▶ **Figure 11.27 Phase diagrams of H₂O and CO₂.** The axes are not drawn to scale in either case. In (a), for water, note the triple point T at 0.0098 °C and 0.00603 atm, the normal melting (or freezing) point of 0 °C at 1 atm, the normal boiling point of 100 °C at 1 atm, and the critical point C (374.4 °C and 217.7 atm). In (b), for carbon dioxide, note the triple point T at −56.4 °C and 5.11 atm, the normal sublimation point of −78.5 °C at 1 atm, and the critical point C (31.1 °C and 73.0 atm).

(a)

(b)
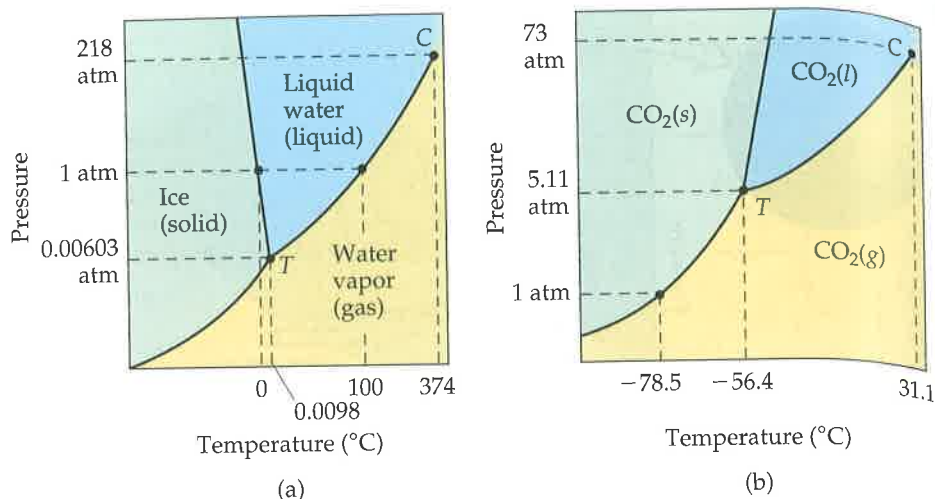
sublimes when heated at 1 atm. Thus, CO_2 does not have a normal melting point; instead, it has a normal sublimation point, −78.5 °C. Because CO_2 sublimes rather than melts as it absorbs energy at ordinary pressures, solid CO_2 (dry ice) is a convenient coolant. For water (ice) to sublime, however, its vapor pressure must be below 0.00603 atm. Food is "freeze-dried" by placing frozen food in a low-pressure chamber (below 0.00603 atm) so that the ice in it sublimes.
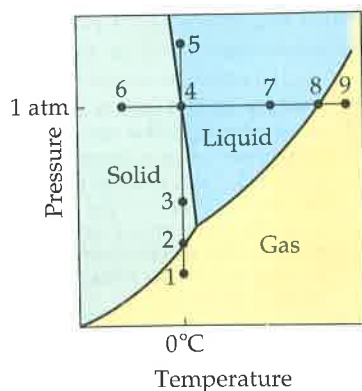
▲ **Figure 11.28 Phase diagram of H₂O.**

■■ **SAMPLE EXERCISE 11.6 | Interpreting a Phase Diagram**

Referring to Figure 11.28 ◀, describe any changes in the phases present when H₂O is **(a)** kept at 0 °C while the pressure is increased from that at point 1 to that at point 5 (vertical line), **(b)** kept at 1.00 atm while the temperature is increased from that at point 6 to that at point 9 (horizontal line).

SOLUTION

Analyze: We are asked to use the phase diagram provided to deduce what phase changes might occur when specific pressure and temperature changes are brought about.

Plan: Trace the path indicated on the phase diagram, and note what phases and phase changes occur.

Solve:

(a) At point 1, H₂O exists totally as a vapor. At point 2 a solid–vapor equilibrium exists. Above that pressure, at point 3, all the H₂O is converted to a solid. At point 4 some of the solid melts and equilibrium between solid and liquid is achieved. At still higher pressures all the H₂O melts, so only the liquid phase is present at point 5.

(b) At point 6 the H₂O exists entirely as a solid. When the temperature reaches point 4, the solid begins to melt and equilibrium exists between the solid and liquid phases. At an even higher temperature, point 7, the solid has been converted entirely to a liquid. A liquid–vapor equilibrium exists at point 8. Upon further heating to point 9, the H₂O is converted entirely to the vapor phase.

Check: The indicated phases and phase changes are consistent with our knowledge of the properties of water.

■■ **PRACTICE EXERCISE**

Using Figure 11.27(b), describe what happens when the following changes are made to a CO_2 sample: **(a)** Pressure increases from 1 atm to 60 atm at a constant temperature of −60 °C. **(b)** Temperature increases from −60 °C to −20 °C at a constant pressure of 60 atm.

Answers: **(a)** $CO_2(g) \longrightarrow CO_2(s)$; **(b)** $CO_2(s) \longrightarrow CO_2(l)$

11.7 STRUCTURES OF SOLIDS

Throughout the remainder of this chapter we will focus on how the properties of solids relate to their structures and bonding. Solids can be either crystalline or amorphous (noncrystalline). In a **crystalline solid** the atoms, ions, or molecules are ordered in well-defined three-dimensional arrangements.

(a) Pyrite (fool's gold)   (b) Fluorite   (c) Amethyst

These solids usually have flat surfaces, or *faces*, that make definite angles with one another. The orderly stacks of particles that produce these faces also cause the solids to have highly regular shapes (Figure 11.29▲). Quartz and diamond are crystalline solids.

An **amorphous solid** (from the Greek words for "without form") is a solid in which particles have no orderly structure. These solids lack well-defined faces and shapes. Many amorphous solids are mixtures of particles that do not stack together well. Most others are composed of large, complicated molecules. Familiar amorphous solids include rubber and glass.
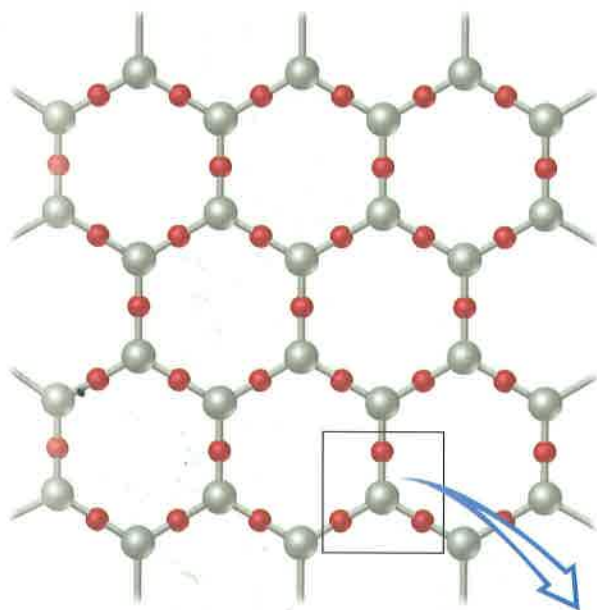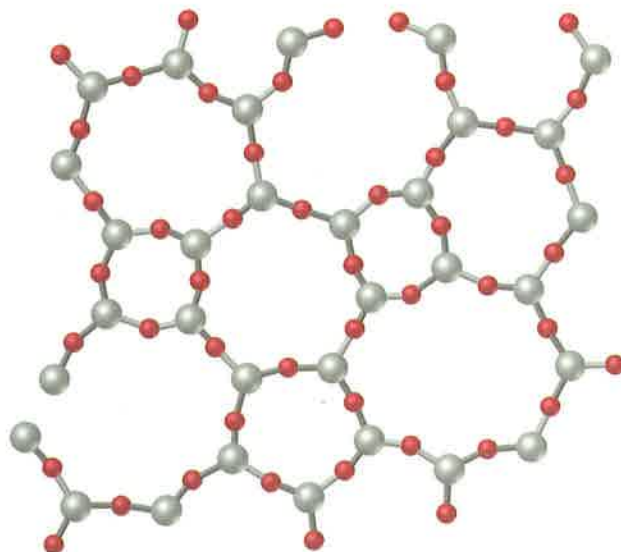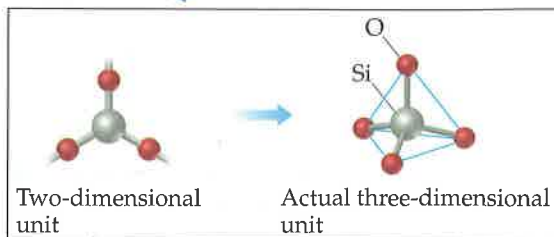
Quartz (SiO_2) is a crystalline solid with a three-dimensional structure like that shown in Figure 11.30(a)▼. When quartz melts (at about 1600 °C), it becomes a viscous, tacky liquid. Although the silicon–oxygen network remains largely intact, many Si—O bonds are broken, and the rigid order of the quartz is lost. If the melt is rapidly cooled, the atoms are unable to return to an orderly arrangement. As a result, an amorphous solid known either as quartz glass or as silica glass results [Figure 11.30(b)].
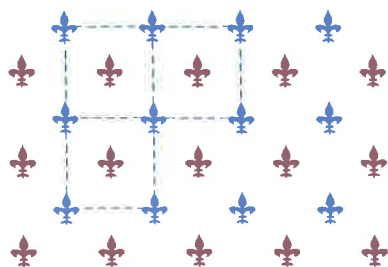
▼ **Figure 11.30 Schematic comparisons of (a) crystalline SiO_2 (quartz) and (b) amorphous SiO_2 (quartz glass).** The structures are actually three-dimensional and not planar as drawn. The two-dimensional unit shown as the basic building block of the structure (silicon and three oxygens) actually has four oxygens, the fourth coming out of the plane of the paper and capable of bonding to other silicon atoms. The actual three-dimensional building block is shown.

(a) Crystalline SiO_2

O
Si
Two-dimensional unit   Actual three-dimensional unit

(b) Amorphous SiO_2

Because the particles of an amorphous solid lack any long-range order, intermolecular forces vary in strength throughout a sample. Thus, amorphous solids do not melt at specific temperatures. Instead, they soften over a temperature range as intermolecular forces of various strengths are overcome. A crystalline solid, in contrast, melts at a specific temperature.

GIVE IT SOME THOUGHT

What is the general difference in the melting behaviors of crystalline and amorphous solids?

Unit Cells

The characteristic order of crystalline solids allows us to convey a picture of an entire crystal by looking at only a small part of it. We can think of the solid as being built by stacking together identical building blocks, much as stacking rows of individual "identical" bricks forms a brick wall. The repeating unit of a solid, the crystalline "brick," is known as the **unit cell**. A simple two-dimensional example appears in the sheet of wallpaper shown in Figure 11.31 ◄. There are several ways of choosing a unit cell, but the choice is usually the smallest unit cell that shows clearly the symmetry characteristic of the entire pattern.

A crystalline solid can be represented by a three-dimensional array of points called a **crystal lattice**. Each point in the lattice is called a *lattice point*, and it represents an identical environment within the solid. The crystal lattice is, in effect, an abstract scaffolding for the crystal structure. We can imagine forming the entire crystal structure by arranging the contents of the unit cell repeatedly on the crystal lattice. In the simplest case the crystal structure would consist of identical atoms, and each atom would be centered on a lattice point. This is the case for most metals.
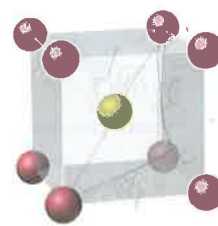
Figure 11.32 ◄ shows a crystal lattice and its associated unit cell. In general, unit cells are parallelepipeds (six-sided figures whose faces are parallelograms). Each unit cell can be described by the lengths of the edges of the cell and by the angles between these edges. Seven basic types of unit cells can describe the lattices of all crystalline compounds. The simplest of these is the cubic unit cell, in which all the sides are equal in length and all the angles are 90°.

Three kinds of cubic unit cells are illustrated in Figure 11.33 ▼. When lattice points are at the corners only, the unit cell is called **primitive cubic** (or *simple cubic*). When a lattice point also occurs at the center of the unit cell, the cell is **body-centered cubic**. When the cell has lattice points at the center of each face, as well as at each corner, it is **face-centered cubic**.
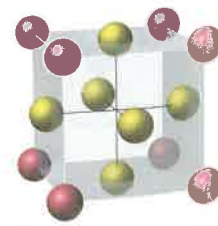
The simplest crystal structures are cubic unit cells with only one atom centered at each lattice point. Most metals have such structures. Nickel, for example, has a face-centered cubic unit cell, whereas sodium has a body-centered cubic one. Figure 11.34 ▶ shows how atoms fill the cubic unit cells. Notice that

▲ Figure 11.31 **A two-dimensional analog of a lattice and its unit cell.** The wallpaper design shows a characteristic repeat pattern. Each dashed blue square denotes a unit cell of the pattern. The unit cell could equally well be selected with red figures at the corners.

▲ Figure 11.32 **Part of a simple crystal lattice and its associated unit cell.** A lattice is an array of points that define the positions of particles in a crystalline solid. Each lattice point represents an identical environment in the solid. The points here are shown connected by lines to help convey the three-dimensional character of the lattice and to help us see the unit cell.
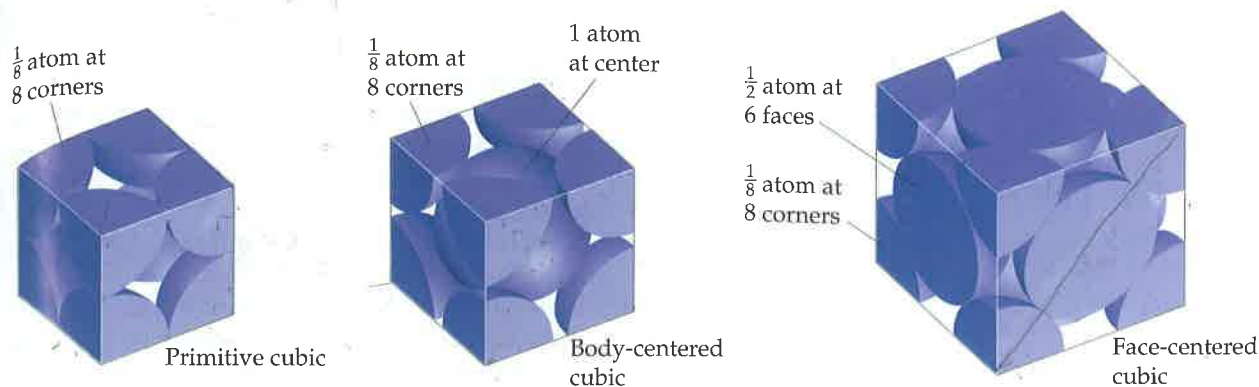
Primitive cubic   Body-centered cubic   Face-centered cubic

▲ Figure 11.33 **The three types of unit cells found in cubic lattices.** For clarity, the corner spheres are red and the body-centered and face-centered ones are yellow. Each sphere represents a lattice point (an identical environment in the solid).

$\frac{1}{8}$ atom at 8 corners

Primitive cubic

$\frac{1}{8}$ atom at 8 corners

1 atom at center

Body-centered cubic

$\frac{1}{2}$ atom at 6 faces

$\frac{1}{8}$ atom at 8 corners

Face-centered cubic

▲ Figure 11.34 **Space-filling view of cubic unit cells.** Only the portion of each atom that belongs to the unit cell is shown.

the atoms on the corners and faces do not lie wholly within the unit cell. Instead, these atoms are shared between unit cells. As an example, let's look at the primitive cubic structure in Figure 11.34. In an actual solid, this primitive cubic structure has other primitive cubic unit cells next to it in all directions, on top of it, and underneath it. If you look at any one corner of the primitive cubic unit cell, you will see that is shared by 8 unit cells. Therefore, in an individual primitive cubic unit cell, each corner contains only one-eighth of an atom. Because a cube has eight corners, each primitive cubic unit cell has a total of $1/8 \times 8 = 1$ atom. Similarly, each body-centered cubic unit cell shown in Figure 11.34 contains two atoms ($1/8 \times 8 = 1$ from the corners, and 1 totally inside the cube). Two unit cells share equally atoms that are on the faces of a face-centered cubic unit cell so that only one-half of the atom belongs to each unit cell. Therefore, the total number of atoms in the face-centered cubic unit cell shown in Figure 11.34 is four (that is, $1/8 \times 8 = 1$ from the corners and $1/2 \times 6 = 3$ from the faces). Table 11.6 ▶ summarizes the fraction of an atom that occupies a unit cell when atoms are shared between unit cells.

TABLE 11.6 ■ **Fraction of an Atom That Occupies a Unit Cell for Various Positions in the Unit Cell**

| Position in Unit Cell	Fraction in Unit Cell
Center	1
Face	$\frac{1}{2}$
Edge	$\frac{1}{4}$
Corner	$\frac{1}{8}$

⚠ **GIVE IT SOME THOUGHT**

If you know the unit cell dimensions for a solid, the number of atoms per unit cell, and the mass of the atoms, show how you can calculate the density of the solid.

The Crystal Structure of Sodium Chloride

In the crystal structure of NaCl (Figure 11.35 ▼) we can center either the Na^+ ions or the Cl^- ions on the lattice points of a face-centered cubic unit cell. Thus, we can describe the structure as being face-centered cubic.

▼ Figure 11.35 **Two ways of defining the unit cell of NaCl.** A representation of an NaCl crystal lattice can show either (a) Cl^- ions (green spheres) or (b) Na^+ ions (purple spheres) at the lattice points of the unit cell. In both cases, the red lines define the unit cell. Both of these choices for the unit cell are acceptable; both have the same volume, and in both cases identical points are arranged in a face-centered cubic fashion.

(a)

(b)
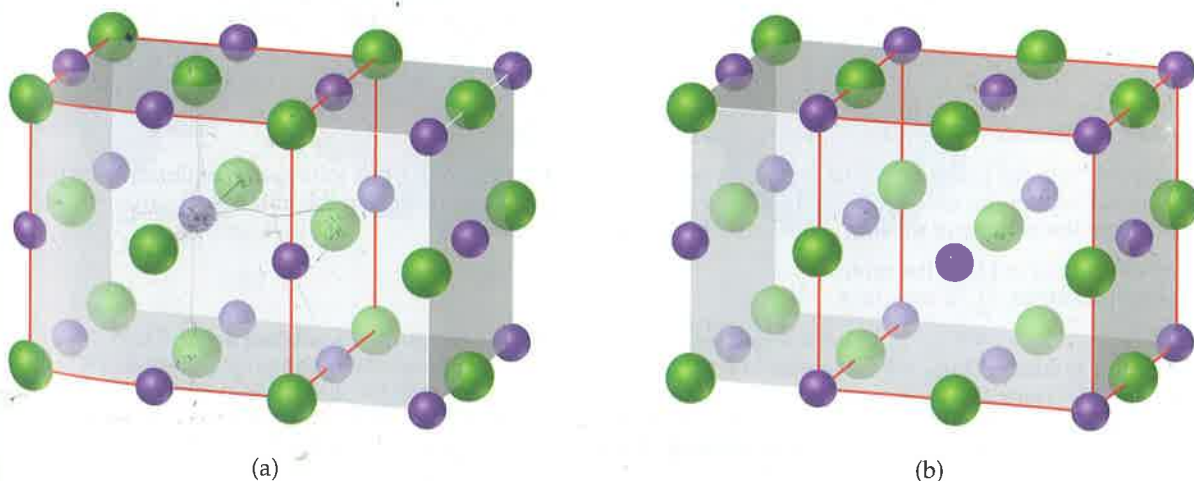
▶ Figure 11.36
Relative size of ions in an NaCl unit cell.
As in Figure 11.35, purple represents Na^+ ions and green represents Cl^- ions. Only portions of most of the ions lie within the boundaries of the single unit cell.
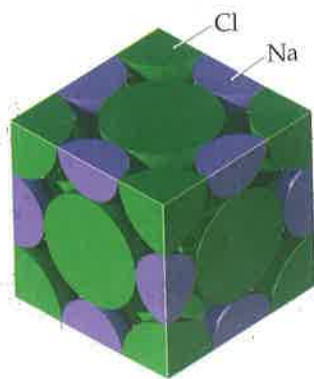
In Figure 11.35 the Na^+ and Cl^- ions have been moved apart so the symmetry of the structure can be seen more clearly. In this representation no attention is paid to the relative sizes of the ions. The representation in Figure 11.36 ◀, on the other hand, shows the relative sizes of the ions and how they fill the unit cell. Notice that other unit cells share the particles at corners, edges, and faces.

The total cation-to-anion ratio of a unit cell must be the same as that for the entire crystal. Therefore, within the unit cell of NaCl there must be an equal number of Na^+ and Cl^- ions. Similarly, the unit cell for $CaCl_2$ would have one Ca^{2+} for every two Cl^-, and so forth.

■ **SAMPLE EXERCISE 11.7** | Determining the Contents of a Unit Cell

Determine the net number of Na^+ and Cl^- ions in the NaCl unit cell (Figure 11.36).

SOLUTION

Analyze: We must sum the various contributing elements to determine the number of Na^+ and Cl^- ions within the unit cell.

Plan: To find the total number of ions of each type, we must identify the different locations within the unit cell and determine the fraction of the ion that lies within the unit cell boundaries.

Solve: There is one-fourth of an Na^+ on each edge, a whole Na^+ in the center of the cube (refer also to Figure 11.35), one-eighth of a Cl^- on each corner, and one-half of a Cl^- on each face. Thus, we have the following:

Na^+: $\left(\frac{1}{4} Na^+ \text{ per edge}\right)$(12 edges) = 3 Na^+
(1 Na^+ per center)(1 center) = 1 Na^+

Cl^-: $\left(\frac{1}{8} Cl^- \text{ per corner}\right)$(8 corners) = 1 Cl^-
$\left(\frac{1}{2} Cl^- \text{ per face}\right)$(6 faces) = 3 Cl^-

Thus, the unit cell contains

4 Na^+ and 4 Cl^-

Check: Since individually the Cl^- ions form a face-centered cubic lattice [see Figure 11.35(a)], as do the Na^+ ions [see Figure 11.35(b)], we would expect there to be four ions of each type in the unit cell. More important, the presence of equal amounts of the two ions agree with the compound's stoichiometry:

1 Na^+ for each Cl^-

■ **PRACTICE EXERCISE**

The element iron crystallizes in a form called α-iron, which has a body-centered cubic unit cell. How many iron atoms are in the unit cell?
Answer: two

■ **SAMPLE EXERCISE 11.8** | Using the Contents and Dimensions of a Unit Cell to Calculate Density

The geometric arrangement of ions in crystals of LiF is the same as that in NaCl. The unit cell of LiF is 4.02 Å on an edge. Calculate the density of LiF.

SOLUTION

Analyze: We are asked to calculate the density of LiF from the size of the unit cell.

Plan: Density is mass per volume, and this is true at the unit cell level as well as the bulk level. We need to determine the number of formula units of LiF within the unit cell. From that, we can calculate the total mass within the unit cell. Because we know the mass and can calculate the volume of the unit cell, we can then calculate density.

Solve: The arrangement of ions in LiF is the same as that in NaCl (Sample Exercise 11.7), so a unit cell of LiF contains

4 Li^+ ions and 4 F^- ions

Density is mass per unit volume. Thus, we can calculate the density of LiF from the mass contained in a unit cell and the volume of the unit cell. The mass contained in one unit cell is

4(6.94 amu) + 4(19.0 amu) = 103.8 amu

The volume of a cube of length a on an edge is a^3, so the volume of the unit cell is $(4.02\ \text{Å})^3$. We can now calculate the density, converting to the common units of g/cm³:

$$\text{Density} = \frac{(103.8\ \text{amu})}{(4.02\ \text{Å})^3}\left(\frac{1\ \text{g}}{6.02 \times 10^{23}\ \text{amu}}\right)\left(\frac{1\ \text{Å}}{10^{-8}\ \text{cm}}\right)^3 = 2.65\ \text{g/cm}^3$$

Check: This value agrees with that found by simple density measurements, 2.640 g/cm³ at 20 °C. The size and contents of the unit cell are therefore consistent with the macroscopic density of the substance.

■ PRACTICE EXERCISE

The body-centered cubic unit cell of a particular crystalline form of iron is 2.8664 Å on each side. Calculate the density of this form of iron.
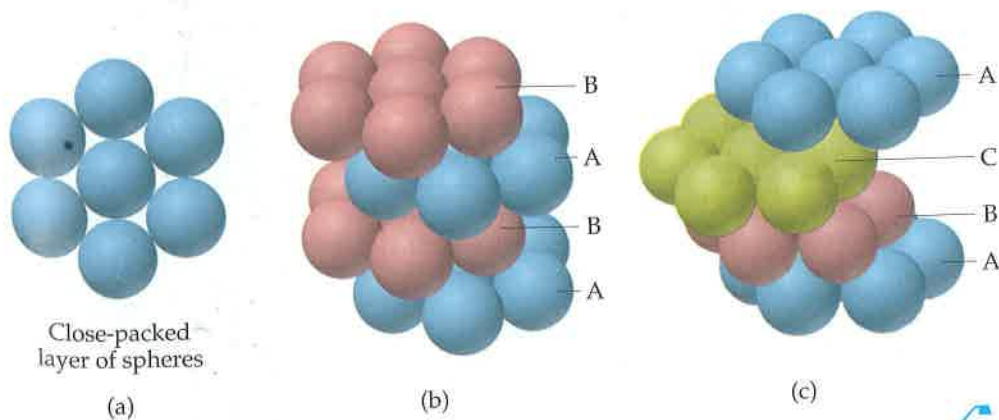*Answer:* 7.8753 g/cm³

Close Packing of Spheres

The structures adopted by crystalline solids are those that bring particles in closest contact to maximize the attractive forces between them. In many cases the particles that make up the solids are spherical or approximately so. Such is the case for atoms in metallic solids. It is therefore instructive to consider how equal-sized spheres can pack most efficiently (that is, with the minimum amount of empty space).

The most efficient arrangement of a layer of equal-sized spheres is shown in Figure 11.37(a)▼. Each sphere is surrounded by six others in the layer. A second layer of spheres can be placed in the depressions on top of the first layer. A third layer can then be added above the second with the spheres sitting in the depressions of the second layer. However, there are two types of depressions for this third layer, and they result in different structures, as shown in Figure 11.37(b) and (c).

If the spheres of the third layer are placed in line with those of the first layer, as shown in Figure 11.37(b), the structure is known as **hexagonal close packing**. The third layer repeats the first layer, the fourth layer repeats the second layer, and so forth, giving a layer sequence that we denote ABAB.

The spheres of the third layer, however, can be placed so they do not sit above the spheres in the first layer. The resulting structure, shown in Figure 11.37(c), is known as **cubic close packing**. In this case it is the fourth layer that repeats the first layer, and the layer sequence is ABCA. Although it cannot be seen in Figure 11.37(c), the unit cell of the cubic close-packed structure is face-centered cubic.

An origami-inspired demonstration, tested by Michael Laing. James Birk and Ellen Yezierski, "Paper-and-Glue Unit Cell Models," *J. Chem. Educ.*, Vol. 80, **2003**, 157–159.

Keenan E. Dungey, George Lisensky, and S. Michael Condren, "Kixium Monolayers: A Simple Alternative to the Bubble Raft Model for Close-Packed Spheres," *J. Chem. Educ.*, Vol. 76, **1999**, 618–619.

An overhead projector demonstration of close packing. Daryl L. Ostercamp, "Close Packing of Identical Spheres," *J. Chem. Educ.*, Vol. 69, **1992**, 162.

▲ **Figure 11.37 Close packing of equal-sized spheres.** (a) Close packing of a single layer of equal-sized spheres. (b) In the hexagonal close-packed structure the atoms in the third layer lie directly over those in the first layer. The order of layers is ABAB. (c) In the cubic close-packed structure the atoms in the third layer are not over those in the first layer. Instead, they are offset a bit, and it is the fourth layer that lies directly over the first. Thus, the order of layers is ABCA.

In both of the close-packed structures, each sphere has 12 equidistant nearest neighbors: six in one plane, three above that plane, and three below. We say that each sphere has a **coordination number** of 12. The coordination number is the number of particles immediately surrounding a particle in the crystal structure. In both types of close packing, spheres occupy 74% of the total volume of the structure; 26% is empty space between the spheres. By comparison, each sphere in the body-centered cubic structure has a coordination number of 8, and only 68% of the space is occupied. In the primitive cubic structure the coordination number is 6, and only 52% of the space is occupied.

When unequal-sized spheres are packed in a lattice, the larger particles sometimes assume one of the close-packed arrangements, with smaller particles occupying the holes between the large spheres. In Li_2O, for example, the larger oxide ions assume a cubic close-packed structure, and the smaller Li^+ ions occupy small cavities that exist between oxide ions.

GIVE IT SOME THOUGHT

Based on the information given above for close-packed structures and structures with cubic unit cells, what qualitative relationship exists between coordination numbers and packing efficiencies?

11.8 BONDING IN SOLIDS

The physical properties of crystalline solids, such as melting point and hardness, depend both on the arrangements of particles (atoms, ions, or molecules) and on the attractive forces between them. Table 11.7 ▼ classifies solids according to the types of forces between particles in solids.

Molecular Solids

Molecular solids consist of atoms or molecules held together by intermolecular forces (dipole–dipole forces, London dispersion forces, and hydrogen bonds). Because these forces are weak, molecular solids are soft. Furthermore, they normally have relatively low melting points (usually below 200 °C). Most substances that are gases or liquids at room temperature form molecular solids at low temperature. Examples include Ar, H_2O, and CO_2.

TABLE 11.7 ■ Types of Crystalline Solids

Type of Solid	Form of Unit Particles	Forces Between Particles	Properties	Examples
Molecular	Atoms or molecules	London dispersion forces, dipole–dipole forces, hydrogen bonds	Fairly soft, low to moderately high melting point, poor thermal and electrical conduction	Argon, Ar; methane, CH_4; sucrose, $C_{12}H_{22}O_{11}$; Dry Ice, CO_2
Covalent-network	Atoms connected in a network of covalent bonds	Covalent bonds	Very hard, very high melting point, variable thermal and electrical conduction	Diamond, C; quartz, SiO_2
Ionic	Positive and negative ions	Electrostatic attractions	Hard and brittle, high melting point, poor thermal and electrical conduction	Typical salts—for example, NaCl, $Ca(NO_3)_2$
Metallic	Atoms	Metallic bonds	Soft to very hard, low to very high melting point, excellent thermal and electrical conduction, malleable and ductile	All metallic elements—for example, Cu, Fe, Al, Pt

## A Closer Look   X-RAY DIFFRACTION BY CRYSTALS

When light waves pass through a narrow slit, they are scattered in such a way that the wave seems to spread out. This physical phenomenon is called *diffraction*. When light passes through many evenly spaced narrow slits (a *diffraction grating*), the scattered waves interact to form a series of bright and dark bands, known as a diffraction pattern. The bright bands correspond to constructive overlapping of the light waves, and the dark bands correspond to destructive overlapping of the light waves (∞ Section 9.8, "A Closer Look: Phases in Atomic and Molecular Orbitals"). The most effective diffraction of light occurs when the wavelength of the light and the width of the slits are similar in magnitude.

The spacing of the layers of atoms in solid crystals is usually about 2–20 Å. The wavelengths of X-rays are also in this range. Thus, a crystal can serve as an effective diffraction grating for X-rays. X-ray diffraction results from the scattering of X-rays by a regular arrangement of atoms, molecules, or ions. Much of what we know about crystal structures has been obtained from studies of X-ray diffraction by crystals, a technique known as *X-ray crystallography*. Figure 11.38▼ depicts the diffraction of a beam of X-rays as it passes through a crystal. The diffracted X-rays were formerly detected by photographic film. Today, crystallographers use an *array detector*, a device analogous to that used in digital cameras, to capture and measure the intensities of the diffracted rays. The diffraction pattern of spots on the detector in Figure 11.38 depends on the particular arrangement of atoms in the crystal. Thus, different types of crystals give rise to different diffraction

patterns. In 1913 the English scientists William and Lawrence Bragg (father and son) determined for the first time how the spacing of layers in crystals leads to different X-ray diffraction patterns. By measuring the intensities of the diffracted beams and the angles at which they are diffracted, it is possible to reason backward to the structure that must have given rise to the pattern. One of the most famous X-ray diffraction patterns is the one for crystals of the genetic material DNA (Figure 11.39▼), first obtained in the early 1950s. Working from X-ray diffraction data obtained by Rosalind Franklin, Franklin, Maurice Wilkins, James Watson, and Francis Crick determined the double-helix structure of DNA, one of the most important discoveries in molecular biology. For this achievement, Watson, Crick, and Wilkins were awarded the Nobel Prize in Physiology or Medicine in 1962. Franklin died in 1958, at age 37, from cancer; Nobel Prizes are awarded only to the living (and can be shared by three people at the most).

Today X-ray crystallography is used extensively to determine the structures of molecules in crystals. The instruments used to measure X-ray diffraction, known as *X-ray diffractometers*, are now computer-controlled, making the collection of diffraction data highly automated. The diffraction pattern of a crystal can be determined very accurately and quickly (sometimes in a matter of hours), even though thousands of diffraction points are measured. Computer programs are then used to analyze the diffraction data and determine the arrangement and structure of the molecules in the crystal.
Related Exercises: 11.95, 11.96
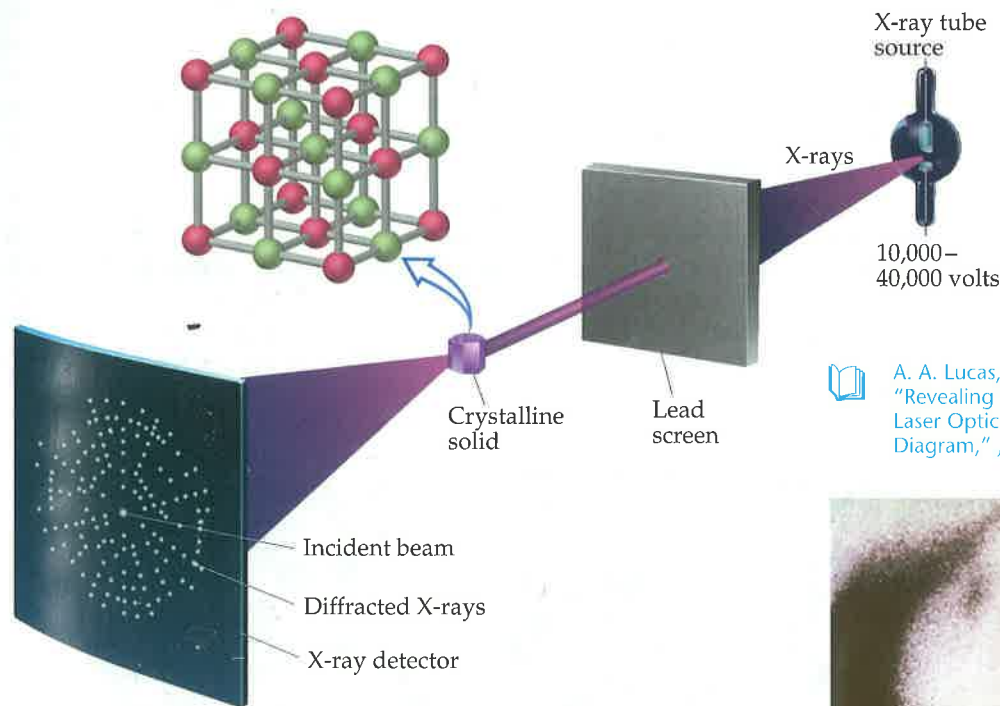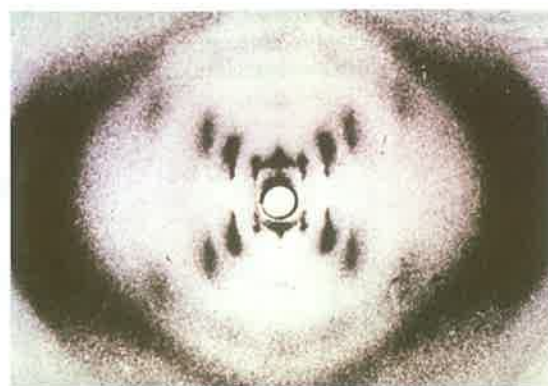

◀ **Figure 11.38 Diffraction of X-rays by a crystal.** In X-ray crystallography, an X-ray beam is diffracted by a crystal. The diffraction pattern can be recorded as spots where the diffracted X-rays strike a detector, which records the positions and intensities of the spots.
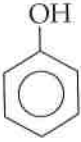
A. A. Lucas, P. Lambin, R. Mairesse and M. Mathot. "Revealing the Backbone Structure of β-DNA from Laser Optical Simulations of Its X-ray Diffraction Diagram," *J. Chem. Educ.*, Vol. 76, **1999**, 378–383.

▶ **Figure 11.39 The X-ray diffraction photograph of one form of crystalline DNA.** This photograph was taken in the early 1950s. From the pattern of dark spots, the double-helical shape of the DNA molecule was deduced.

CH₃   OH

Benzene   Toluene   Phenol

	Benzene	Toluene	Phenol
Melting point (°C)	5	−95	43
Boiling point (°C)	80	111	182

▲ Figure 11.40 **Comparative melting and boiling points for benzene, toluene, and phenol.**

The properties of molecular solids depend on the strengths of the forces that exist between molecules and on the abilities of the molecules to pack efficiently in three dimensions. Benzene (C_6H_6), for example, is a highly symmetrical planar molecule. ∞ (Section 8.6) It has a higher melting point than toluene, a compound in which one of the hydrogen atoms of benzene has been replaced by a CH_3 group (Figure 11.40 ◄). The lower symmetry of toluene molecules prevents them from packing as efficiently as benzene molecules. As a result, the intermolecular forces that depend on close contact are not as effective and the melting point is lower. In contrast, the boiling point of toluene is higher than that of benzene, indicating that the intermolecular attractive forces are larger in liquid toluene than in liquid benzene. Both the melting and boiling points of phenol, another substituted benzene shown in Figure 11.40, are higher than those of benzene because the OH group of phenol can form hydrogen bonds.

GIVE IT SOME THOUGHT

Which of the following substances would you expect to form molecular solids: Co, C_6H_6, or K_2O?

Covalent-Network Solids

Covalent-network solids consist of atoms held together, throughout the entire sample of material, in large networks or chains by covalent bonds. Because covalent bonds are much stronger than intermolecular forces, these solids are much harder and have higher melting points than molecular solids. Diamond and graphite, two allotropes of carbon, are covalent-network solids. Other examples include silicon and germanium; quartz, SiO_2; silicon carbide, SiC; and boron nitride, BN.

In diamond, each carbon atom is bonded tetrahedrally to four other carbon atoms, as shown in Figure 11.41(a) ▼. This interconnected three-dimensional array of strong carbon–carbon single bonds that are sp^3 hybridized contributes to diamond's unusual hardness. Industrial-grade diamonds are employed in the blades of saws for the most demanding cutting jobs. Diamond also has a high melting point, 3550 °C.

In graphite, the carbon atoms are bonded in trigonal planar geometries to three other carbons to form interconnected hexagonal rings, as shown in Figure 11.41(b). The distance between adjacent carbon atoms in the plane, 1.42 Å, is very close to the C—C distance in benzene, 1.395 Å. In fact, the bonding resembles that of benzene, with delocalized π bonds extending over the layers. ∞ (Section 9.6) Electrons move freely through the delocalized orbitals,
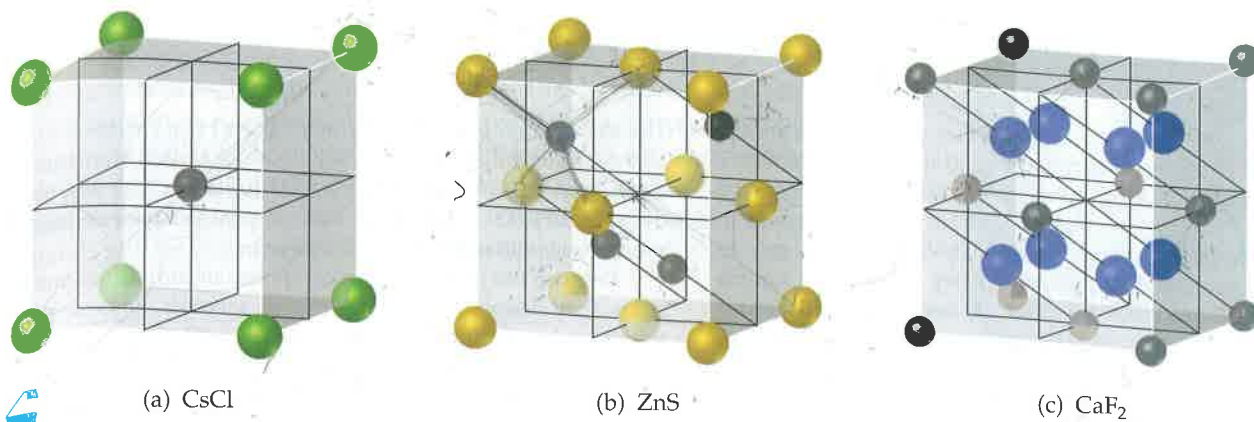
▶ Figure 11.41 **Structures of (a) diamond and (b) graphite.** The blue color in (b) is added to emphasize the planarity of the carbon layers.
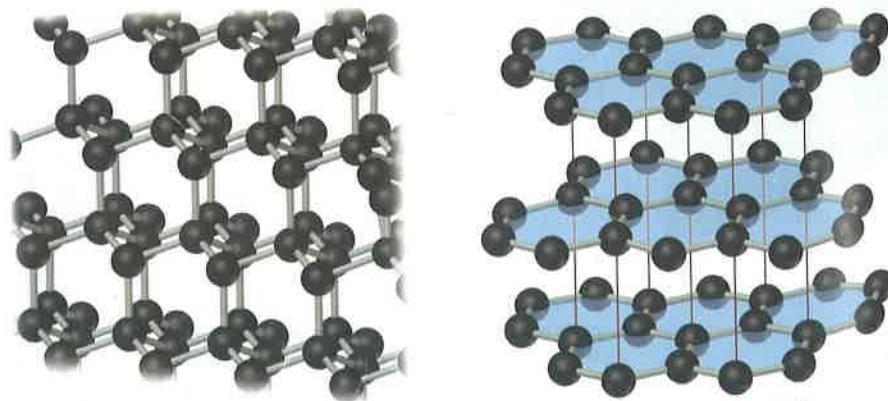
(a) Diamond   (b) Graphite

▲ Figure 11.42 **Unit cells of some common ionic structures.** The ZnS shown in (b) is called zinc blende, and the CaF₂ of (c) is known as fluorite.

making graphite a good conductor of electricity along the layers. (In fact, graphite is used as a conducting electrode in batteries.) These sp^2-hybridized sheets of carbon atoms are separated by 3.35 Å from one another, and the sheets are held together only by weak dispersion forces. Thus, the layers readily slide past one another when rubbed, giving graphite a greasy feel. Graphite is used as a lubricant and in the "lead" in pencils. The enormous differences in physical properties of graphite and diamond—both of which are pure carbon—arise from their differences in their three-dimensional structure and bonding.

Ionic Solids

Ionic solids consist of ions held together by ionic bonds. ⟺ (Section 8.2) The strength of an ionic bond depends greatly on the charges of the ions. Thus, NaCl, in which the ions have charges of 1+ and 1−, has a melting point of 801 °C, whereas MgO, in which the charges are 2+ and 2−, melts at 2852 °C.

The structures of simple ionic solids can be classified as a few basic types. The NaCl structure is a representative example of one type. Other compounds that possess this same structure include LiF, KCl, AgCl, and CaO. Three other common types of crystal structures are shown in Figure 11.42▲.

The structure adopted by an ionic solid depends largely on the charges and relative sizes of the ions. In the NaCl structure, for example, the Na$^+$ ions have a coordination number of 6 because each Na$^+$ ion is surrounded by six nearest neighbor Cl$^-$ ions. In the CsCl structure [Figure 11.42(a)], by comparison, the Cl$^-$ ions adopt a primitive cubic arrangement with each Cs$^+$ ion surrounded by eight Cl$^-$ ions. The increase in the coordination number as the alkali metal ion changes from Na$^+$ to Cs$^+$ is a consequence of the larger size of Cs$^+$ compared to Na$^+$.

In the zinc blende (ZnS) structure [Figure 11.42(b)], the S^{2-} ions adopt a face-centered cubic arrangement, with the smaller Zn^{2+} ions arranged so they are each surrounded tetrahedrally by four S^{2-} ions (compare with Figure 11.33). CuCl also adopts this structure.

In the fluorite (CaF₂) structure [Figure 11.42(c)], the Ca^{2+} ions are shown in a face-centered cubic arrangement. As required by the chemical formula of the substance, there are twice as many F$^-$ ions (blue) in the unit cell as there are Ca^{2+} ions. Other compounds that have the fluorite structure include BaCl₂ and PbF₂.
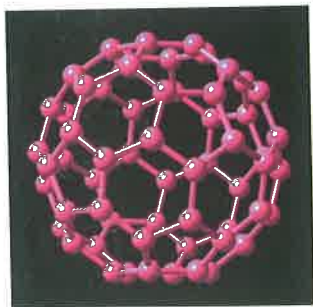
Metallic Solids

Metallic solids, also simply called metals, consist entirely of metal atoms. Metallic solids usually have hexagonal close-packed, cubic close-packed (face-centered cubic), or body-centered cubic structures. Thus, each atom typically is surrounded by eight or 12 adjacent atoms.

A Closer Look   THE THIRD FORM OF CARBON

Until the mid-1980s pure solid carbon was thought to exist in only two forms: diamond and graphite, both of which are covalent-network solids. In 1985 a group of researchers led by Richard Smalley and Robert Curl of Rice University in Houston and Harry Kroto of the University of Sussex in England made a startling discovery. They vaporized a sample of graphite with an intense pulse of laser light and used a stream of helium gas to carry the vaporized carbon into a mass spectrometer (⚬⚬ Section 2.4, "A Closer Look: The Mass Spectrometer"). The mass spectrum showed peaks corresponding to clusters of carbon atoms, with a particularly strong peak corresponding to molecules composed of 60 carbon atoms, C_{60}.

Because C_{60} clusters were so preferentially formed, the group proposed a radically different form of carbon, namely, C_{60} *molecules* that were nearly spherical in shape. They proposed that the carbon atoms of C_{60} form a "ball" with 32 faces, 12 of which are pentagons and 20 are hexagons (Figure 11.43 ▼), exactly like a soccer ball. The shape of this molecule is reminiscent of the geodesic dome invented by the U.S. engineer and philosopher R. Buckminster Fuller, so C_{60} was whimsically named "buckminsterfullerene," or "buckyball" for short. Since the discovery of C_{60}, other related molecules of carbon atoms have been discovered. These molecules are now known as fullerenes.

Appreciable amounts of buckyball can be prepared by electrically evaporating graphite in an atmosphere of helium gas. About 14% of the resulting soot consists of C_{60} and a related molecule, C_{70}, which has a more elongated structure.

The carbon-rich gases from which C_{60} and C_{70} condense also contain other fullerenes, mostly with more carbon atoms such as C_{76} and C_{84}. The smallest possible fullerene, C_{20}, was first detected in 2000. This small, ball-shaped molecule is much more reactive than the larger fullerenes.

Because the fullerenes are composed of individual molecules, they dissolve in various organic solvents, whereas diamond and graphite do not (Figure 11.44 ▼). This solubility permits the fullerenes to be separated from the other components of soot and even from each other. It also allows the study of their reactions in solution. Study of these substances has led to the discovery of some very interesting chemistry. For example, it is possible to place a metal atom inside a buckyball, generating a molecule in which a metal atom is completely enclosed by the carbon sphere. The C_{60} molecules also react with potassium to give K_3C_{60}, which contains a face-centered cubic array of buckyballs with K^+ ions in the cavities between them. This compound is a superconductor at 18 K (to ⚬⚬ Section 12.1), suggesting the possibility that other fullerenes may also have interesting electrical, magnetic, or optical properties. For their discovery and pioneering work with fullerenes, Professors Smalley, Curl, and Kroto were awarded the 1996 Nobel Prize in Chemistry.
Related Exercise: 11.97

▲ Figure 11.43 **The buckminsterfullerene molecule, C_{60}.** The molecule has a highly symmetric structure in which the 60 carbon atoms sit at the vertices of a truncated icosahedron—the same geometry as a soccer ball.

▲ Figure 11.44 **Solutions of fullerenes.** Unlike diamond and graphite, the new molecular forms of carbon can be dissolved in organic solvents. The orange solution on the left is a solution of C_{70} in *n*-hexane, which is a colorless liquid. The magenta solution on the right is a solution of buckyball, C_{60}, in *n*-hexane.

📖 Robert F. Curl and Richard E. Smalley, "Fullerenes," *Scientific American*, **October 1991**, 54–63. An early review on fullerenes.

The bonding in metals is too strong to be due to London dispersion forces, and yet there are not enough valence electrons for ordinary covalent bonds between atoms. The bonding is due to valence electrons that are delocalized throughout the entire solid. In fact, we can visualize the metal as an array of positive ions immersed in a sea of delocalized valence electrons, as shown in Figure 11.45 ▶. This type of bonding is called *metallic bonding* and will be discussed in more detail in Section 23.5.

Metals vary greatly in the strength of their bonding, as shown by their wide range of physical properties such as hardness and melting point. In general, however, the strength of the bonding increases as the number of electrons available for bonding increases. Thus, sodium, which has only one valence electron per atom, melts at 97.5 °C, whereas chromium, with six electrons beyond the noble-gas core, melts at 1890 °C. The mobility of the electrons explains why metals are good conductors of heat and electricity. The bonding and properties of metals will be examined more closely in Chapter 23.

■ SAMPLE INTEGRATIVE EXERCISE | Putting Concepts Together

The substance CS_2 has a melting point of −110.8 °C and a boiling point of 46.3 °C. Its density at 20 °C is 1.26 g/cm³. It is highly flammable. (a) What is the name of this compound? (b) List the intermolecular forces that CS_2 molecules would have with each other. (c) Predict what type of crystalline solid $CS_2(s)$ would form. (d) Write a balanced equation for the combustion of this compound in air. (You will have to decide on the most likely oxidation products.) (e) The critical temperature and pressure for CS_2 are 552 K and 78 atm, respectively. Compare these values with those for CO_2 (Table 11.5), and discuss the possible origins of the differences. (f) Would you expect the density of CS_2 at 40 °C to be greater or less than at 20 °C? What accounts for the difference?

SOLUTION

(a) The compound is named carbon disulfide, in analogy with the naming of other binary molecular compounds such as carbon dioxide. ∞ (Section 2.8)
(b) Only London dispersion forces affect CS_2; it does not have a dipole moment, based upon its molecular shape, and obviously cannot undergo hydrogen bonding.
(c) Because $CS_2(s)$ consists of individual CS_2 molecules, it will be a molecular solid.
(d) The most likely products of the combustion will be CO_2 and SO_2. ∞ (Sections 3.2 and 7.8) Under some conditions SO_3 might be formed, but this would be the less likely outcome. Thus, we have the following equation for combustion:

$$CS_2(l) + 3\,O_2(g) \longrightarrow CO_2(g) + 2\,SO_2(g)$$
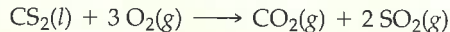
(e) The critical temperature and pressure of CS_2 (552 K and 78 atm) are both higher than those given for CO_2 in Table 11.5 (304 K and 73 atm). The difference in critical temperatures is especially notable. The higher values for CS_2 arise from the greater London dispersion attractions between the CS_2 molecules compared with CO_2. These greater attractions are due to the larger size of the sulfur compared to oxygen and therefore its greater polarizability.
(f) The density would be lower at the higher temperature. Density decreases with increasing temperature because the molecules possess higher kinetic energies. Their more energetic movements result in larger average distances between molecules, which translate into lower densities.
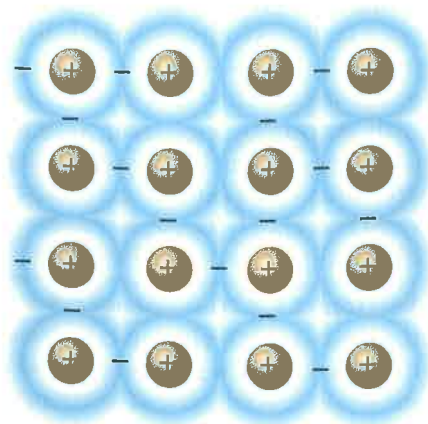
▲ Figure 11.45 **Representation of a cross section of a metal.** Each sphere represents the nucleus and inner-core electrons of a metal atom. The surrounding blue "fog" represents the mobile sea of electrons that binds the atoms together.

The *sea of electrons* description also helps explain the electrical conductivity characteristic of metals. Conductivity is the result of the relative mobility of the electrons.

CHAPTER REVIEW

SUMMARY AND KEY TERMS

Introduction and Section 11.1 Substances that are gases or liquids at room temperature are usually composed of molecules. In gases the intermolecular attractive forces are negligible compared to the kinetic energies of the molecules; thus, the molecules are widely separated and undergo constant, chaotic motion. In liquids the **intermolecular forces** are strong enough to keep the molecules in close proximity; nevertheless, the molecules are free to move with respect to one another. In solids the interparticle attractive forces are strong enough to restrain molecular motion and to force the particles to occupy specific locations in a three-dimensional arrangement.

Section 11.2 Three types of intermolecular forces exist between neutral molecules: **dipole–dipole forces**, **London dispersion forces**, and **hydrogen bonding**. **Ion–dipole forces** are important in solutions in which ionic compounds are dissolved in polar solvents. London dispersion forces operate between all molecules (and atoms, for atomic substances such as He, Ne, Ar, and so forth). The relative

strengths of the dipole–dipole and dispersion forces depend on the polarity, **polarizability**, size, and shape of the molecule. Dipole–dipole forces increase in strength with increasing polarity. Dispersion forces increase in strength with increasing molecular weight, although molecular shape is also an important factor. Hydrogen bonding occurs in compounds containing O—H, N—H, and F—H bonds. Hydrogen bonds are generally stronger than dipole–dipole or dispersion forces.

Section 11.3 The stronger the intermolecular forces, the greater is the **viscosity**, or resistance to flow, of a liquid. The surface tension of a liquid also increases as intermolecular forces increase in strength. **Surface tension** is a measure of the tendency of a liquid to maintain a minimum surface area. The adhesion of a liquid to the walls of a narrow tube and the cohesion of the liquid account for **capillary action** and the formation of a meniscus at the surface of a liquid.

Section 11.4 A substance may exist in more than one state of matter, or phase. **Phase changes** are transformations from one phase to another. Changes of a solid to liquid (melting), solid to gas (sublimation), and liquid to gas (vaporization) are all endothermic processes. Thus, the **heat of fusion** (melting), the **heat of sublimation**, and the **heat of vaporization** are all positive quantities. The reverse processes are exothermic. A gas cannot be liquefied by application of pressure if the temperature is above its **critical temperature**. The pressure required to liquefy a gas at its critical temperature is called the **critical pressure**.

Section 11.5 The **vapor pressure** of a liquid indicates the tendency of the liquid to evaporate. The vapor pressure is the partial pressure of the vapor when it is in **dynamic equilibrium** with the liquid. At equilibrium the rate of transfer of molecules from the liquid to the vapor equals the rate of transfer from the vapor to the liquid. The higher the vapor pressure of a liquid, the more readily it evaporates and the more **volatile** it is. Vapor pressure increases nonlinearly with temperature. Boiling occurs when the vapor pressure equals the external pressure.

The **normal boiling point** is the temperature at which the vapor pressure equals 1 atm.

Section 11.6 The equilibria between the solid, liquid, and gas phases of a substance as a function of temperature and pressure are displayed on a **phase diagram**. A line indicates equilibria between any two phases. The line through the melting point usually slopes slightly to the right as pressure increases, because the solid is usually more dense than the liquid. The melting point at 1 atm is the **normal melting point**. The point on the diagram at which all three phases coexist in equilibrium is called the **triple point**.

Section 11.7 In a **crystalline solid**, particles are arranged in a regularly repeating pattern. An **amorphous solid** is one whose particles show no such order. The essential structural features of a crystalline solid can be represented by its **unit cell**, the smallest part of the crystal that can, by simple displacement, reproduce the three-dimensional structure. The three-dimensional structures of a crystal can also be represented by its **crystal lattice**. The points in a crystal lattice represent positions in the structure where there are identical environments. The simplest unit cells are cubic. There are three kinds of cubic unit cells: **primitive cubic, body-centered cubic**, and **face-centered cubic**. Many solids have a close-packed structure in which spherical particles are arranged so as to leave the minimal amount of empty space. Two closely related forms of close packing, **cubic close packing** and **hexagonal close packing**, are possible. In both, each sphere has a **coordination number** of 12.

Section 11.8 The properties of solids depend both on the arrangements of particles and on the attractive forces between them. **Molecular solids**, which consist of atoms or molecules held together by intermolecular forces, are soft and low melting. **Covalent-network solids**, which consist of atoms held together by covalent bonds that extend throughout the solid, are hard and high melting. **Ionic solids** are hard and brittle and have high melting points. **Metallic solids**, which consist of metal cations held together by a sea of electrons, exhibit a wide range of properties.

KEY SKILLS

- Understand and be able to describe the intermolecular attractive interactions (ion–dipole, dipole–dipole, London dispersion, hydrogen bonding) that exist between molecules or ions, and be able to compare the relative strengths of intermolecular attractions in substances based on their molecular structure, or physical properties.
- Understand the concept of polarizability.
- Understand the concepts of viscosity and surface tension in liquids.
- Know the names of the various phase changes for a pure substance.
- Interpret heating curves and be able to calculate quantities related to temperature and enthalpies of phase changes.
- Define critical pressure, critical temperature, vapor pressure, normal boiling point, normal melting point, critical point, triple point.
- Be able to interpret and sketch phase diagrams; know how water's phase diagram differs from most other substances, and why.

- Know the difference between crystalline and amorphous solids, and be able to explain the differences between primitive cubic, body-centered cubic, and face-centered cubic unit cells.
- Classify solids based on their bonding/intermolecular forces and understand how difference in bonding relates to physical properties.

VISUALIZING CONCEPTS

11.1 CQ Does the following diagram best describe a crystalline solid, liquid, or gas? Explain. [Section 11.1]
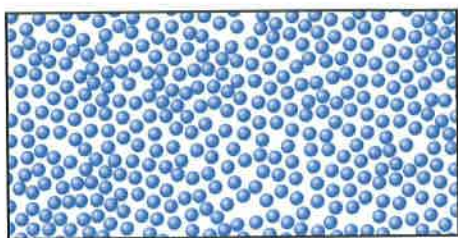
11.2 CQ (a) What kind of intermolecular attractive force is shown in each of the following cases? **(b)** Predict which two interactions are stronger than the other two. [Section 11.2]


(a) H F ······ H F   (c) Na⁺ ······ O (H H)

(b) F F ······ F F   (d) SO₃ ······ SO₂
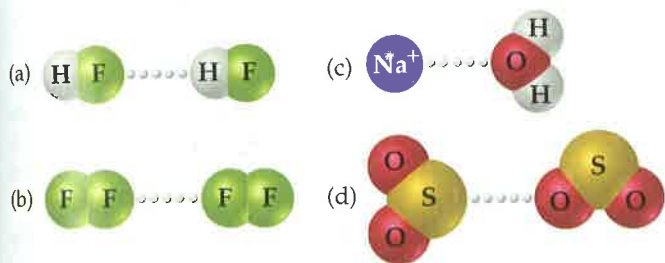
11.3 CQ The molecular models of glycerol and 1-propanol are given here.


(a) Glycerol   (b) 1-propanol
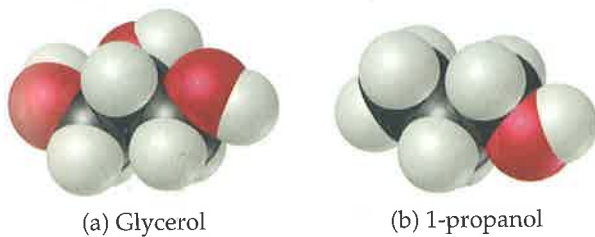
Do you expect the viscosity of glycerol to be larger or smaller than that of 1-propanol? Explain. [Section 11.3]

**11.4 CQ** Using the following graph of CS_2 data, determine **(a)** the approximate vapor pressure of CS_2 at 30 °C, **(b)** the temperature at which the vapor pressure equals 300 torr, **(c)** the normal boiling point of CS_2. [Section 11.5]
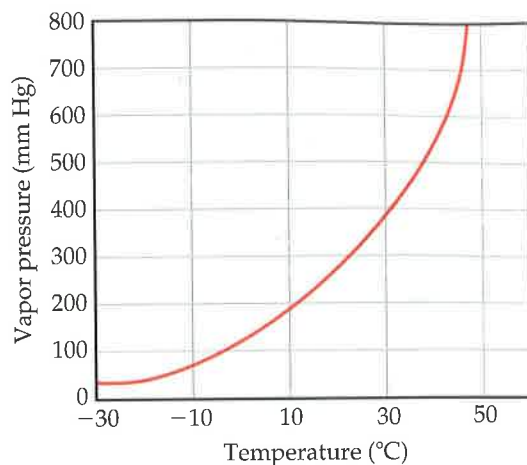
11.5 CQ The following molecules have the same molecular formula (C_3H_8O), yet they have different normal boiling points, as shown. Rationalize the difference in boiling points. [Sections 11.2 and 11.5]

(a) Propanol 97.2 °C   (b) Ethyl methyl ether 10.8 °C
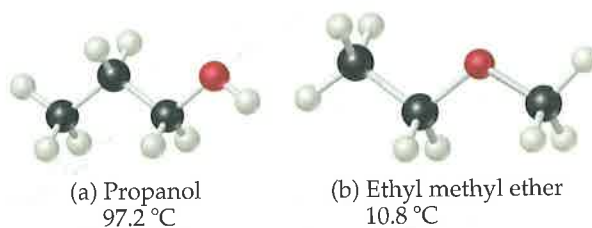
11.6 CQ The phase diagram of a hypothetical substance is shown below.
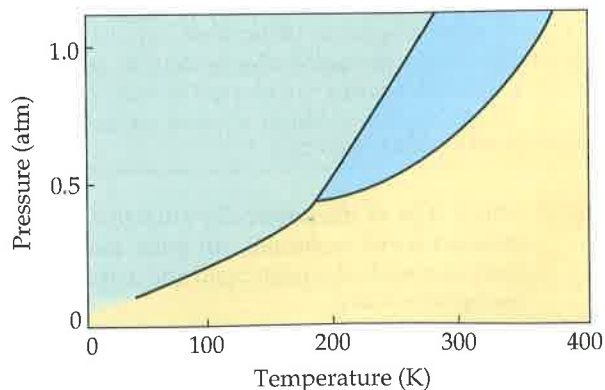
(a) Estimate the normal boiling point and freezing point of the substance.
(b) What is the physical state of the substance under the following conditions?
(i) $T = 150$ K, $P = 0.2$ atm
(ii) $T = 100$ K, $P = 0.8$ atm
(iii) $T = 300$ K, $P = 1.0$ atm
(c) What is the triple point of the substance? [Section 11.6]