However, the 3*s* and 3*p* valence orbitals overlap and mix to form molecular orbitals. Electrons in these energy levels can travel throughout the crystal. (right) Crystals of magnesium grown from a vapor.

Metal Alloys

- An **alloy** is best defined as *a substance that contains a mixture of elements and has metallic properties*.
- Alloys can be conveniently classified into two types.

1. In a **substitutional alloy**, some of the host metal atoms are replaced by other metal atoms of similar size.
   In brass, approximately one-third of the atoms in the host copper metal have been replaced by zinc atoms, as shown in Fig. 10.21(a).

Figure 10.21



Two types of alloys.

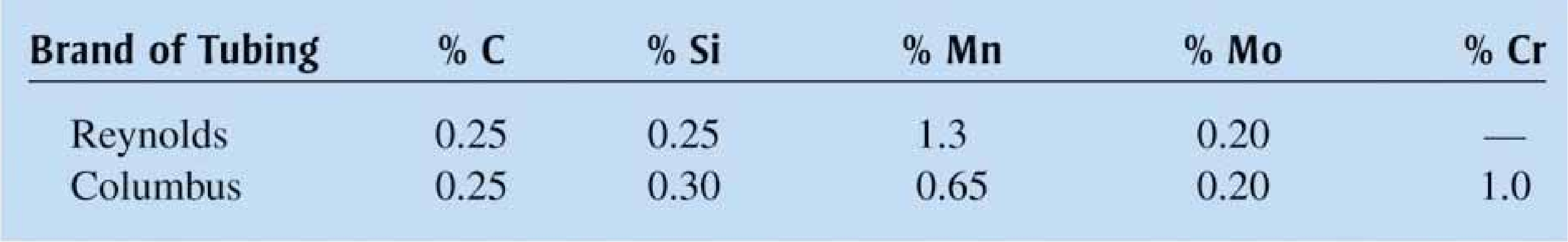
2. An **interstitial alloy** is formed when some of the interstices (holes) in the closest packed metal structure are occupied by small atoms, as shown in Fig. 10.21(b).

- *Mild steels*, containing less than 0.2% carbon, are ductile and malleable and are used for nails, cables, and chains.

- *Medium steels*, containing 0.2 to 0.6% carbon, are harder than mild steels and are used in rails and structural steel beams.
- *High-carbon steels*, containing 0.6 to 1.5% carbon, are tough and hard and are used for springs, tools, and cutlery.
- Many types of steel also contain elements in addition to iron and carbon. Such steels are often called alloy steels.

- The compositions of the two brands of steel tubing most commonly used in expensive racing bicycles are given in Table 10.4.

TABLE 10.4 The Composition of the Two Brands of Steel Tubing Commonly Used to Make Lightweight Racing Bicycles

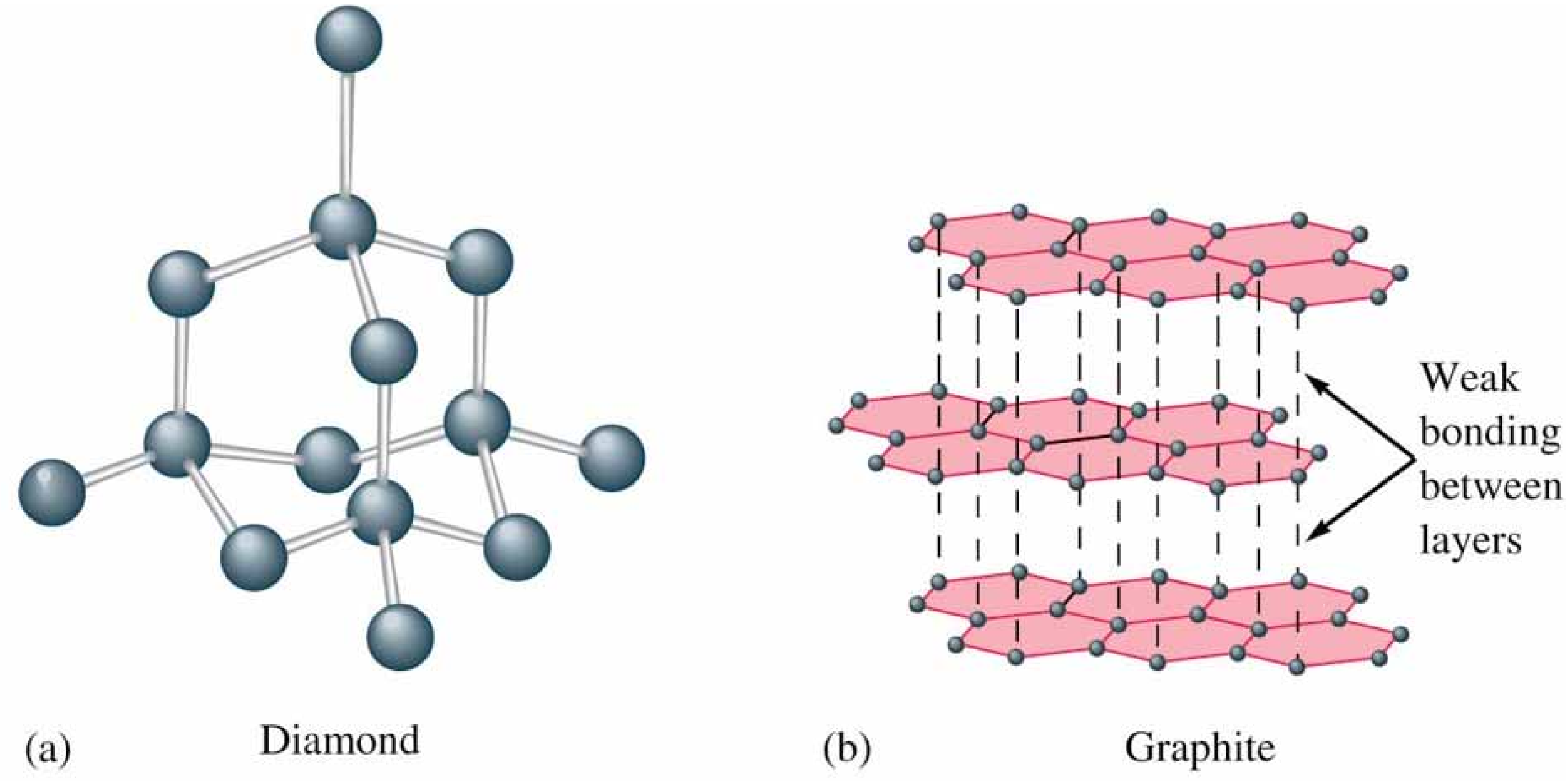


Brand of Tubing	% C	% Si	% Mn	% Mo	% Cr
Reynolds	0.25	0.25	1.3	0.20	—
Columbus	0.25	0.30	0.65	0.20	1.0

10.5 Carbon and Silicon: Network Atomic Solids

- Many atomic solids contain strong directional covalent bonds to form a solid that might best be viewed as a "giant molecule." We call these substances **network solids**.
- The two most common forms of carbon, diamond and graphite, are typical network solids. In diamond, the hardest naturally occurring substance, each carbon atom is surrounded by a tetrahedral arrangement of other carbon atoms to form a huge molecule [see Fig. 10.22(a)].

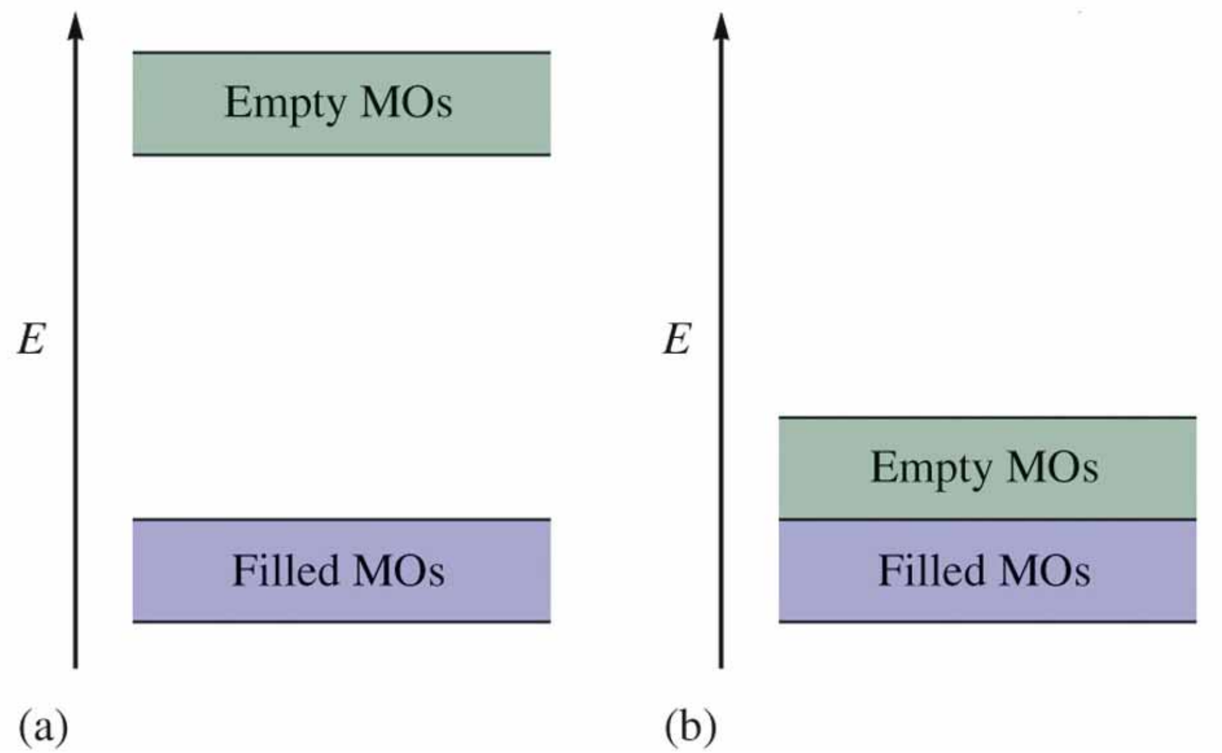
Figure 10.22



The structures of diamond and graphite. In each case only a small part of the entire structure is shown.

- Energy-level diagrams for diamond and a typical metal are given in Fig. 10.23.
- Note that in the energy-level diagram for diamond there is *a large gap between the filled and the empty levels*.
- This means that electrons cannot be transferred easily to the empty conduction bands.
- Graphite is very different from diamond.

Figure 10.23

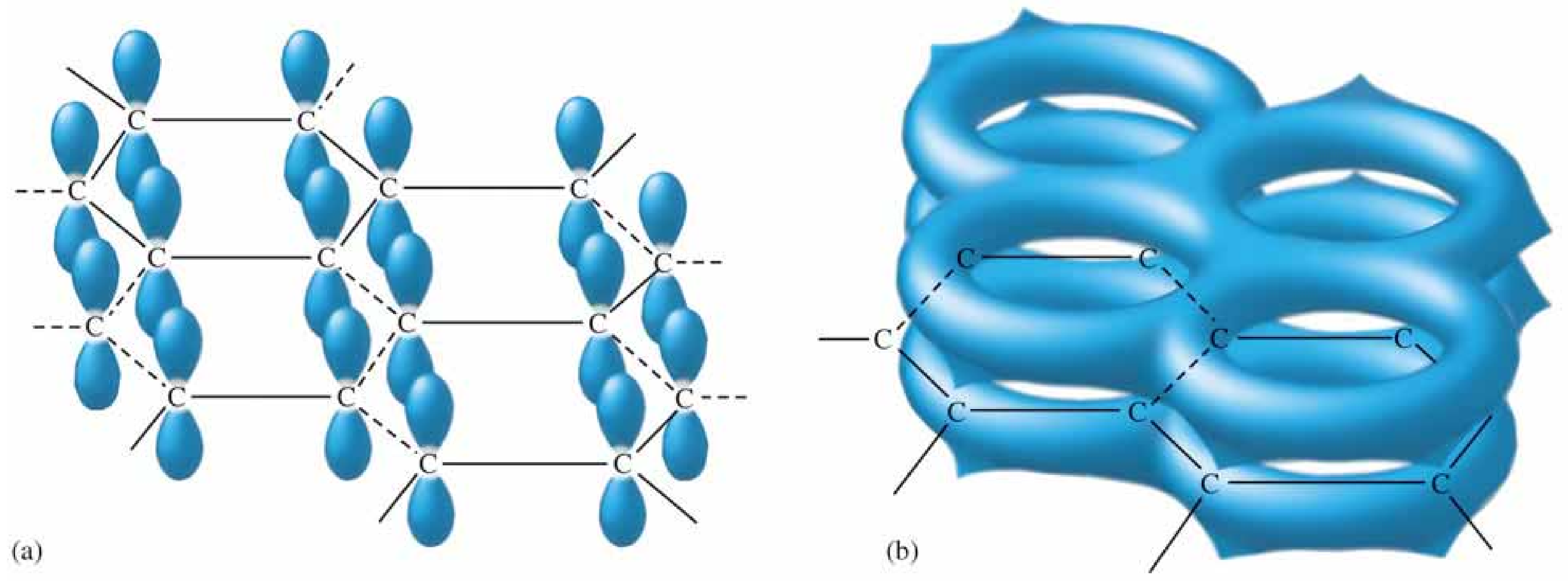


Partial representation of the molecular orbital energies in (a) diamond and (b) a typical metal.

- In contrast to the tetrahedral arrangement of carbon atoms in diamond, the structure of graphite is based on layers of carbon atoms arranged in fused six-membered rings, as shown in Fig. 10.22(b).
- The localized electron model predicts sp^2 hybridization in this case.
- The three sp^2 obitals on each carbon are used to form σ bonds with three other carbon atoms.

- One 2*p* orbital remains unhybridized on each carbon and is perpendicular to the plane of carbon atoms, as shown in Fig. 10.24.

Figure 10.24

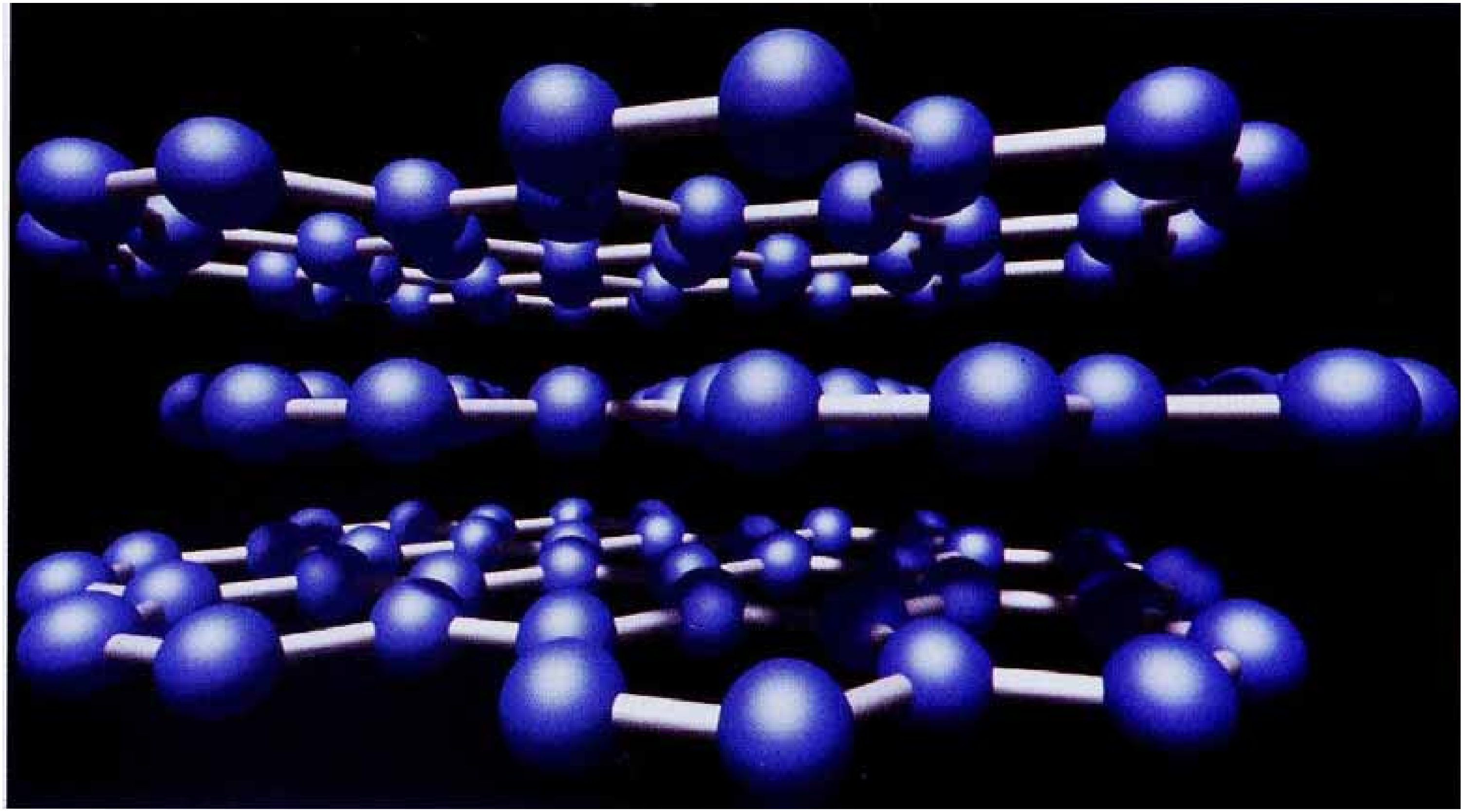


The *p* orbitals (a) perpendicular to the plane of the carbon ring system in graphite can combine to form (b) an extensive π – bonding network.

- These orbitals combine to form a group of closely spaced π molecular orbitals that are important in two ways.
- First, they contribute significantly to the stability of the graphite layers because of the π bond formation.
- Second, the π molecular orbitals with their delocalized electrons account for the electrical conductivity of graphite.

- Graphite is often used as a lubricant in locks.
- The slipperiness that is characteristic of graphite can be explained by noting that graphite has very strong bonding within the layers of carbon atoms but little bonding between the layers.
- Graphite’s layered structure is shown in Fig. 10.25.
- Silicon is an important constituent of the compounds that make up the earth’s crust. In fact, silicon is to geology as carbon is to biology.

Figure 10.25

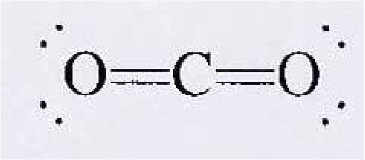


Graphite consists of layers of carbon atoms.

- The fundamental silicon-oxygen compound is **silica**, which has the empirical formula SiO_2.
- Knowing the properties of the similar compound carbon dioxide, one might expect silica to be a gas that contains discrete SiO_2 molecules.
- In fact, nothing could be further from the truth-quartz and some types of sand are typical of the materials composed of silica.

- What accounts for this difference? The answer lies in the bonding.

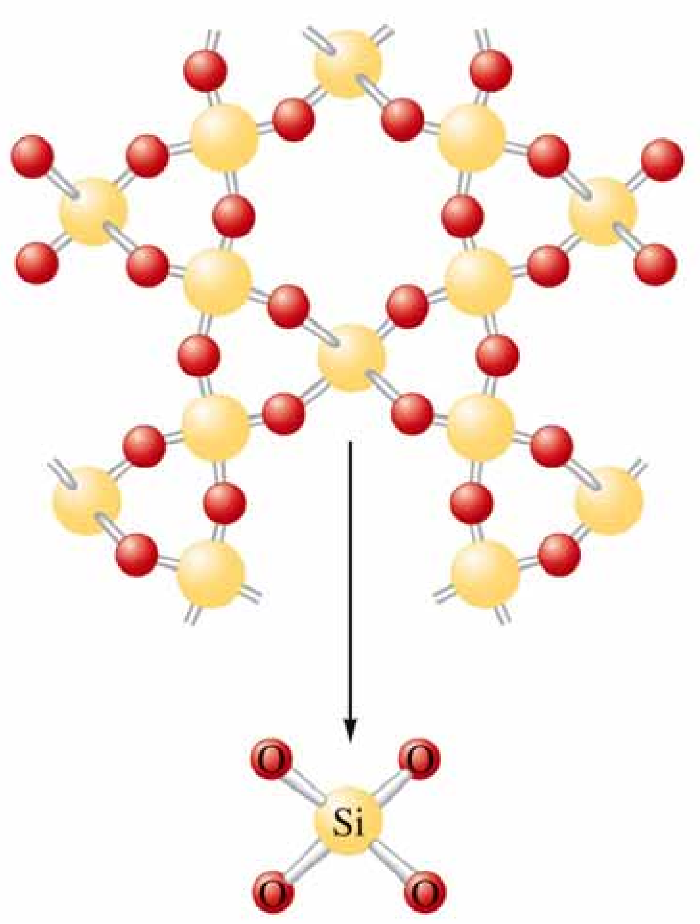
- The Lewis structure of CO_2 is



- each C ＝ O bond can be viewed as a combination of a σ bond involving a carbon *sp* hybrid orbital and a π bond involving a carbon 2*p* orbital.
- silicon cannot use its valence 3*p* orbitals to form strong π bonds with oxygen, mainly because of the larger size of the silicon atom and its orbitals.

- Instead of forming π bonds, the silicon atom satisfies the octet rule by forming single bonds with four oxygen atoms, as shown in the representation of the structure of quartz in Fig. 10.26.
- Compounds closely related to silica and found in most rocks, soils, and clays are the **silicates**.
- Like silica, the silicates are based on interconnected SiO_4 tetrahedra.

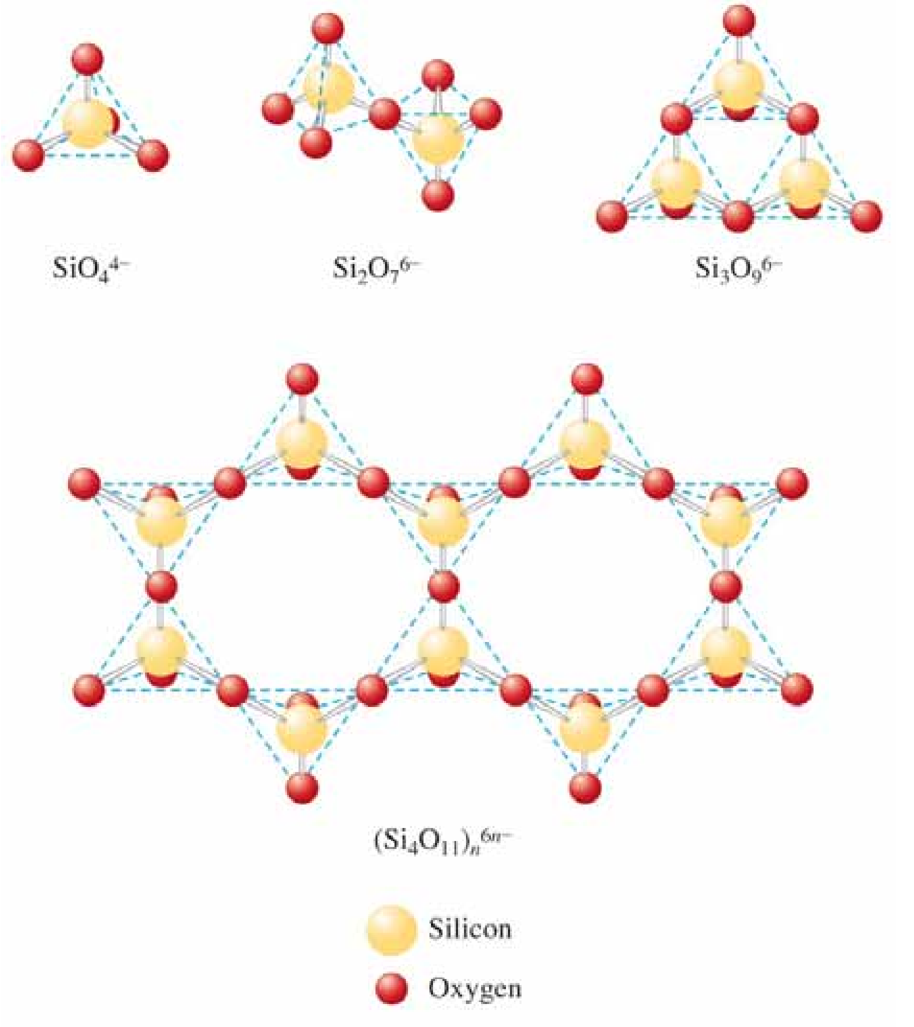
Figure 10.26



(top) The structure of quartz (empirical formula SiO_2). Quartz contains chains of SiO_4 tetrahedra (bottom) that share oxygen atoms.

- In contrast to silica, where the O/Si ratio is 2:1, silicates have O/Si ratios greater than 2:1 and contain silicon-oxygen anions.
- To form the neutral solid silicates, cations are needed to balance the excess negative charge.
- silicates are salts containing metal cations and polyatomic silicon-oxygen anions.
- Examples of important silicate anions are shown in Fig. 10.27.

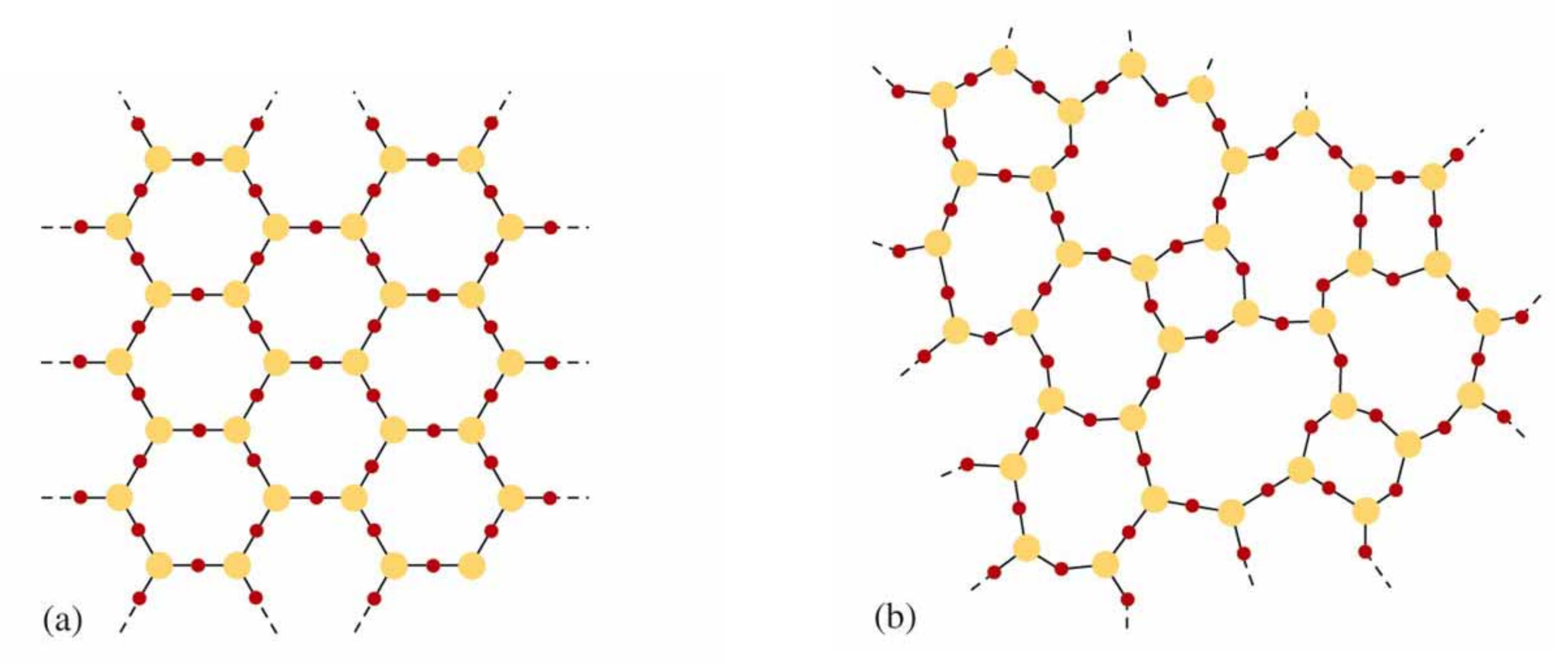
Figure 10.27



Examples of silicate anions, all of which are based on SiO_4^{4-} tetrahedra.

- When silica is heated above its melting point (about 1600℃) and cooled rapidly, an amorphous solid called a **glass** results (see Fig. 10.28).

Figure 10.28

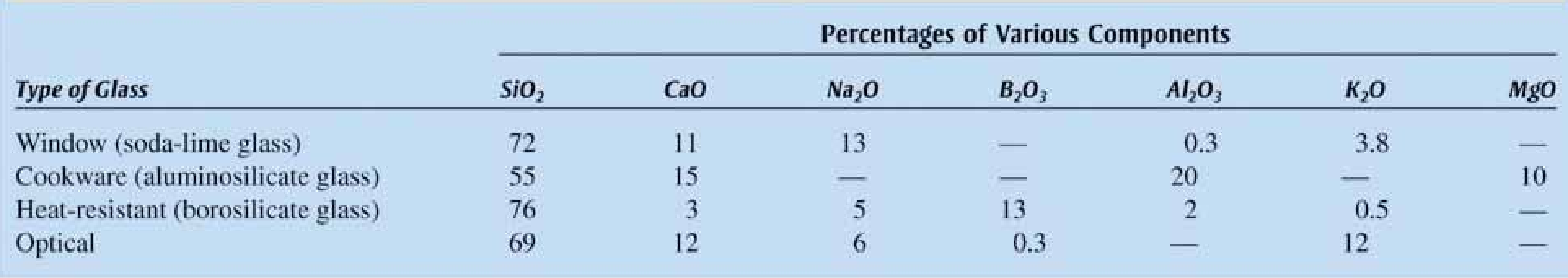


Examples of silicate anions, all Two-dimensional representations of (a) a quartz crystal and (b) a quartz glass.

- Common glass results when substances such as Na_2CO_3 are added to the silica melt,
- addition of B_2O_3 produces a glass (called *borosilicate glass*) that expands and contracts little under large temperature changes.
- The most common brand name for this can be ground to the precise shapes needed for eyeglass and contact lenses. The compositions of several types of glass are shown in Table 10.5.

A glass pitcher being manufactured.

TABLE 10.5 Compositions of Some Common Types of Glass



	Percentages of Various Components						
Type of Glass	SiO_2	CaO	Na_2O	B_2O_3	Al_2O_3	K_2O	MgO
Window (soda-lime glass)	72	11	13	—	0.3	3.8	—
Cookware (aluminosilicate glass)	55	15	—	—	20	—	10
Heat-resistant (borosilicate glass)	76	3	5	13	2	0.5	—
Optical	69	12	6	0.3	—	12	—

Ceramics

- Ceramics are typically made from clays (which contain silicates) and hardened by firing at high temperatures.
- Ceramics are nonmetallic materials that are strong, brittle, and resistant to heat and attack by chemicals.
- A glass is a *homogenous*, noncrystalline “frozen solution,” and a ceramic is *heterogenous*.
- A ceramic contains two phases: minute crystals of silicates that are suspended in a glassy cement.

- Clays are formed by the weathering action of water and carbon dioxide on the mineral feldspar, which is a mixture of silicates with empirical formulas such as $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ and $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$.
- Feldspar is really an *alumi-nosilicate* in which aluminum as well as silicon atoms are part of the oxygen-bridged polyanion.

An artist paints a ceramic vase before glazing.

- Ceramics constitute one of the most important classes of “high-tech’ materials.
- Because of their stability at high temperatures and resistance to corrosion, ceramics seem an obvious choice for constructing jet and automobile engines in which the greatest fuel efficiencies are possible at very high temperatures.

Semiconductors

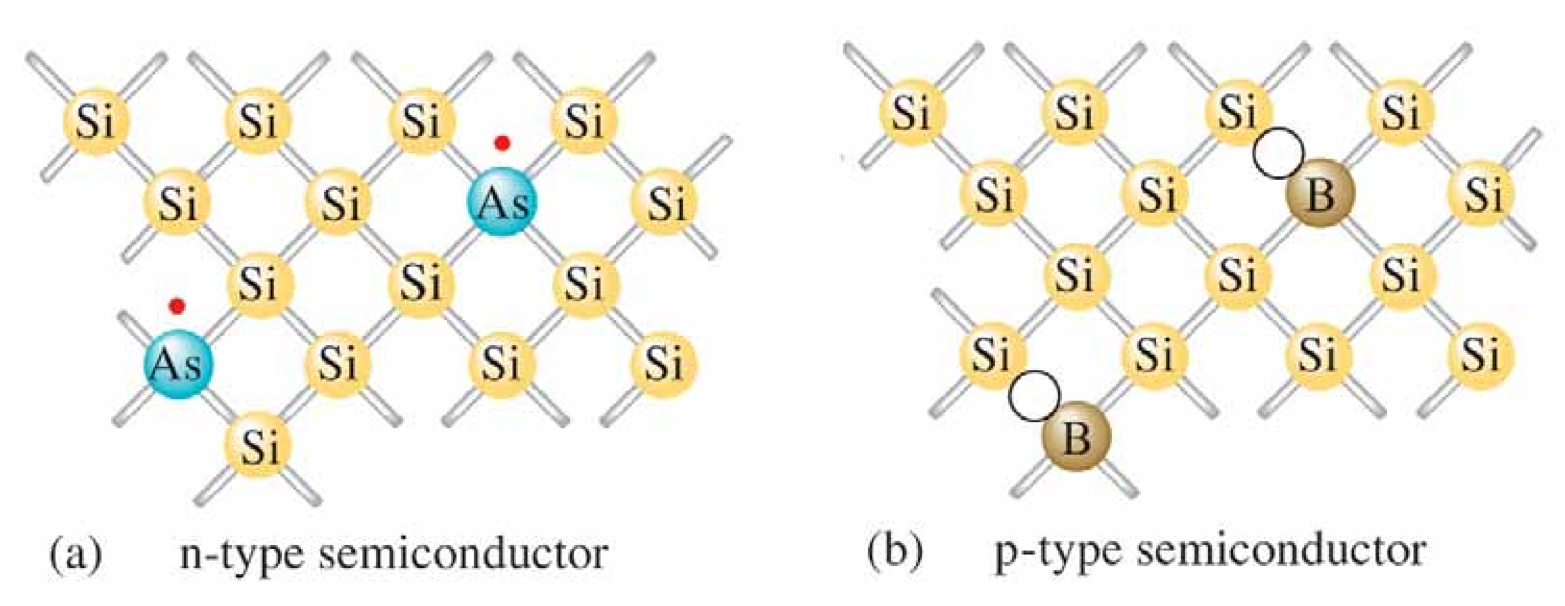
- Elemental silicon has the same structure as diamond, as might be expected from its position in the periodic table.
- Recall that in diamond there is a large energy gap between the filled and empty molecular orbitals (see Fig. 10.23).
- In silicon the situation is similar, but the energy gap is smaller. A few electrons can cross the gap at 25℃, making silicon a **semiconducting element**, or semiconductor.

- The small conductivity of silicon can be enhanced at normal temperatures if the silicon crystal is doped with certain other elements.
- When a small fraction of silicon atoms is replaced by arsenic atoms, each having one more valence electron than silicon, extra electrons become available for conduction, as shown in Fog. 10.29(a).

- This produces an **n-type semiconductor**, a substance whose conductivity is increased by doping it with atoms having more valence electrons than the atoms in the host crystal.
- These extra electrons lie close in energy to the conduction bands and can be easily excited into these levels, where they can conduct an electric current[see Fig. 10.30(a)].

- We also can enhance the conductivity of silicon by doping the crystal with an element such as boron,
- Boron has one less electron than is required to form the bonds with the surrounding silicon atoms, an electron vacancy, or hole, is created, as shown in Fig. 10.29(b).
- Replacing silicon atoms with boron atoms leaves vacancies in these molecular orbitals, as shown in Fig. 10.30(b).

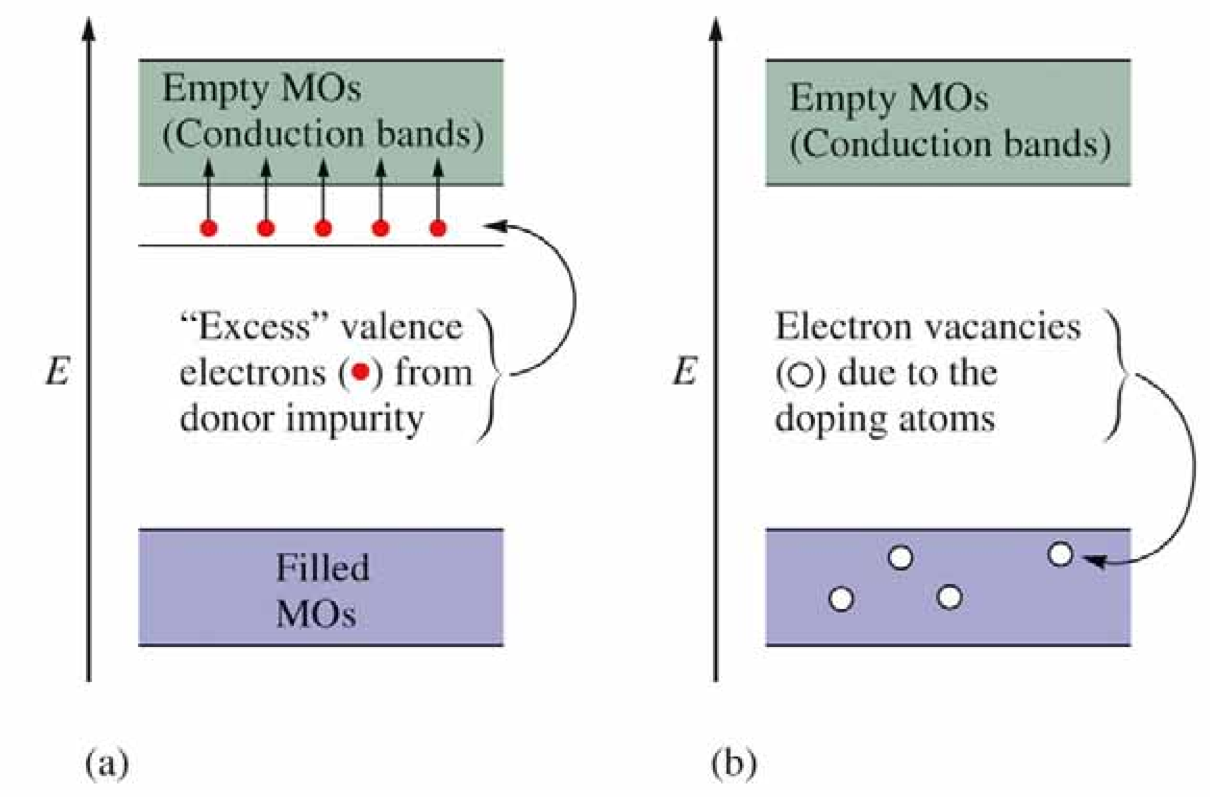
Figure 10.29



(a) n-type semiconductor (b) p-type semiconductor

(a) A silicon crystal doped with arsenic, which has one more valence electron than silicon. (b) A silicon crystal doped with boron, which has one less electron than silicon.

Figure 10.30



Energy-level diagrams for (a) an n-type semiconductor and (b) a p-type semiconductor.

- There is only one electron in some of the molecular orbitals, and these unpaired electrons can function as conducting electrons.
- Thus the substance becomes a better conductor.
- When semiconductors are doped with atoms having fewer valence electrons than the atoms of the host crystal, they are called **p-type semiconductors**.

- Most important applications of semiconductors involve connection of a p-type and an n-type to form a p-n junction.
- Figure 10.31(a) shows a typical junction; the red dots represent excess electrons in the n-type semiconductor, and the white circles represent holes (electron vacancies) in the p-type semiconductor.

- Now suppose an external electric potential is applied by connecting the negative terminal of a battery to the p-type region and the positive terminal to the n-type region.
- The situation represented in Fig. 10.31(b) results.
- The junction resists the imposed current flow in this direction and is said to be under *reverse bias*.

Figure 10.31

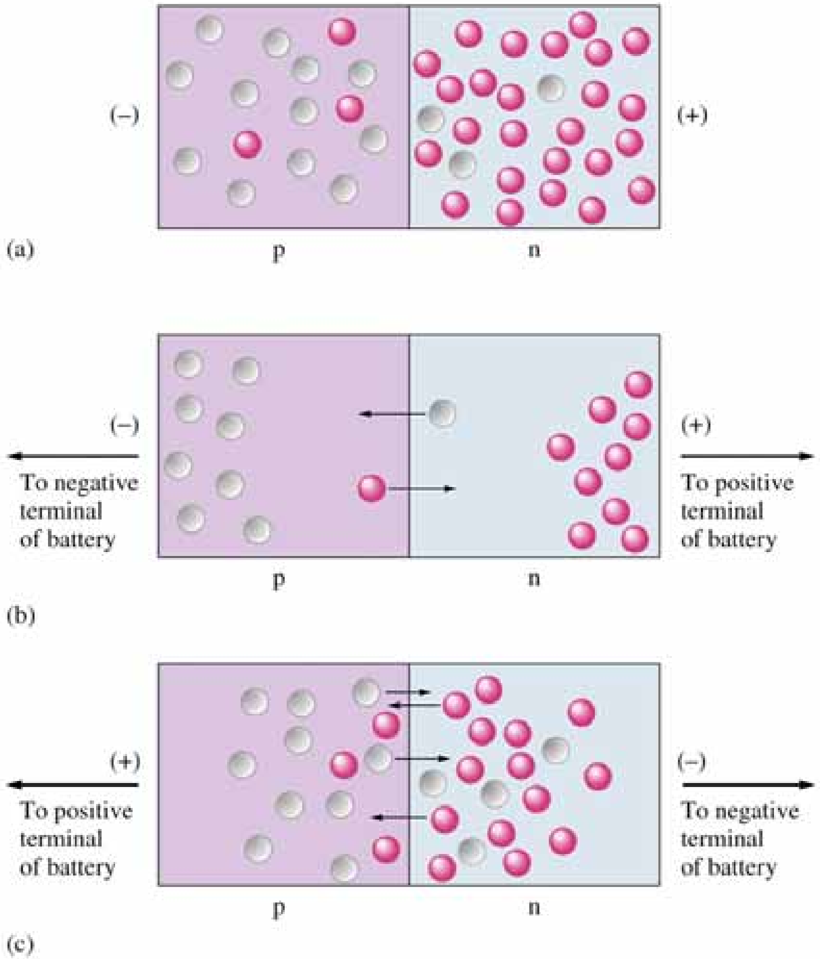
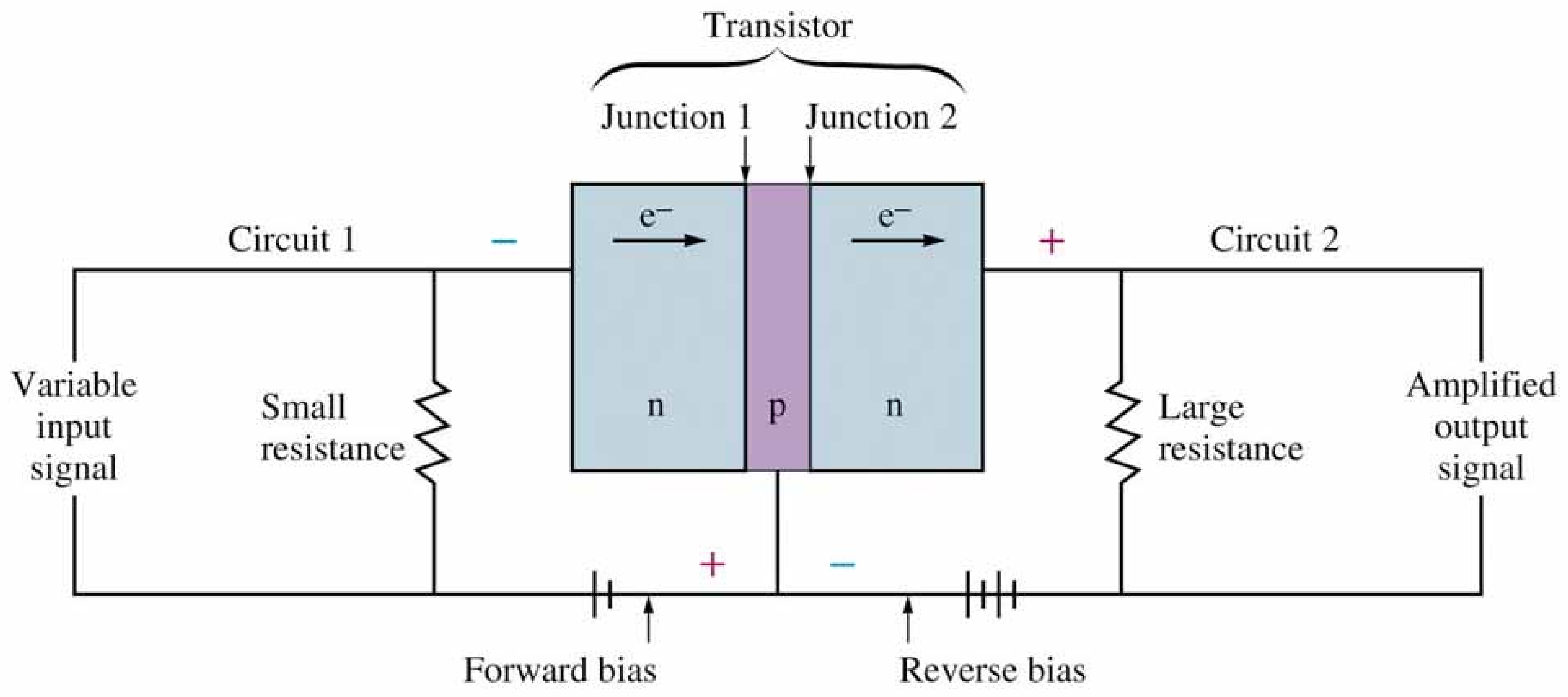

(–)
(+)
(a)
p
n
(–)
To negative terminal of battery
(+)
To positive terminal of battery
p
n
(b)
(+)
To positive terminal of battery
(–)
To negative terminal of battery
p
n
(c)

Figure 10.31

The p-n junction involves the contact of a p-type and an n-type semiconductor. (a) The charge carries of the p-type region are holes. In the n-type region the charge carries are electrons. (b) No current flows (reverse bias). (c) Current readily flows (forward bias). Note that each electron that crosses the boundary leaves a hole behind. Thus the electrons and the holes move in opposite directions.

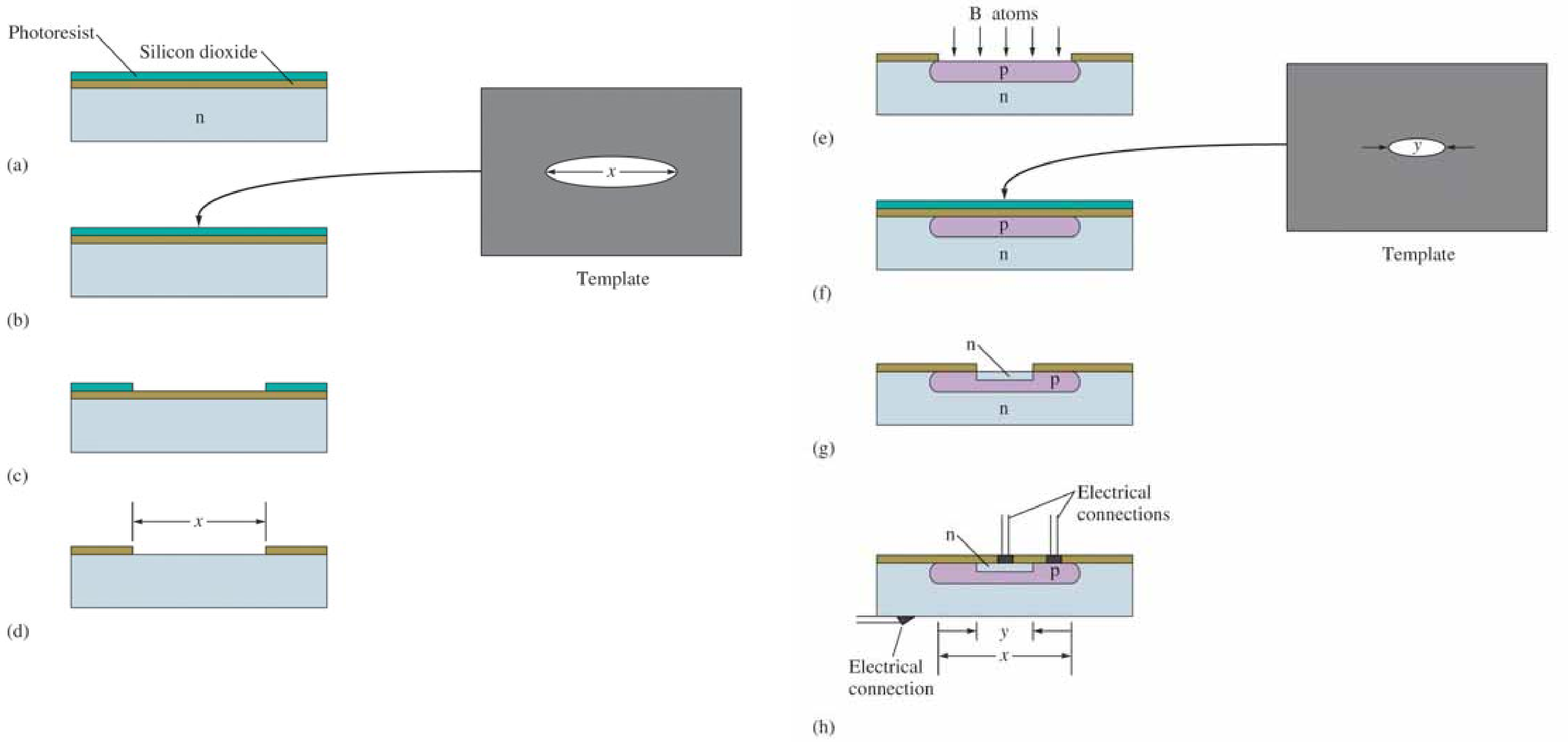
- On the other hand, if the battery id connected so that the negative terminal is connected to the n-type region and the positive terminal is connected to the p-type region [Fig. 10.31(c)], the movement of electrons (and holes) is in the favored direction.
- The junction is said to be under *forward bias*.
- A p-n junction makes an excellent *rectifier*, a device that produces a pulsating direct current from alternating current.

Figure 10.32



A schematic of two circuits connected by a transistor. The signal in circuit 1 is amplified in circuit 2.

Figure 10.33



The steps for forming a transistor in a crystal of initially pure silicon.

10.6 Molecular Solids

- There are many types of solids that contain discrete molecular units at each lattice position.
- A common example is ice, where the lattice positions are occupied by water molecules [see Fig. 10.12(c)].
- Other examples are dry ice (solid carbon dioxide), some forms of sulfur that contain S_8 molecules [Fig. 10.34(b)].

Figure 10.34

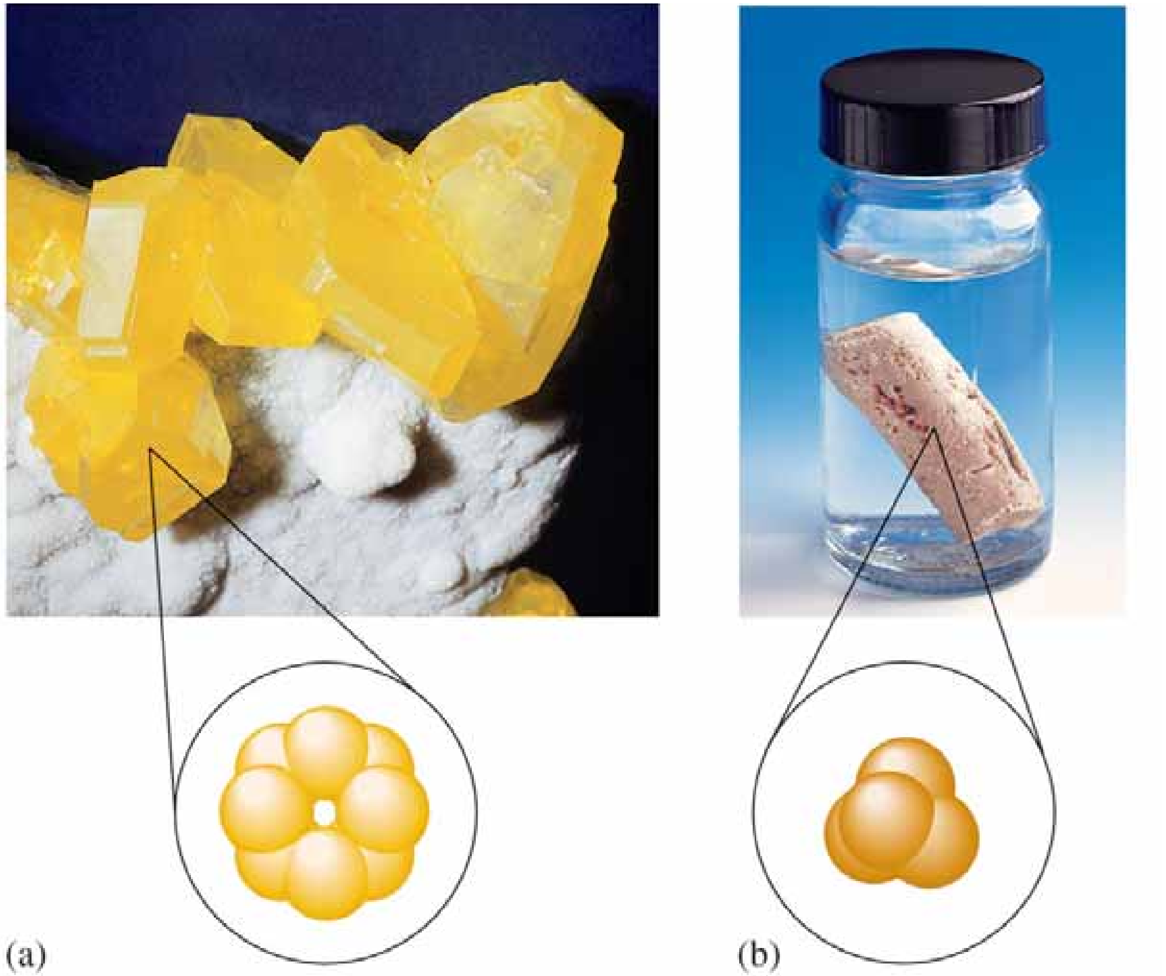


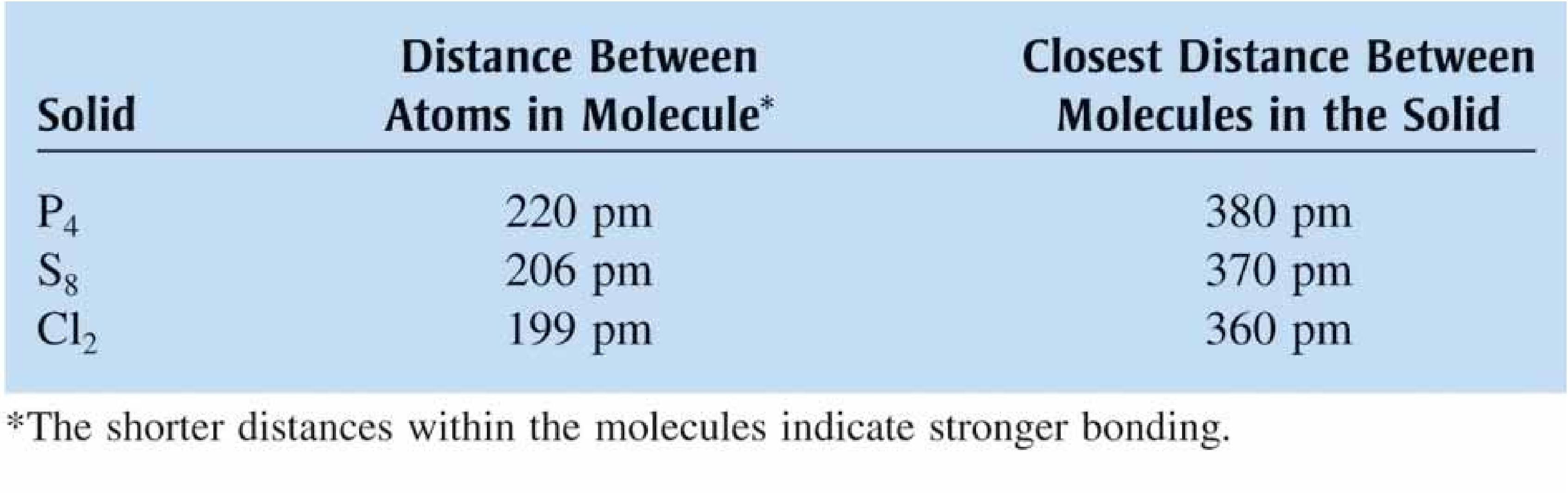
Figure 10.34

(a) Sulfur crystals (yellow) contain S_8 molecules. (b) White phosphorus (containing P_4 molecules) is so reactive with the oxygen in air that it must be stored under water.

- The differences between the covalent bonds within the molecules and the forces between the molecules are apparent from the comparison of the interatomic and intermolecular distances in solids shown in Table 10.6.

A “steaming” piece of dry ice.

TABLE 10.6 Comparison of Atomic Separations Within Molecules (Covalent Bonds) and Between Molecules (Intermolecular Interactions)

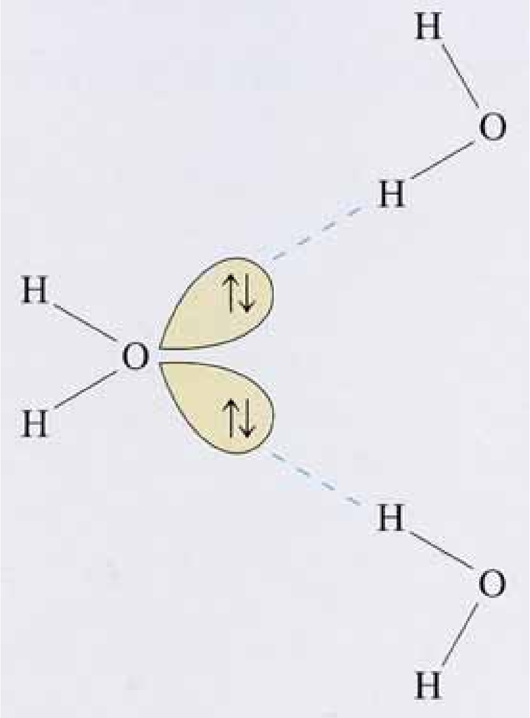


Solid	Distance Between Atoms in Molecule*	Closest Distance Between Molecules in the Solid
P_4	220 pm	380 pm
S_8	206 pm	370 pm
Cl_2	199 pm	360 pm

*The shorter distances within the molecules indicate stronger bonding.

- When molecules do have dipole moments, their intermolecular forces are significantly greater, especially when hydrogen bonding is possible.
- Water molecules are particularly well suited to interact with each other because each molecule has two polar O—H bonds and two lone pairs on the oxygen atom.

- This can lead to the association of four hydrogen atoms with each oxygen: two by covalent bonds and two by dipole forces:



- Note the two relatively short covalent oxygen-hydrogen bonds and the two longer oxygen-hydrogen dipole interactions that can be seen in the ice structure in Fig. 10.12(c).

10.7 Ionic Solids

- Ionic solids are stable, high-melting substances held together by the strong electrostatic forces that exist between oppositely charged ions.
- There are three types of holes in closest packed structures:

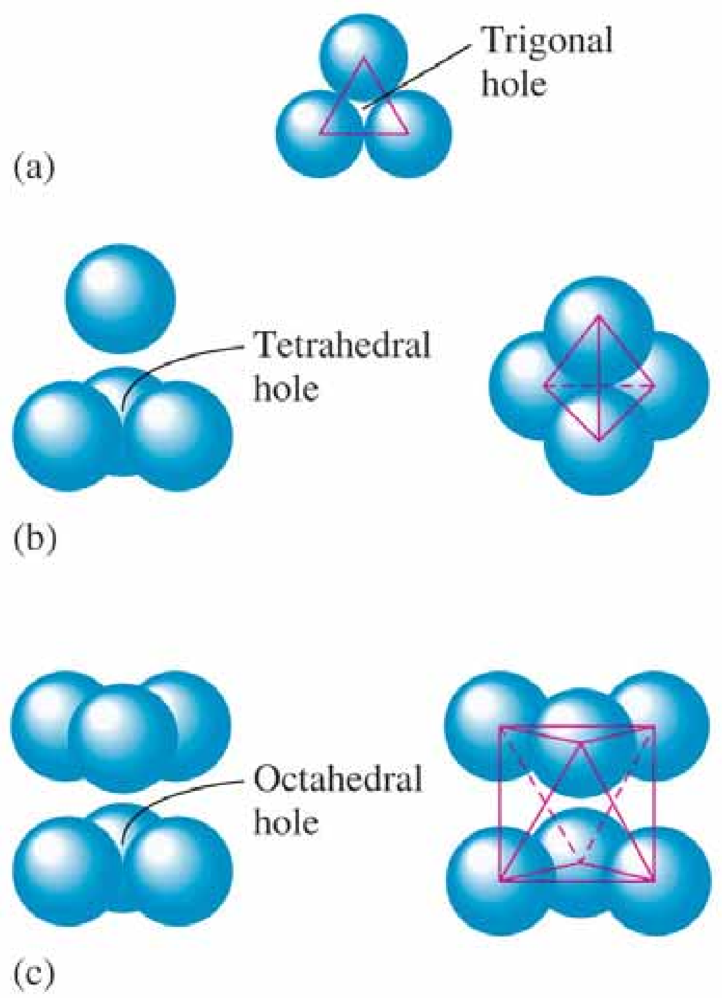
1. Trigonal holes are formed by three spheres in the same layer [Fig. 10.35(a)].

2. Tetrahedral holes are formed when a sphere sits in the dimple of three spheres in an adjacent layer [Fig. 10.35(b)].

3. Octahedral holes are formed between two sets of three spheres in adjoining layers of the closest packed structures [Fig. 10.35(c)].

Figure 10.35

(The holes that exist among closest packed uniform spheres. (a) The trigonal hole formed by three spheres in a given plane. (b) The tetrahedral hole formed when a sphere occupies a dimple formed by three spheres in an adjacent layer. (c) The octahedral hole formed by six spheres in two adjacent layers.



- For spheres of a given diameter, the holes in increase in size in the order

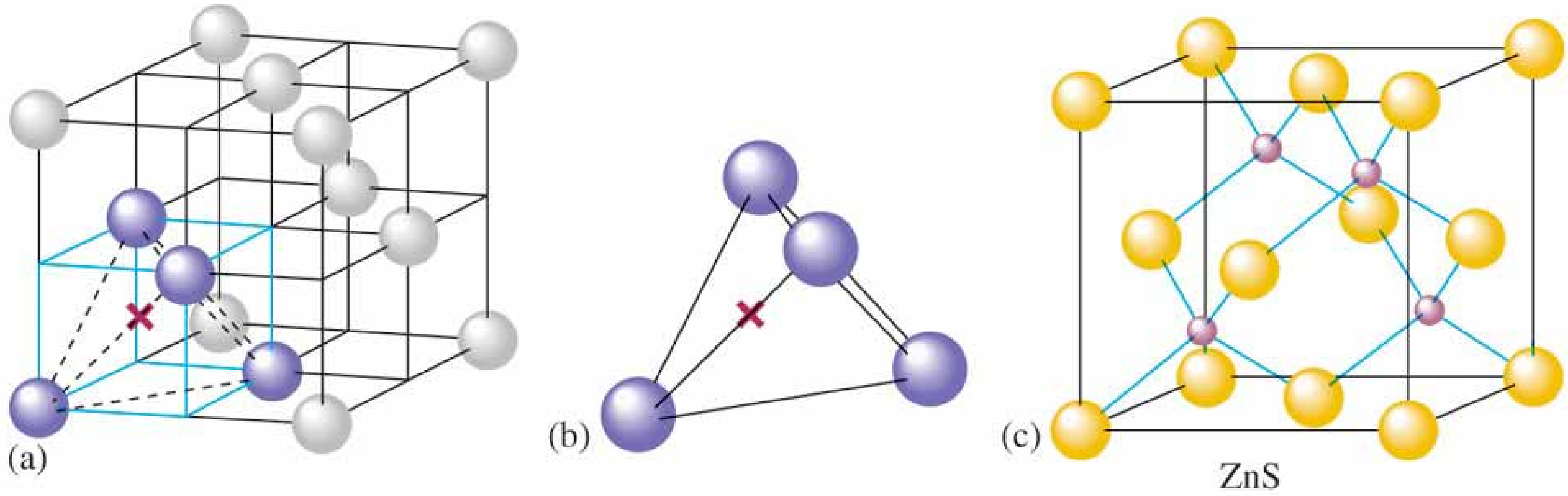
$$\text{trigonal} < \text{tetrahedral} < \text{octahedral}$$

- in zinc sulfide the S^{2-} ions (ionic radius ＝ 180pm) are arranged in a cubic closest packed structure with the smaller Zn^{2+} ions (ionic radius ＝ 70pm) in the tetrahedral holes.

- The locations of the tetrahedral holes in the face-centered cubic unit cell of the ccp structure are shown in Fig. 10.36(a).
- There are twice as many tetrahedral holes as packed anions in the closest packed structure.
- Zinc sulfide must have the same number of S^{2-} ions and Zn^{2+} ions to achieve electrical neutrality.

- Thus in the zinc sulfide structure only half the tetrahedral holes contain Zn^{2+} ions, as shown in Fig. 10.36(c).

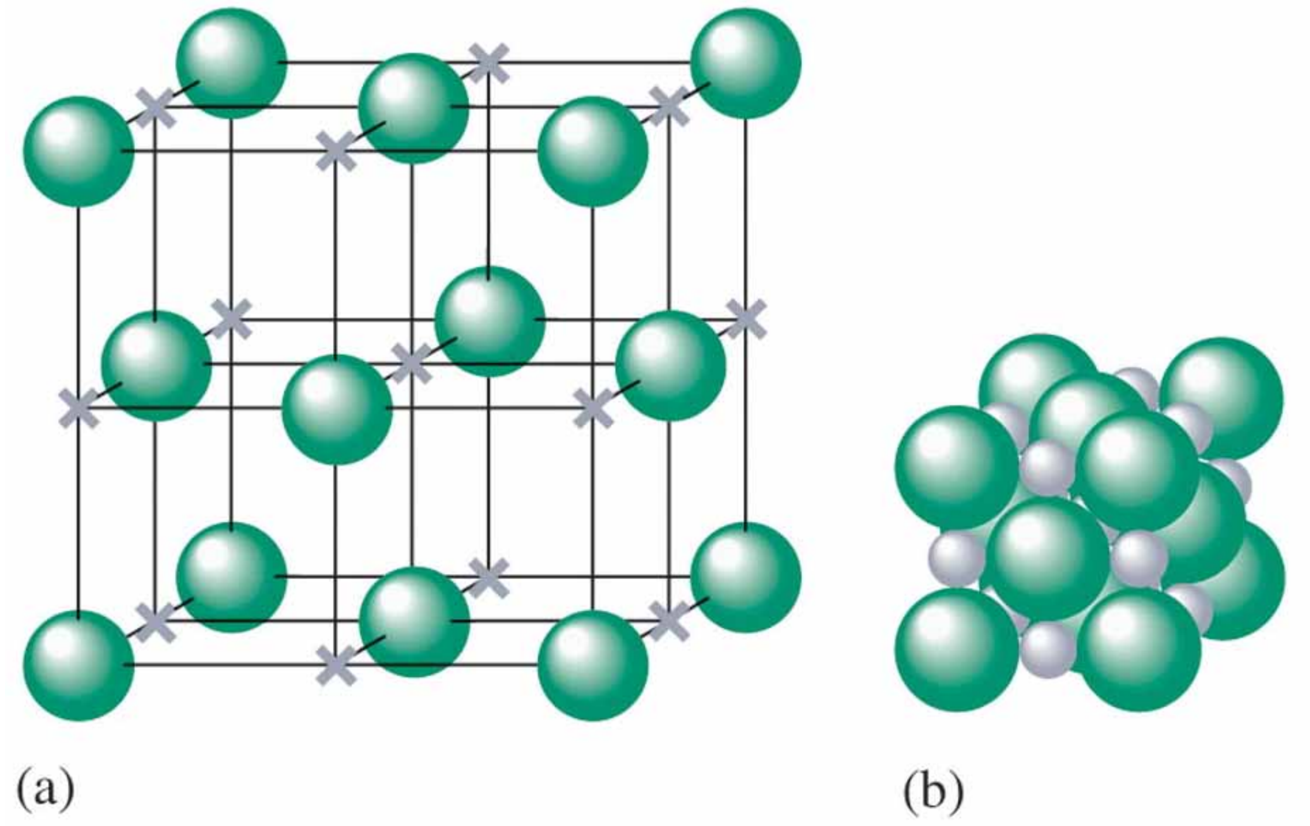
Figure 10.36



(a) The location (X) of a tetrahedral hole in the face-centered cubic unit cell. (b) One of the tetrahedral holes. (c) The unit cell for ZnS where the S^{2-} ions (yellow) are closest packed with the Zn^{2+} ions (red) in alternating tetrahedral holes.

- The structure of sodium chloride can be described in terms of a cubic closest packed array of Cl^- ions with Na^+ ions in all the octahedral holes.
  - The locations of the octahedral holes in the face-centered cubic unit cell are shown in Fig. 10.37(a).
- Figure 10.37(b) shows the structure for sodium chloride that results from Na^+ ions filling all the octahedral holes in a ccp array of Cl^- ions.

Figure 10.37


(a)

(b)

Figure 10.37

(a) The locations (gray X) of the octahedral holes in the face-centered cubic unit cell. (b) Representation of the unit cell for solid NaCl. The Cl^- ions (green spheres) have a ccp arrangement with Na^+ ions (gray spheres) in all the octahedral holes. Note that this representation shows the idealized closest packed structure of NaCl. In the actual structure, the Cl^- ions do not quite touch.

Sample Exercise 10.3

Determining the Number of Ions in a Unit Cell

Determine the net number of Na^+ and Cl^- ions in the sodium chloride unit cell.

Solution

Note form Fig. 10.37(b) that the Cl^- ions are cubic closest packed and thus form a face-centered cubic unit cell. There is a Cl^- ion on each corner and one at the center of each face of the cube. Thus the net number of Cl^- ions present in a unit cell is

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

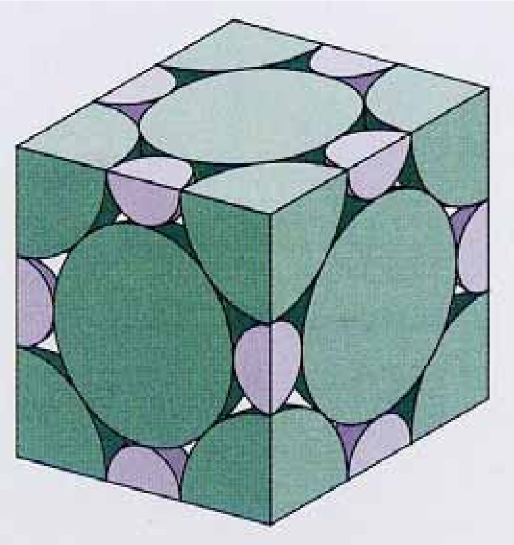
Sample Exercise 10.3

The Na ions occupy the octahedral holes located in the center of the cube and midway along each edge. The Na^+ ion in the center of the cube is contained entirely in the unit cell, whereas those on the edges are shared by four unit cells (four cubes share a common edge). Since the number of edges in a cube is 12, the net number of Na^+ ions present is

$$1(1) + 12(\tfrac{1}{4}) = 4$$

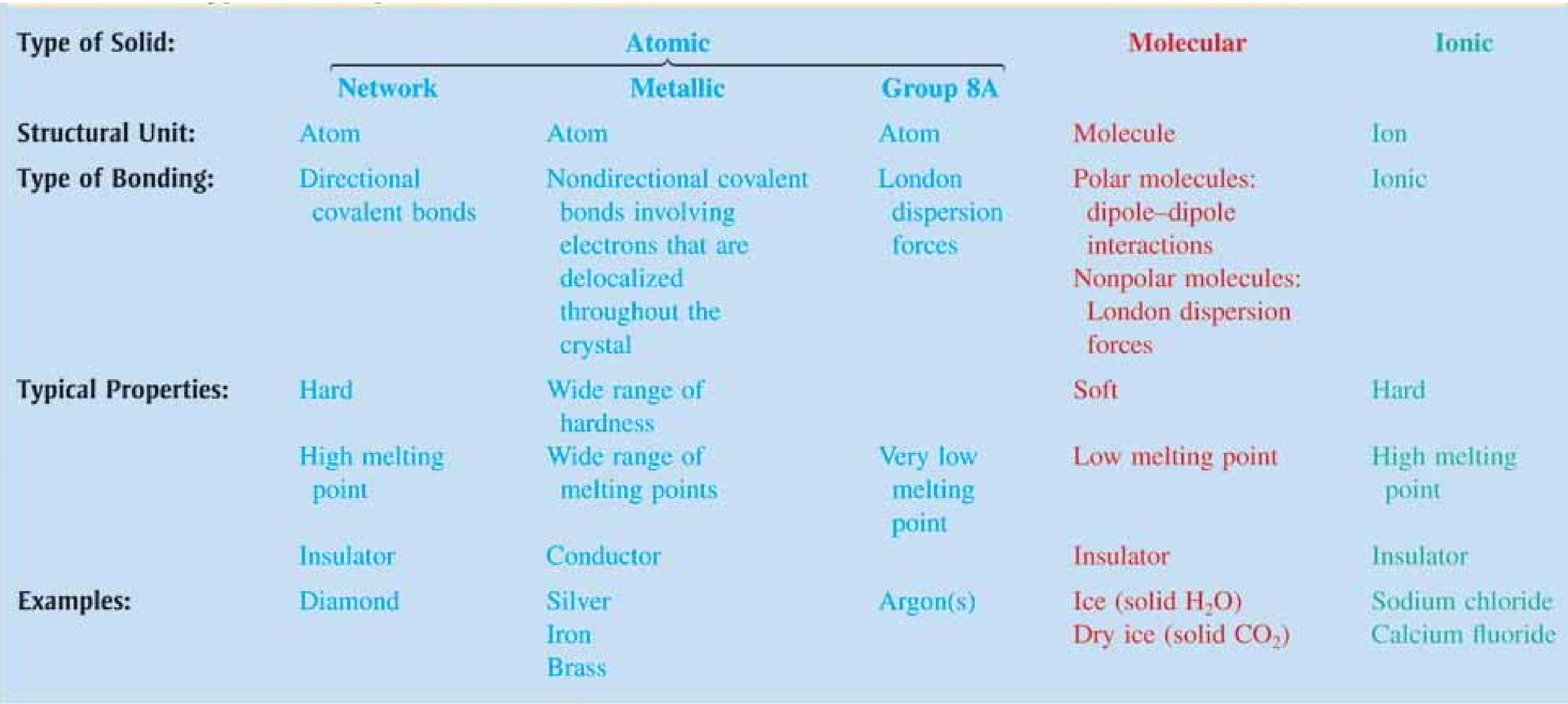
Sample Exercise 10.3

We have shown that the net number of ions in a unit cell is 4 Na^+ ions and 4 Cl^- ions, which agrees with the 1:1 stoichiometry of sodium chloride.



See Exercises 10.61 through 10.68.

TABLE 10.7 Types and Properties of Solids



Type of Solid:	Atomic			Molecular	Ionic
	Network	Metallic	Group 8A		
Structural Unit:	Atom	Atom	Atom	Molecule	Ion
Type of Bonding:	Directional covalent bonds	Nondirectional covalent bonds involving electrons that are delocalized throughout the crystal	London dispersion forces	Polar molecules: dipole–dipole interactions Nonpolar molecules: London dispersion forces	Ionic
Typical Properties:	Hard	Wide range of hardness		Soft	Hard
	High melting point	Wide range of melting points	Very low melting point	Low melting point	High melting point
	Insulator	Conductor		Insulator	Insulator
Examples:	Diamond	Silver Iron Brass	Argon(s)	Ice (solid H_2O) Dry ice (solid CO_2)	Sodium chloride Calcium fluoride

Sample Exercise 10.4

Types of Solids

Using Table 10.7, classify each of the following substances according to the type of solid it forms.

a. Gold **b.** Carbon dioxide

c. Lithium fluoride **d.** Krypton

Solution

a. Solid gold is an atomic solid with metallic properties.

b. Solid carbon dioxide contains nonpolar carbon dioxide molecules and is a molecular solid.

c. Solid lithium fluoride contains Li^+ and F^- ions and is a binary ionic solid.

Sample Exercise 10.4

d. Solid krypton contains krypton atoms that can interact only through London dispersion forces. It is an atomic solid but has properties characteristic of a molecular solid with nonpolar molecules.

See Exercises 10.71 and 10.72.

10.8 Vapor Pressure and Changes of State

- **vaporization**, or **evaporation**: the molecules of a liquid can escape the liquid's surface and form a gas
- The energy required to vaporize 1 mole of a liquid at a pressure of 1 atm is called the **heat of vaporization**, or the **enthalpy of vaporization**, and is usually symbolized as ΔH_{vap}.

Vapor Pressure

- When a liquid is placed in a closed container, the amount of liquid at first decreases but eventually becomes constant.
- The decrease occurs because there is an initial net transfer of molecules from the liquid to the vapor phase (Fig. 10.38).
- This evaporation process occurs at a constant rate at a given temperature (see Fig. 10.39).

Figure 10.38

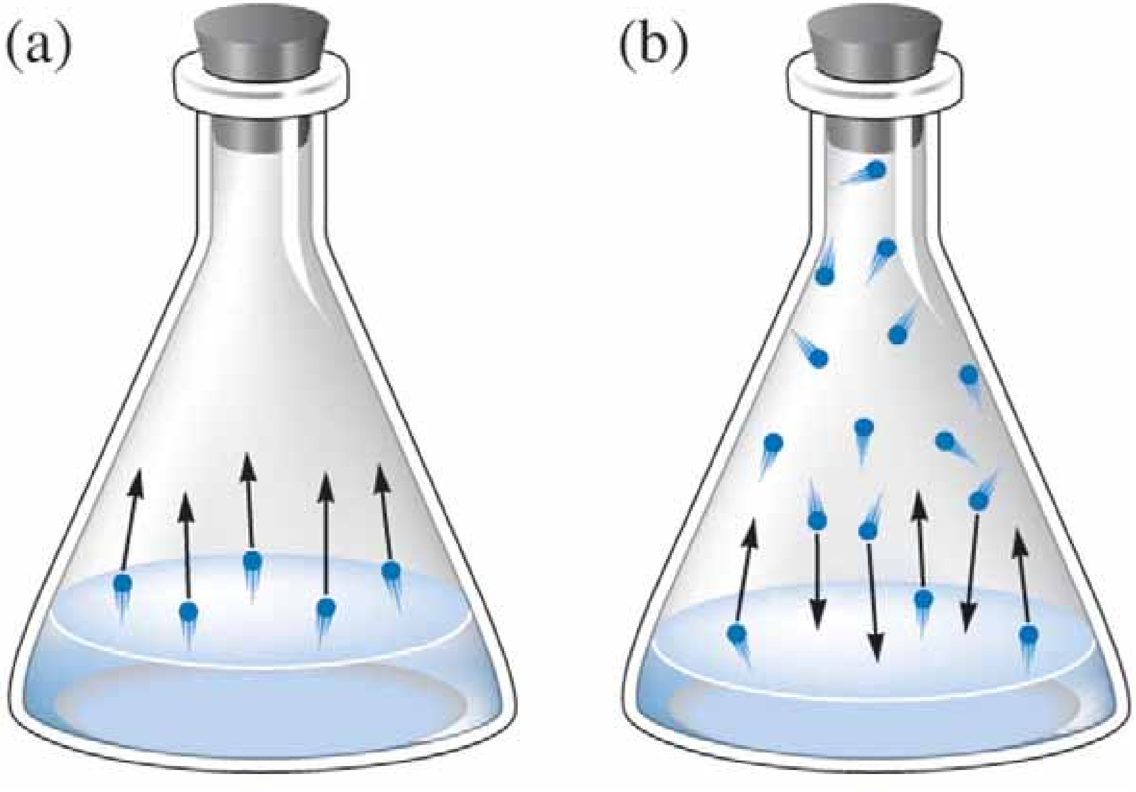


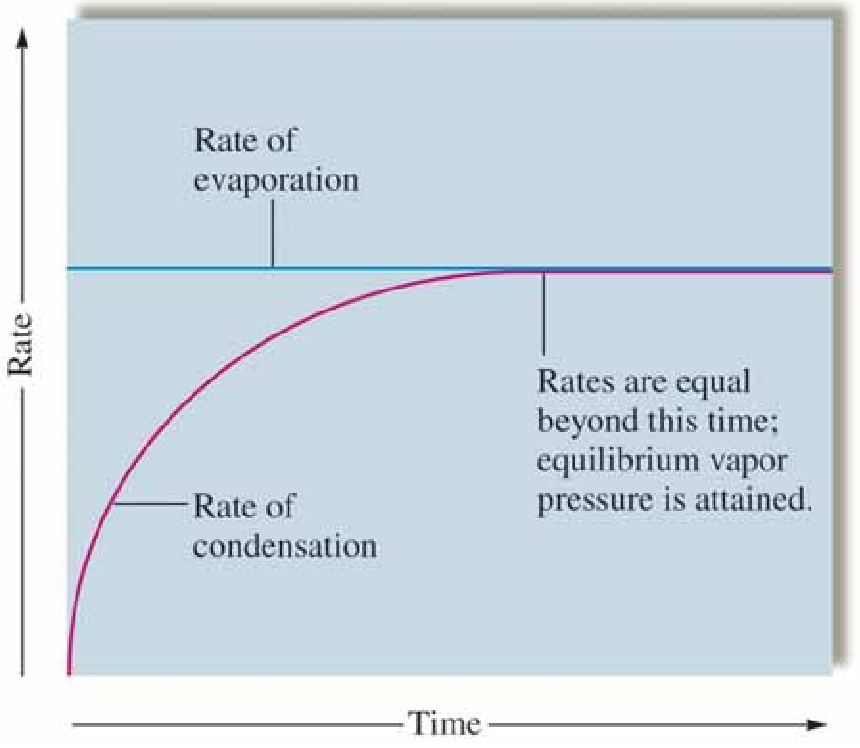
Figure 10.38

Behavior of a liquid in a closed container. (a) Initially, net evaporation occurs as molecules are transferred from the liquid to the vapor phase, so the amount of liquid decreases. (b) As the number of vapor molecules increase, the rate of return to the liquid (condensation) increases, until finally the rate of condensation equals the rate of evaporation. The system is at equilibrium, and no further changes occur in the amounts of vapor or liquid.

- The process by which vapor molecules re-form a liquid is called **condensation**.
- Eventually, enough vapor molecules are present above the liquid so that the rate of condensation equals the rate of evaporation (see Fig. 10.39).
- *At this point no further net change occurs in the amount of liquid or vapor because the two opposite processes exactly balance each other*; the system is at **equilibrium**.

- Note that this system is highly *dynamic* on the molecular level-molecules are constantly escaping from and entering the liquid at a high rate.
- However, there is no *net* change because the two opposite processes just *balance* each other.

Figure 10.39



(a) A silicon crystal doped with arsenic, which has one more valence electron than silicon. (b) A silicon crystal doped with boron, which has one less electron than silicon.

- The pressure of the vaopr present at equilibrium is called the **equilibrium vapor pressure**, or more commonly, the **vapor pressure** of the liquid.
- A simple barometer can measure the vapor pressure of a liquid, as shown in Fig. 10.40(a).

$$P_{\text{atmosphere}} = P_{\text{vapor}} + P_{\text{Hg column}}$$

$$P_{\text{vapor}} = P_{\text{atmosphere}} - P_{\text{Hg column}}$$

- The vapor pressures of liquids vary widely [see Fig. 10.40(b)].
- Liquids with high vapor pressures are said to be *volatile*—they evaporate rapidly from an open dish.
- The vapor pressure of a liquid is principally determined by the size of the *intermolecular forces* in the liquid.

Figure 10.40

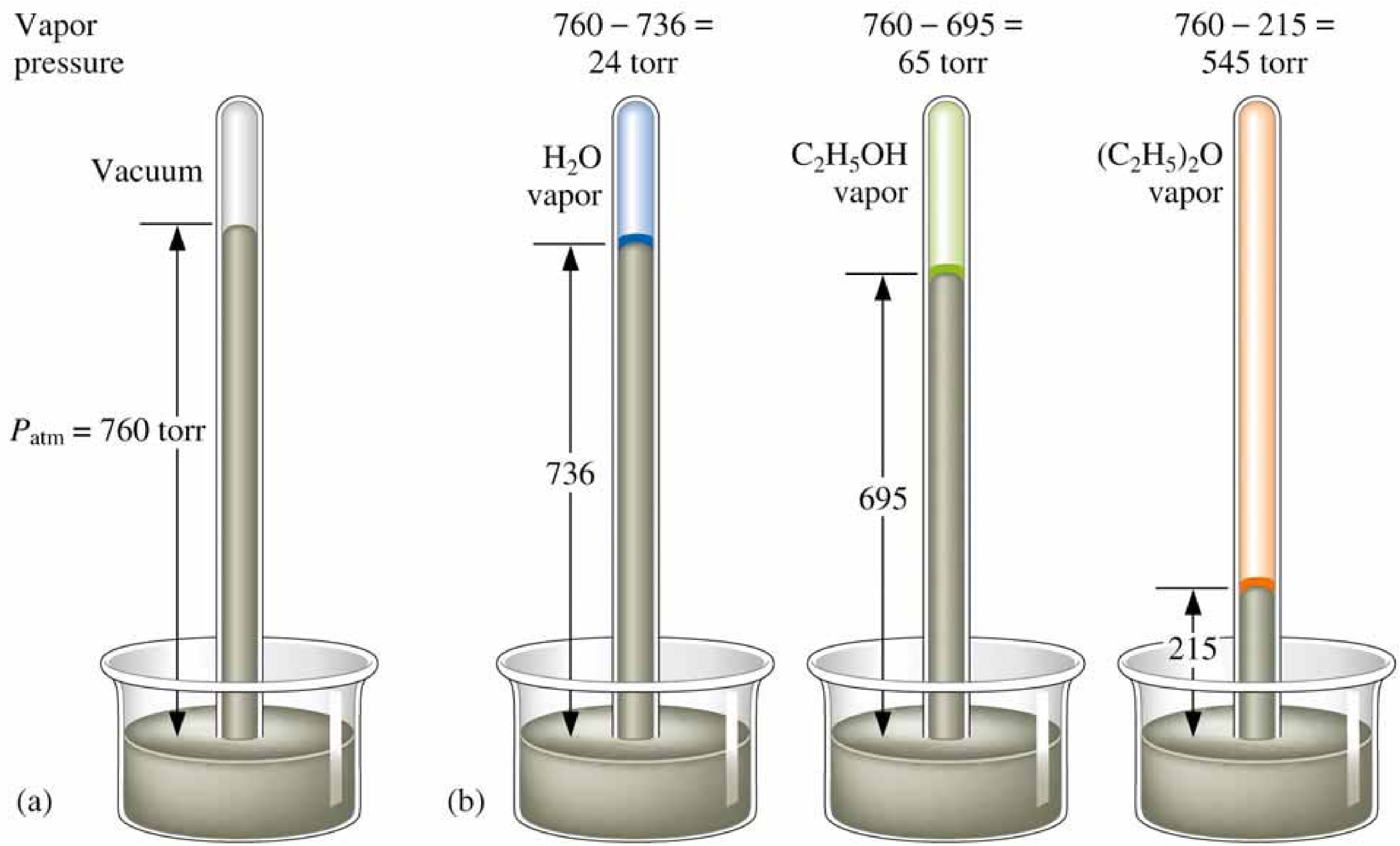
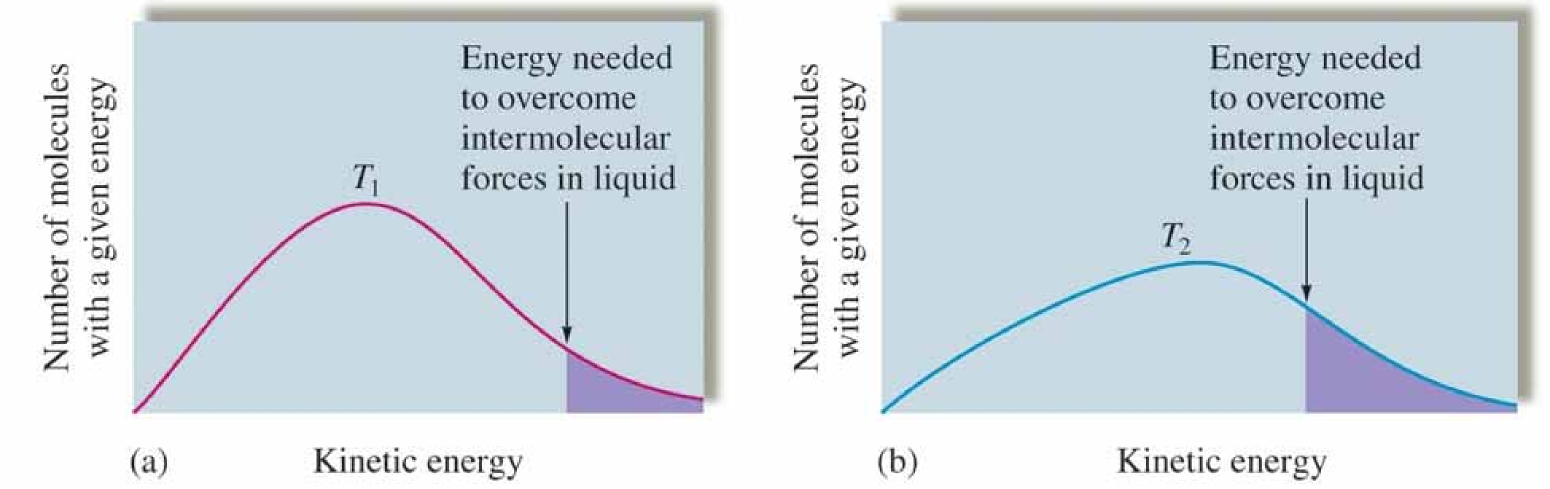

Vapor pressure
760 – 736 = 24 torr
760 – 695 = 65 torr
760 – 215 = 545 torr
Vacuum
H_2O vapor
C_2H_5OH vapor
$(C_2H_5)_2O$ vapor
P_{atm} = 760 torr
736
695
215
(a)
(b)

Figure 10.40

(a) The vapor pressure of a liquid can be measured easily using a simple barometer of the type shown here. (b) The three liquids, water, ethanol (C_2H_5OH), and diethyl ether [$(C_2H_5)_2O$], have quite different vapor pressures. Ether is by far the most volatile of the three. Note that in each case a little liquid remains (floating on the mercury).

- Measurements of the vapor pressure for a given liquid at several temperatures show that *vapor pressure increases significantly with temperature*.
- Figure 10.41 illustrates the distribution of moleculat kinetic energy present in a liquid at two different temperatures.
- The vapor pressure of a liquid increases dramatically with temperature.

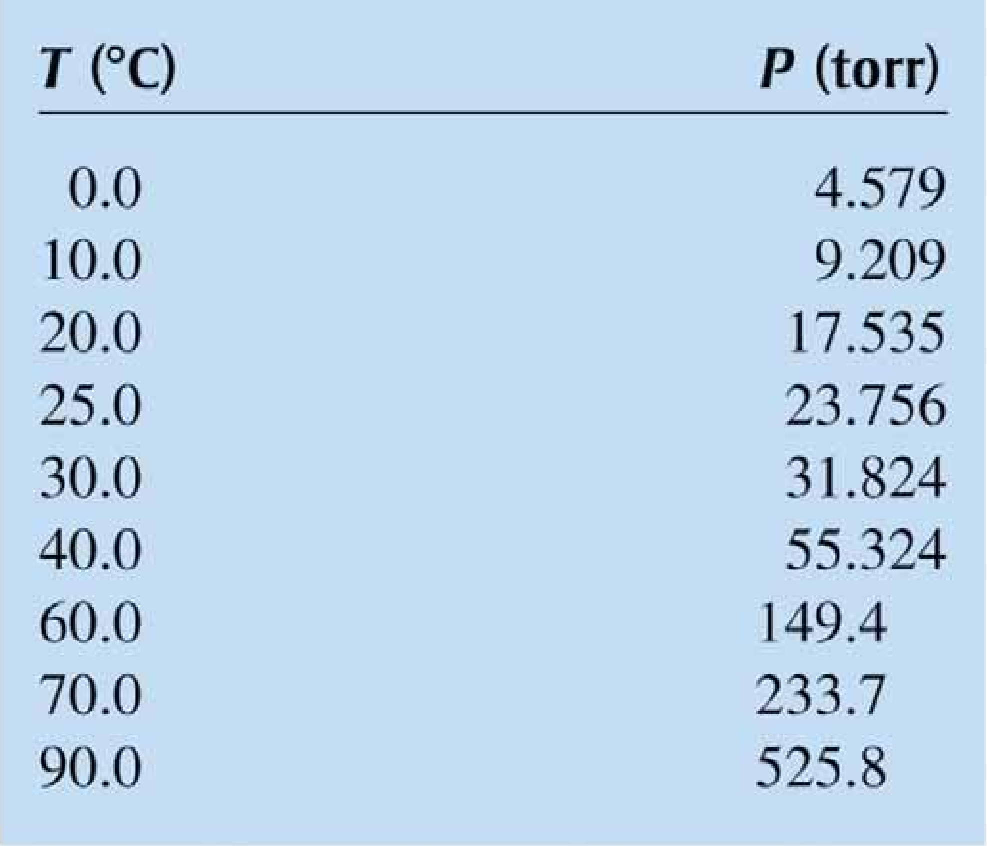
Figure 10.41



The number of molecules in a liquid with a given energy versus kinetic energy at two temperatures. Part (a) shows a lower temperature than that in part (b). Note that the proportion of molecules with enough energy to escape the liquid to the vapor phase (indicated by shaded areas) increases dramatically with temperature. This causes vapor pressure to increase markedly with temperature.

- Values for water at several temperatures are given in Table 10.8.

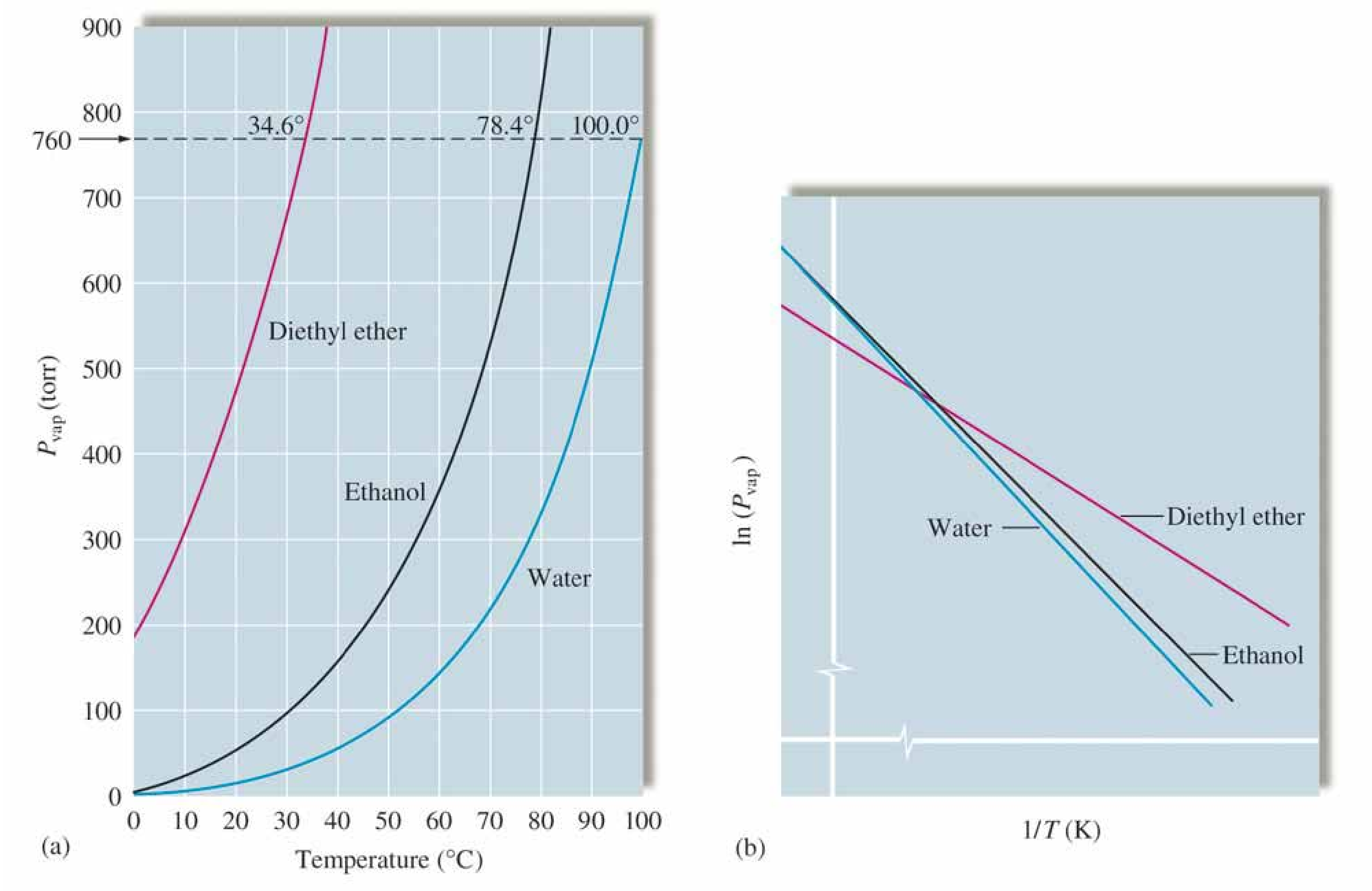
TABLE 10.8 The Vapor Pressure of Water as a Function of Temperature



T (°C)	*P* (torr)
0.0	4.579
10.0	9.209
20.0	17.535
25.0	23.756
30.0	31.824
40.0	55.324
60.0	149.4
70.0	233.7
90.0	525.8

- Plots of vapor pressure versus temperature for water, ethanol, and diethyl ether are shown in Fig. 10.42(a).
- Note the nonlinear increase in vapor pressure for all the liquids as the temperature is increased.
- We find that a straight line can be obtained by plotting $\ln(P_{\text{vap}})$ versus $1/T$, where T is the Kelvin temperature, as shown in Fig. 10.42(b).

Figure 10.42



900
800
760
700
600
500
400
300
200
100
0
P_{vap} (torr)
34.6°
78.4°
100.0°
Diethyl ether
Ethanol
Water
0
10
20
30
40
50
60
70
80
90
100
Temperature (°C)
(a)
ln (P_{vap})
Water
Diethyl ether
Ethanol
1/T (K)
(b)

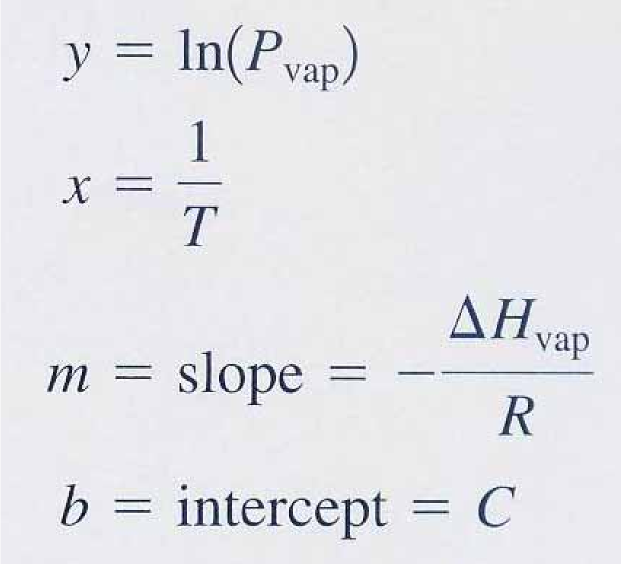
Figure 10.42

(a) The vapor pressure of water, ethanol, and diethyl ether as a function of temperature. (b) Plots of ln(P_{vap}) versus 1/T (Kelvin temperature) for water, ethanol, and diethyl ether.

$$\ln(P_{\text{vap}}) = -\frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T}\right) + C \qquad (10.4)$$

- where ΔH_{vap} is the enthalpy of vaporization, R is the universal gas constant, and C is a constant characteristic of a given liquid.
- The symbol *l*n means that the natural logarithm of the vapor pressure is taken.

- Equation (10.4) is the equation for a straight line of the form $y = mx + b$, where



$$y = \ln(P_{\text{vap}})$$

$$x = \frac{1}{T}$$

$$m = \text{slope} = -\frac{\Delta H_{\text{vap}}}{R}$$

$$b = \text{intercept} = C$$

Sample Exercise 10.5

Determining Enthalpies of Vaporization

Using the plots in Fig. 10.42(b), determine whether eater or diethyl ether has the larger enthalpy of vaporization.

Solution

When $\ln(P_{\text{vap}})$ is plotted versus $1/T$, the slope of the resulting straight line is

$$-\frac{\Delta H_{\text{vap}}}{R}$$

Note from Fig. 10.42(b) that the slopes of the lines for water and diethyl ether are both negative, as expected, and that the line for ether has the smaller slope.

Sample Exercise 10.5

Thus ether has the smaller value of ΔH_{vap}. This makes sense because the hydrogen bonding in water causes it to have a relatively large enthalpy of vaporization.

See Exercises 10.79.

- At two temperatures T_1 and T_2 we can solve equation (10.4) for C and then write the equality

$$\ln(P_{\text{vap},T_1}) + \frac{\Delta H_{\text{vap}}}{RT_1} = C = \ln(P_{\text{vap},T_2}) + \frac{\Delta H_{\text{vap}}}{RT_2}$$

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

$$\ln\left(\frac{P_{\text{vap},T_1}}{P_{\text{vap},T_2}}\right) = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (10.5)$$

Sample Exercise 10.6

Calculating Vapor Pressure

The vapor pressure of water at 25°C is 23.8 torr, and the heat of vaporization of water at 25°C is 43.9 kJ/mol. Calculate the vapor pressure of water at 50. °C .

Solution

We will use Equation (10.5):

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

For water we have

Sample Exercise 10.6

$$\begin{aligned} P_{\text{vap},T_1} &= 23.8 \text{ torr} \\ T_1 &= 25 + 273 = 298 \text{ K} \\ T_2 &= 50. + 273 = 323 \text{ K} \\ \Delta H_{\text{vap}} &= 43.9 \text{ KJ/mol} = 43{,}900 \text{ J/mol} \\ R &= 8.3145 \text{ J/K mol} \end{aligned}$$

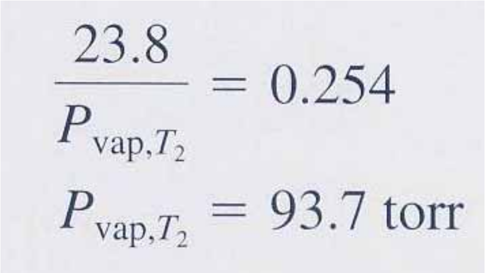
Thus

$$\ln\left(\frac{23.8 \text{ torr}}{P_{\text{vap},T_2}\,(\text{torr})}\right) = \frac{43{,}900 \text{ J/mol}}{8.3145 \text{ J/K mol}}\left(\frac{1}{323 \text{ K}} - \frac{1}{298 \text{ K}}\right)$$

$$\ln\left(\frac{23.8}{P_{\text{vap},T_2}}\right) = -1.37$$

Sample Exercise 10.6

Taking the antilog (see Appendix 1.2) of both sides gives



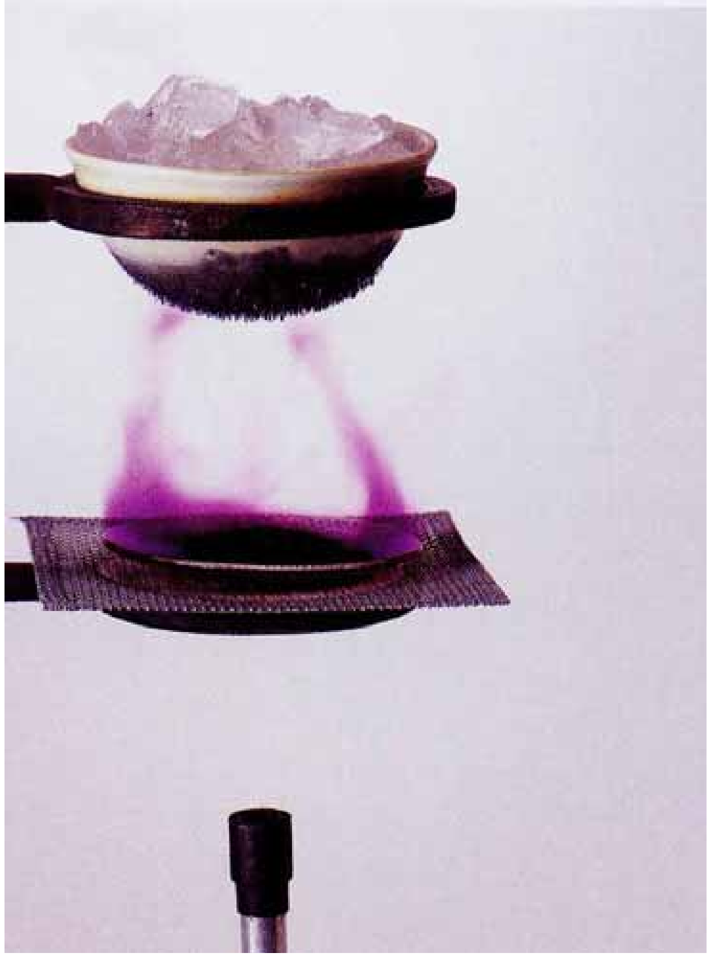
$$\frac{23.8}{P_{\mathrm{vap},T_2}} = 0.254$$

$$P_{\mathrm{vap},T_2} = 93.7 \text{ torr}$$

See Exercises 10.81 through 10.84.

- Like liquids, solids have vapor pressures.
- Figure 10.43 shows iodine vapor in equilibrium with solid iodine in a closed flask.
- Under normal conditions iodine sublimes; that is, it goes directly from the solid to the gaseous state without passing through the liquid state.
- **Sublimation** also occurs with dry ice (solid carbon dioxide).

Figure 10.43



Iodine being heated, causing it to sublime, forming crystals of $I_2(s)$ on the bottom of an evaporating dish cooled by ice.

Changes of State

- This process can be represented by a **heating curve**: a plot of temperature versus time for a process where energy is added at a constant rate.
- The heating curve for water is given in Fig. 10.44.
- The enthalpy change that occurs at the melting point when a solid melts is called the heat of fusion, or more accurately, the enthalpy of fusion, ΔH_{fus}.

- The melting points and enthalpies of fusion for several representative solid are listed in Table 10.9.

Figure 10.44

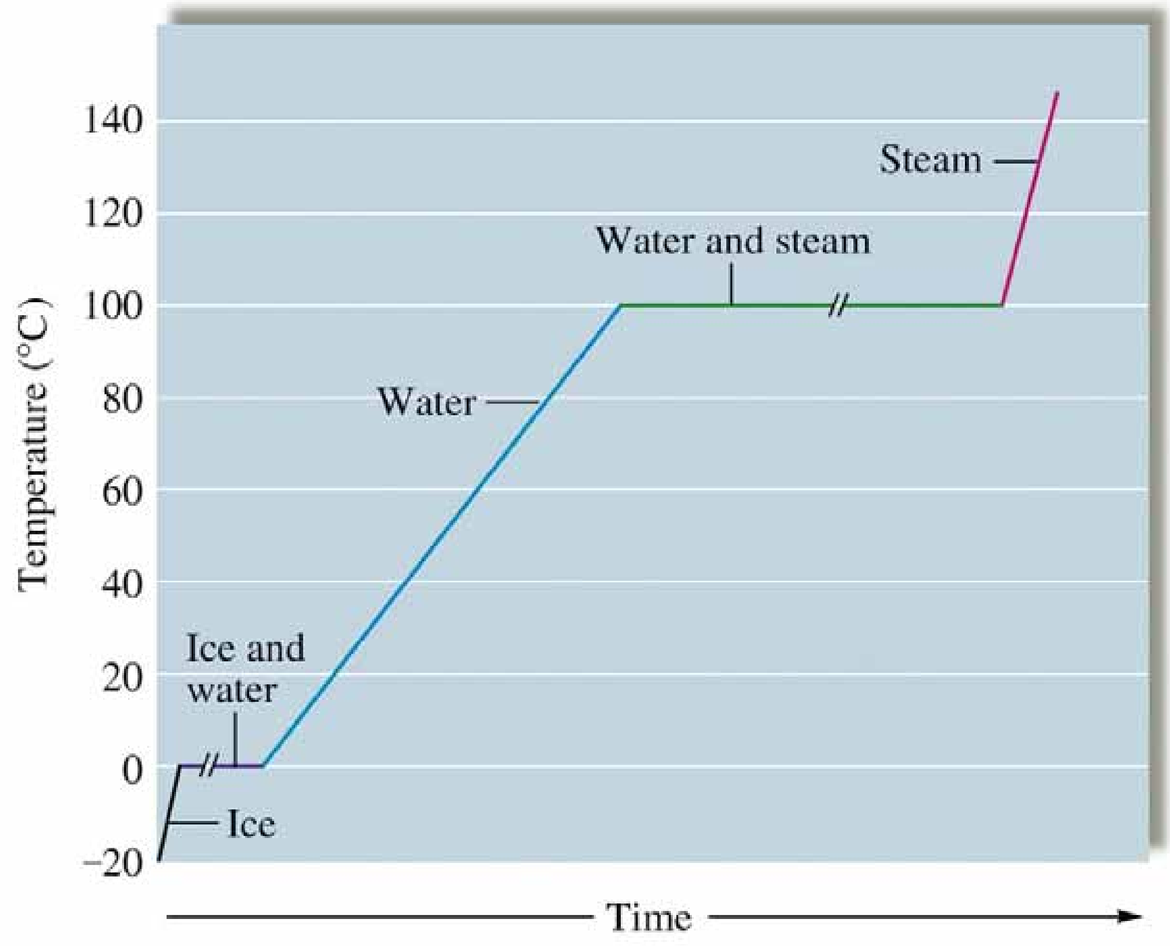
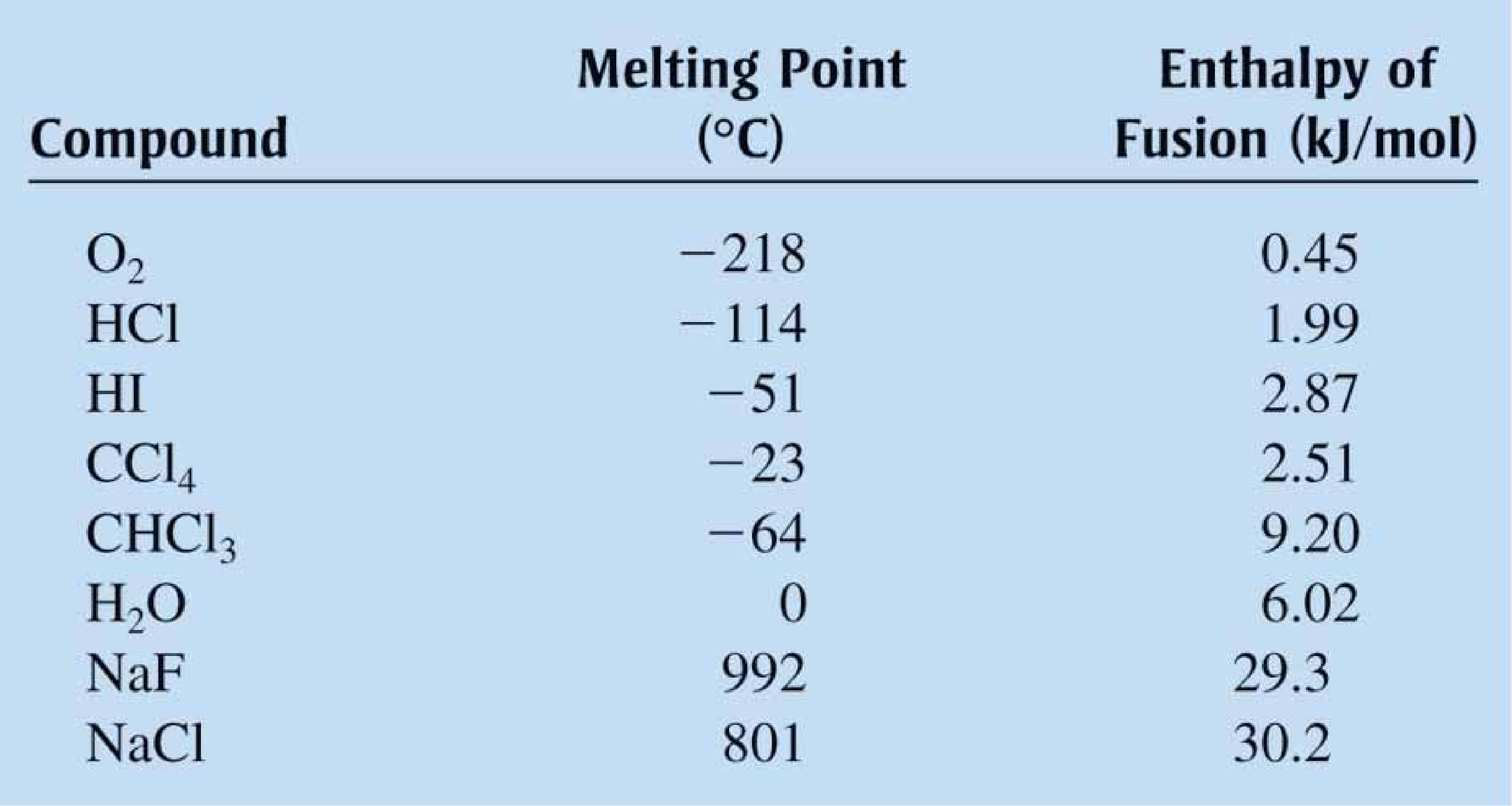

Temperature (°C)
140
120
100
80
60
40
20
0
−20
Steam
Water and steam
Water
Ice and water
Ice
Time

Figure 10.44

The heating curve (not drawn to scale) for a given quantity of eater where energy is added at a constant rate, The plateau at the boiling point is longer than the plateau at the melting point because it takes almost seven times more energy (and this seven times the heating time) to vaporize liquid water than to melt ice. The slopes of the other lines are different because the different states of eater have different molar heat capacities (the energy required to raise the temperature of 1 mole of a substance by 1℃.

TABLE 10.9 Melting Points and Enthalpies of Fusion for Several Representative Solids

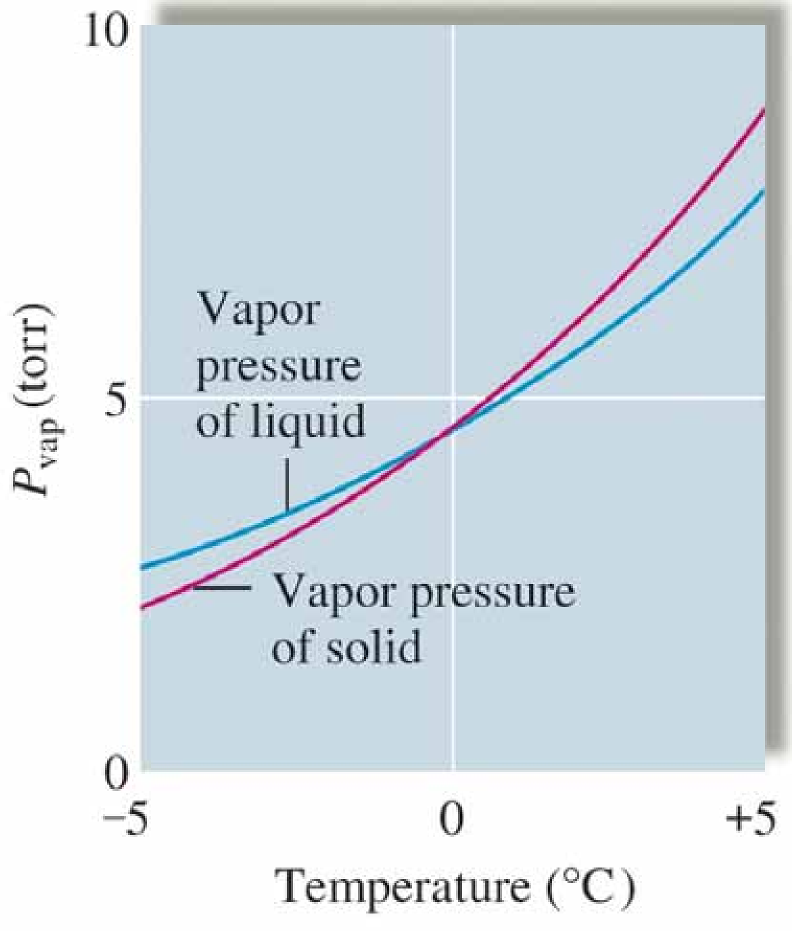


Compound	Melting Point (°C)	Enthalpy of Fusion (kJ/mol)
O_2	−218	0.45
HCl	−114	1.99
HI	−51	2.87
CCl_4	−23	2.51
$CHCl_3$	−64	9.20
H_2O	0	6.02
NaF	992	29.3
NaCl	801	30.2

- The melting and boiling points for a substance are determined by the vapor pressures of the solid and liquid states.
- Figure 10.45 shows the vapor pressures of solid and liquid water as functions of temperature near 0℃.
- Note that below 0℃ the vapor pressure of ice is less than the vapor pressure of liquid water.
- Also note that the vapor pressure of ice has a larger temperature dependence than that of the liquid.

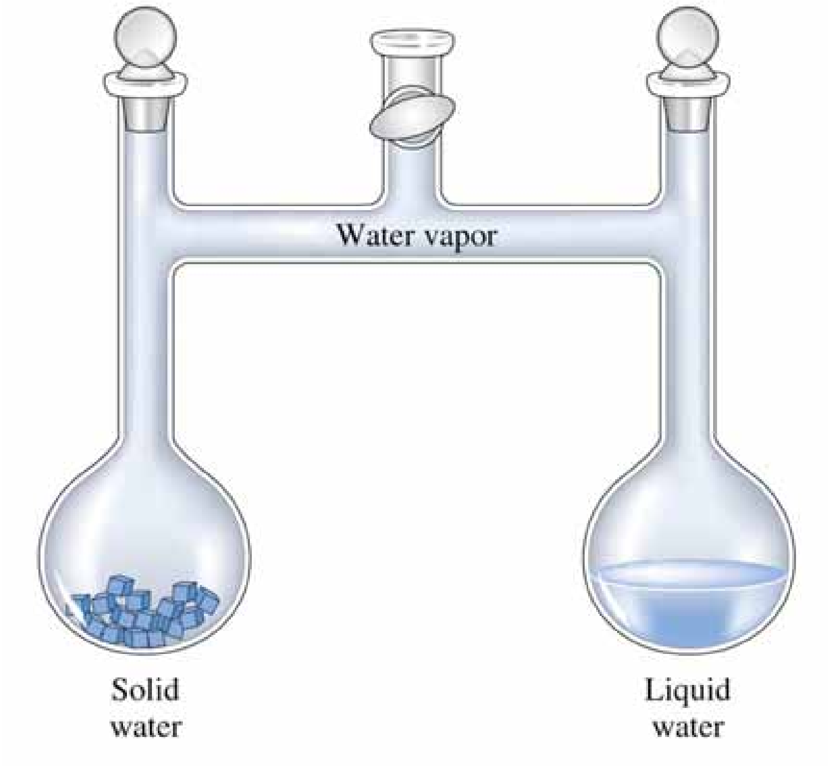
Figure 10.45

The vapor pressures of solid and liquid water as a function of temperature. The data for liquid water below 0℃ are obtained from supercooled water. The data for solid water above 0℃ are estimated by extrapolation of vapor pressure from below 0℃ .



- Thus, as the temperature of the solid is increased, a point is eventually reached *where the liquid and solid have identical vapor pressures*.
- This is the melting point.
- These concepts can be demonstrated experimentally using the apparatus illustrated in Fig.10.46, where ice occupies one compartment and liquid water the other.

Figure 10.46



An apparatus that allows solid and liquid water to interact only through the vapor state.

- **Case 1**

  A temperature at which the vapor pressure of the solid is greater than that of the liquid.

- **Case 2**

  A temperature at which the vapor pressure of the solid is less than that of the liquid.

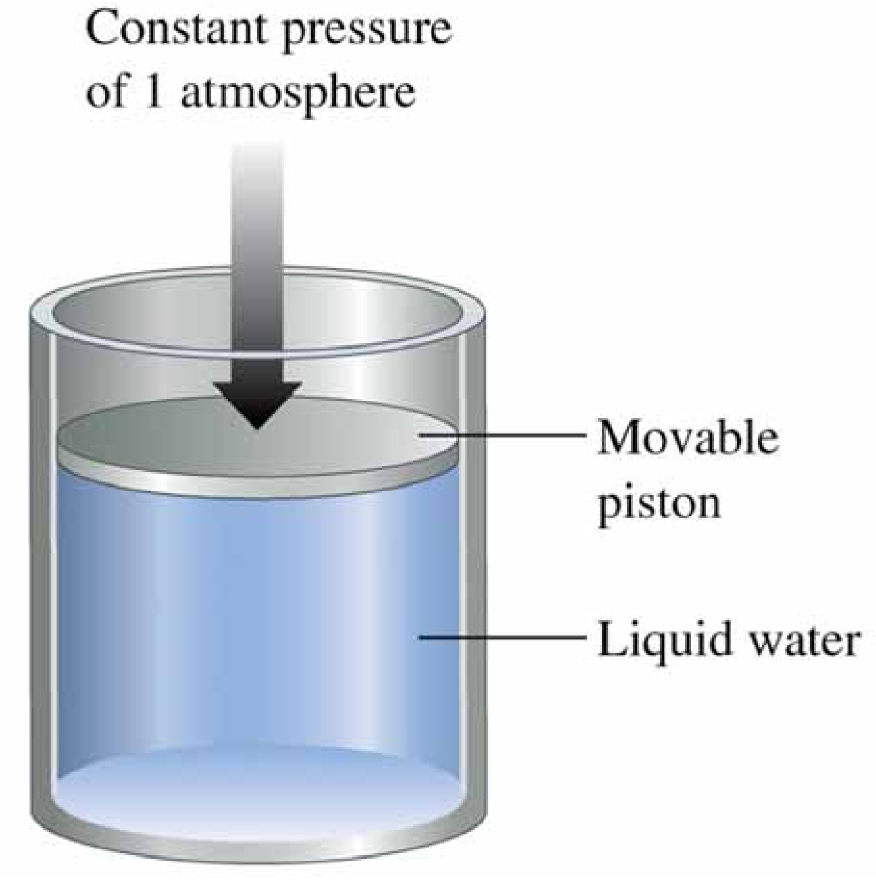
- **Case 3**

  A temperature at which the vapor pressure of the solid and liquid are identical.

- The **normal melting point** is defined as *the temperature at which the solid and liquid states have the same vapor pressure under conditions where the total pressure is 1 atmosphere.*
- The **normal boiling point** of a liquid is *the temperature at which the vapor pressure of the liquid is exactly 1 atmosphere.*
- This concept is illustrated in Fig. 10.47.

Figure 10.47

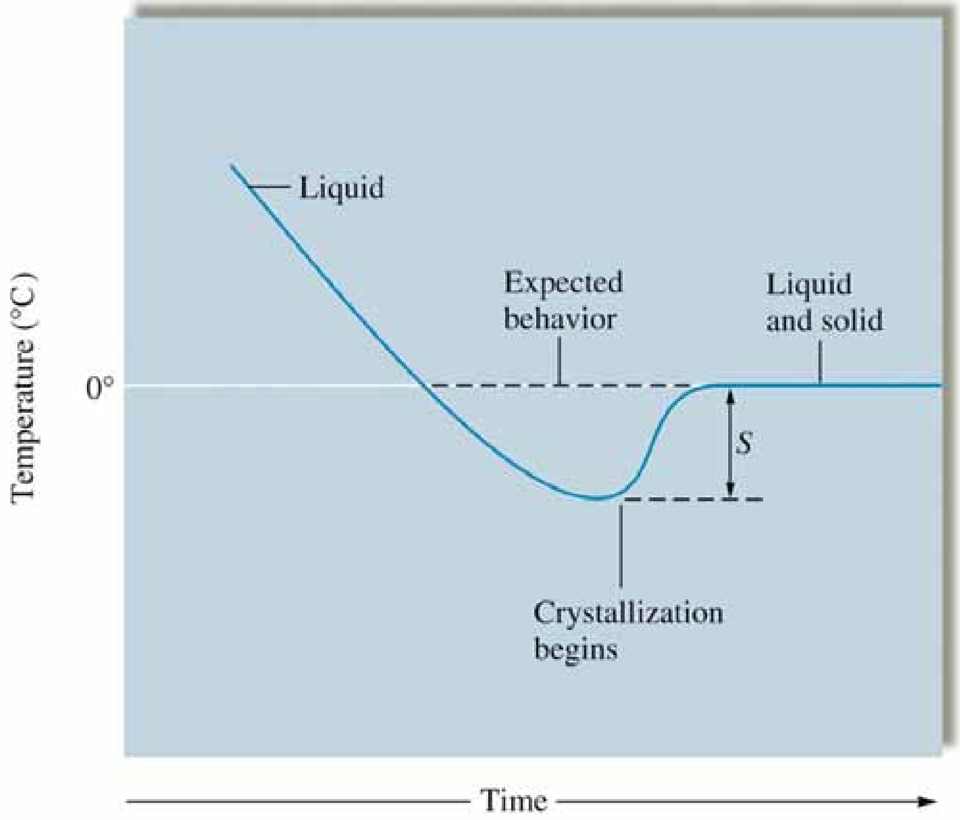
Water in a closed system with a pressure of 1 atm exerted on the piston. No bubbles can form within the liquid as long as the vapor pressure is less than 1 atm.



- **supercooled** : it can be cooled below 0℃ at 1 atm pressure and remain in the liquid state.
- A liquid also can be **superheated**, or raised to temperatures above its boiling point, especially if it is heated rapidly.

Boiling chip releasing air bubbles acts as a nucleating agent for the bubbles that form when water boils.

Figure 10.48



The supercooling of water. The extent of supercooling is given by *S*.

10.9 Phase Diagrams

- **A phase diagram** is a convenient way of representing the phases of a substance as a function of temperature and pressure.
- For example, the phase diagram for water (Fig. 10.49) shows which state exists at a given temperature and pressure.
- It is important to recognize that a phase diagram describes conditions and events in a closed system of the type represented in Fig 10.47.

Figure 10.49

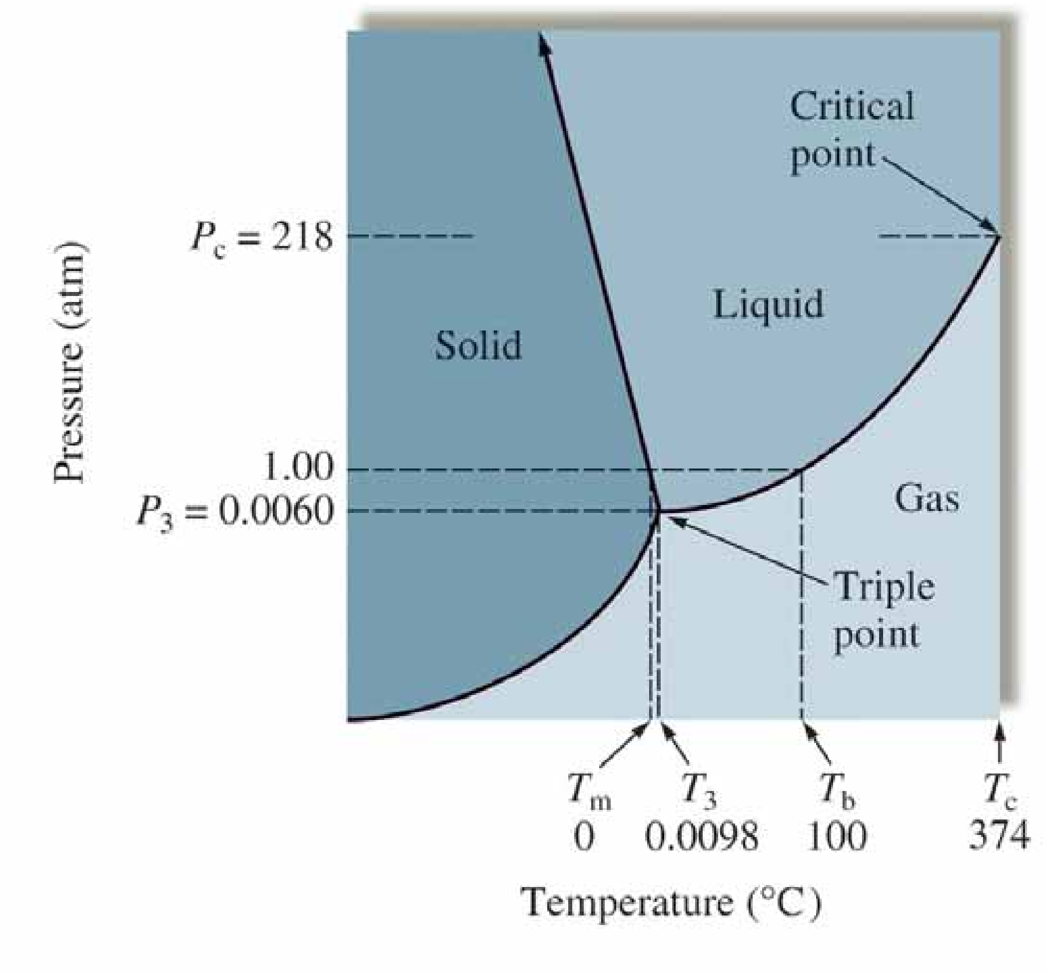
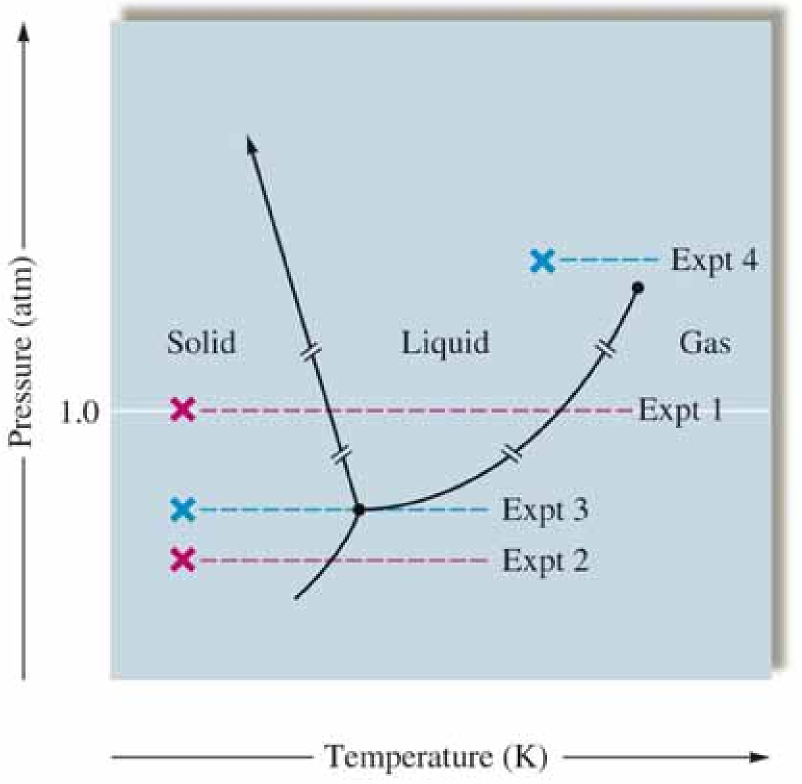

Critical point
$P_c = 218$
Liquid
Solid
1.00
$P_3 = 0.0060$
Gas
Triple point
Pressure (atm)
T_m 0
T_3 0.0098
T_b 100
T_c 374
Temperature (°C)

Figure 10.49

The phase diagram for water. T_m represents the normal melting point; T_3 and P_3 denote the triple point; T_b represents the normal boiling point; T_c represents the critical temperature; P_c represents the critical pressure. The negative slope of the solid/liquid line reflects the face that the density of ice is less than that of liquid water. (Note that this line extends indefinitely, as indicated by the arrow.)

- To show how to interpret the phase diagram for water, we will consider heating experiments at several pressures, shown by the dashed lines in Fig. 10.50.

Figure 10.50



Diagrams of various heating experiments on samples of water in a closed system.

Experiment 1

- *Pressure is 1 atm.*
- This experiment begins with the cylinder shown in Fig. 10.47 completely filled with ice at a temperature of －20°C and the piston exerting a pressure of 1 atm directly on the ice.
- The vapor pressures of the solid and liquid are equal, but this vapor pressure is less than 1 atm, so no water vapor can exist.

- *No vapor is present* because the vapor pressure of liquid water under these conditions is less than 1 atm, the constant external pressure on the piston.
- The cylinder now contains only water vapor.

Experiment 2

- *Pressure is 2.0 torr.*
- We start with ice as the only component in the cylinder at －20°C .
- As heating pro-ceeds, the temperature rises to －10°C, where the ice changes directly to vapor, a process known as *sublimation*.
- No liquid water appears under these conditions because the vapor pressure of liquid water is always greater than 2.0 torr, and thus it cannot exist at this pressure.

Experiment 3

- *Pressure is 4.58 torr.*
- We start with ice as the only component in the cylinder at －20℃ .
- At this point, called the triple point, solid and liquid water have identical vapor pressures of 4.58 torr.
- *At 0.01 ℃ (273.26 K) and 4.58 torr all three states of water are present.*
- Only under these conditions can all three states of water coexist in a closed system.

Experiment 4

- *Pressure is 225 atm.*
- liquid water in the cylinder at 300 °C; the pressure exerted by the piston on the water is 225 atm.
- The **critical temperature** can be defined as the temperature above which the vapor cannot be liquefied no matter what pressure is applied.
- The **critical pressure** is the pressure required to produce liquefaction at the critical temperature.

- Together, the critical temperature and the critical pressure define the **critical point**.

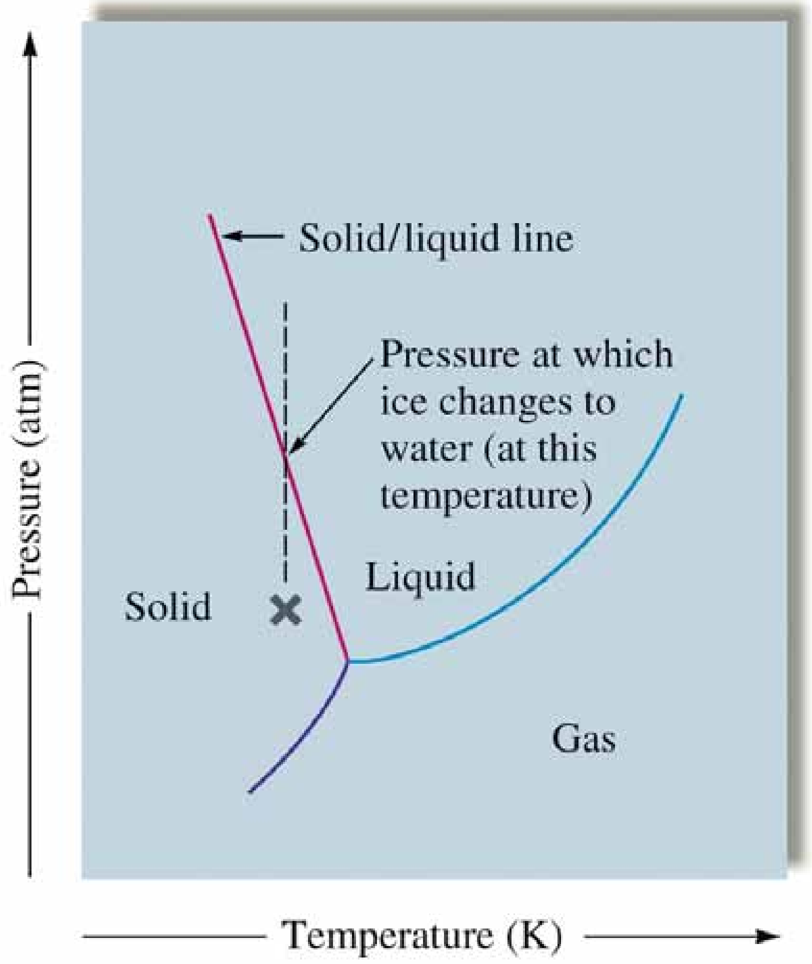
Applications of the Phase Diagram for Water

- There are several additional interesting features of the phase diagram for water.
- Note that the solid/liquid boundary line has a negative slop.
- This means that the melting point of ice *decreases* as the external pressure *increases*.
- The maximum density of water occurs at 4℃; when liquid water freezes, its volume increases.

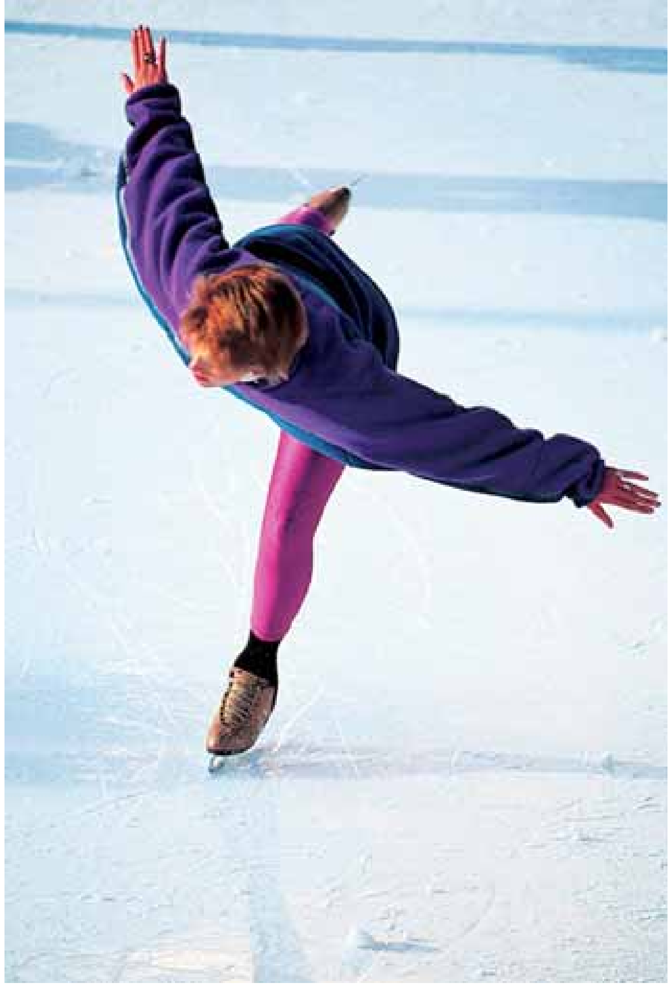
- Figure 10.51 illustrates the effect of pressure on ice.
- At the point *X* on the phase diagram, ice is subjected to increased pressure at constant temperature.
- Note that as the pressure is increased, the solid/liquid line is crossed, indicating that the ice melts.
- This phenomenon may be important in ice skating.

Figure 10.51

The phase diagram for water. At point X on the phase diagram, water is a solid. However, as the external pressure is increased while the temperature remains constant (indicated by the vertical dotted line), the solid/liquid line is crossed and the ice melts.

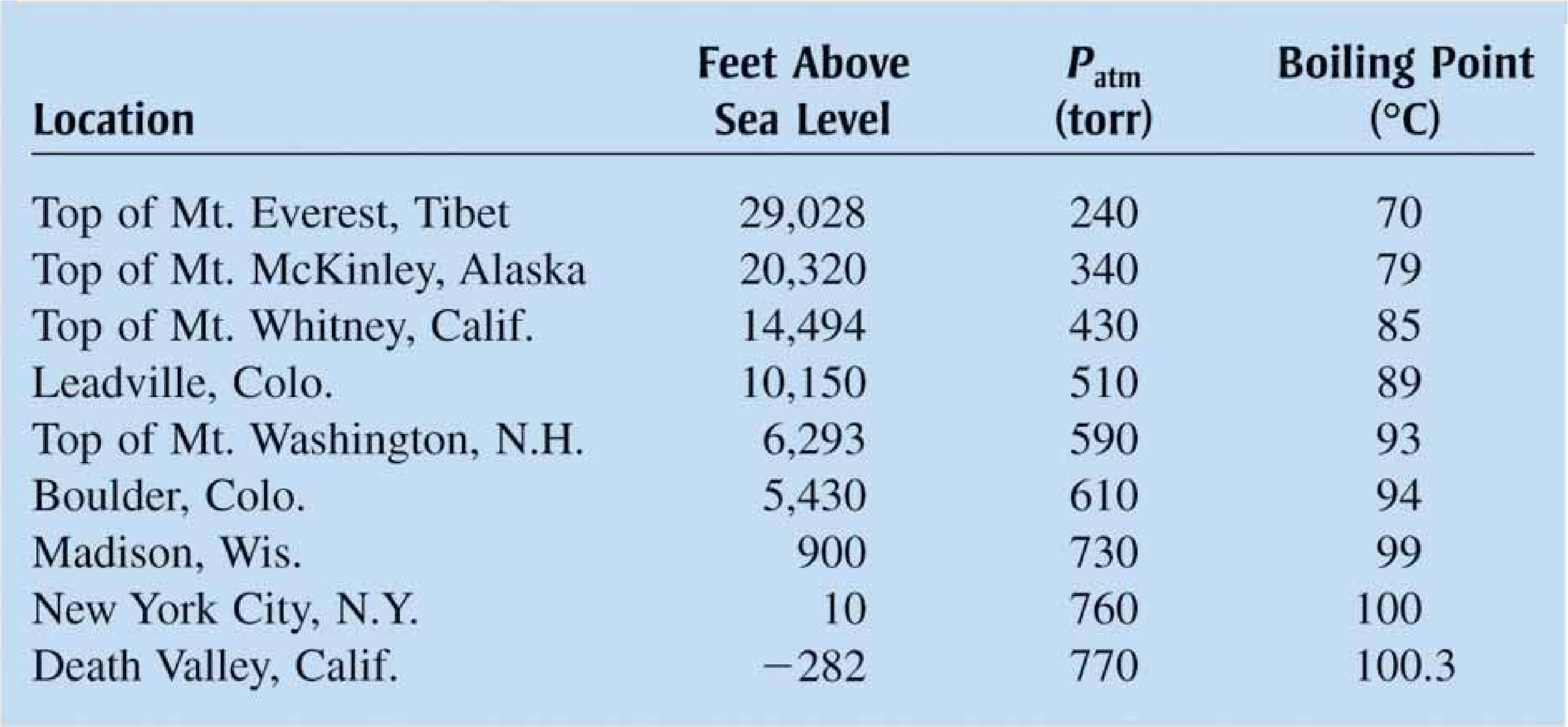


- A liquid boils at the temperature where the vapor pressure of the liquid equals the external pressure.
- The boiling point of a substance, like the melting point, depends on the external pressure.
- This is why water boils at different temperatures at different elevations (see Table 10.10), and any cooking carried out in boiling water will be affected by this variation.



The effect of pressure on ice allows this skater to glide smoothly.

TABLE 10.10 Boiling Point of Water at Various Locations



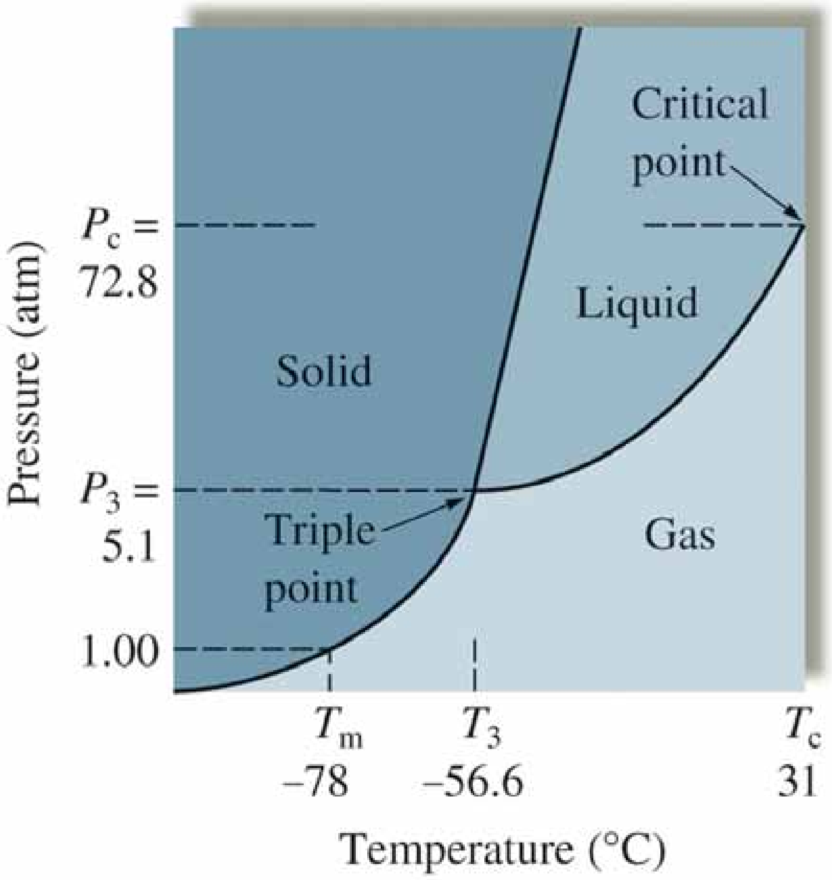
Location	Feet Above Sea Level	P_{atm} (torr)	Boiling Point (°C)
Top of Mt. Everest, Tibet	29,028	240	70
Top of Mt. McKinley, Alaska	20,320	340	79
Top of Mt. Whitney, Calif.	14,494	430	85
Leadville, Colo.	10,150	510	89
Top of Mt. Washington, N.H.	6,293	590	93
Boulder, Colo.	5,430	610	94
Madison, Wis.	900	730	99
New York City, N.Y.	10	760	100
Death Valley, Calif.	−282	770	100.3

The Phase Diagram for Carbon Dioxide

- The phase diagram for carbon dioxide (fig.10.52) differs from that for water.
- The triple point for carbon dioxide occurs at 5.1 atm and －56.6℃, and the critical point occurs at 72.8 atm and 31 ℃.
- At a pressure of 1 atm, solid carbon dioxide sublimes at －78℃, a property that leads to its common name, *dry ice*.

A carbon dioxide fire extinguisher.

Figure 10.52



The phase diagram for carbon dioxide. The liquid state does not exist at a pressure of 1 atm. The solid/liquid line has a positive slope, since the density of solid carbon dioxide is greater than that of liquid carbon dioxide.