

CHEM 1212 - Principles of Chemistry II Chapter 10 - Liquids and Solids

10.1 Intermolecular Forces

- recall intramolecular (within the molecule) bonding whereby atoms can form stable units called molecules by sharing electrons
- this chapter we will consider the properties of condensed states (liquids and solids)
- the forces that cause the aggregation of the components of a substance to form a liquid or solid are intermolecular forces
- recognize that when a substance such as water changes from solid to liquid the molecules remain intact
- note that the densities of a solid and liquid (same substance) are similar whereas the density of the gas is much, much less

Dipole-Dipole Forces

molecules with polar bonds can have dipole-dipole attractions between them

- see Figure 10.2

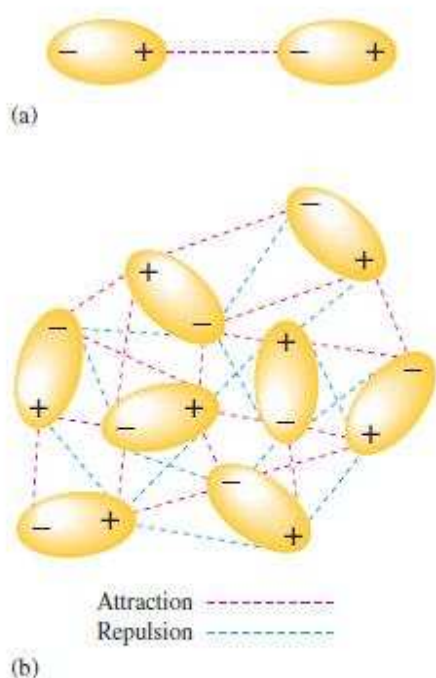


FIGURE 10.2

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

- dipole-dipole forces are typically only about 1 % as strong as covalent or ionic bonds
- strong dipole-dipole forces are seen among molecules in which hydrogen is bound to a highly electronegative atom, such as nitrogen, oxygen, or fluorine
- two factors account for the strengths of these interactions,
 - (1) the great polarity of the bond and
 - (2) the close approach of the dipoles, allowed by the very small size of the hydrogen atom
- the attraction between molecules caused by these strong dipole-dipole forces are termed **hydrogen bonding**

see
Figure
10.3

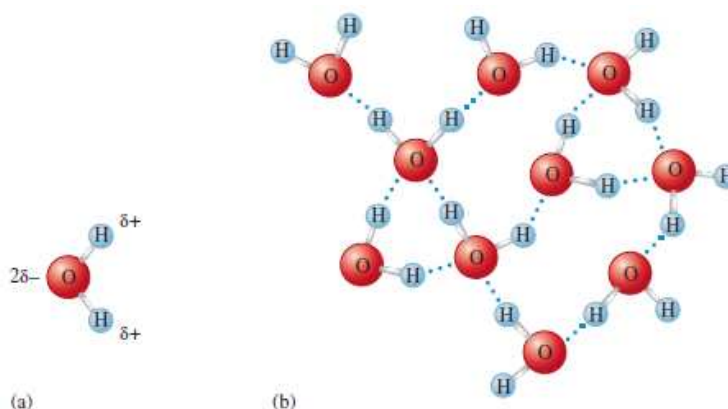


FIGURE 10.3

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

- hydrogen bonding has an important effect on physical properties
 - see Figure 10.4

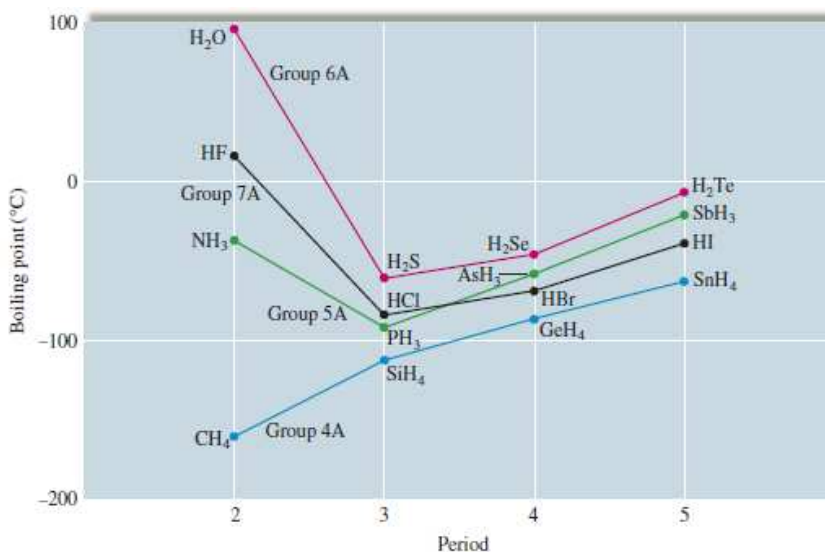


FIGURE 10.4
The boiling points of the covalent hydrides of the elements in Groups 4A, 5A, 6A, and 7A.

- the lightest member of each group (SA, 6A, 7 A) has an unexpectedly high boiling point due to especially large hydrogen bonding interactions that exist among the smallest molecules with most polar X-H bonds; due to (1) relatively large electronegativity values of the lightest elements in each group, which leads to especially polar X-H bonds and (2) the small size of the first element of each group, which allows for the close approach of the dipoles
- a large amount of energy must be supplied to overcome these interactions hence the higher boiling points.

London Dispersion Forces

- even molecules without dipole moments must exert forces on each other
- all substances, even the noble gases, exist in the liquid and solid states under certain conditions
- the forces that exist among noble gas atoms and nonpolar molecules are called **London Dispersion Forces**
- temporary dipolar arrangement of charge can occur which can in tum affect the electron distribution in a neighboring atom
 - see Figure 10.5

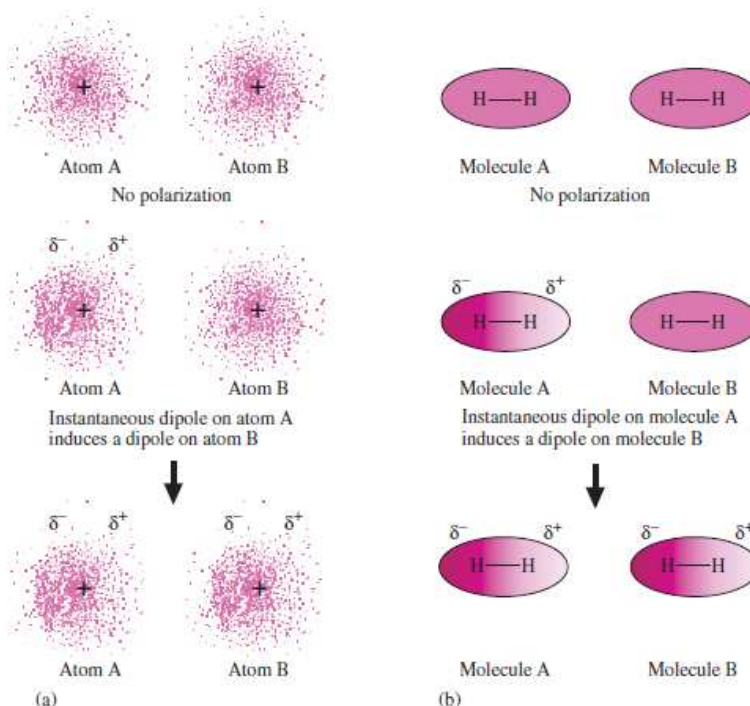


FIGURE 10.5
 (a) An instantaneous polarization can occur on atom A, creating an instantaneous dipole. This dipole creates an induced dipole on neighboring atom B. (b) Nonpolar molecules such as H_2 also can develop instantaneous and induced dipoles.

- see Table 10.2; the freezing point rises going down the group; as the atomic number increases, the number of electrons increases, and there is an increased chance of momentary dipole interactions; this phenomenon termed polarizability
 - therefore the important of London Dispersion Forces increases with increasing size of the atom
- same logic applies to nonpolar molecules such as H_2 , CH_4 , CCl_4 , and CO_2

Element	Freezing Point ($^{\circ}C$)
Helium*	-269.7
Neon	-248.6
Argon	-189.4
Krypton	-157.3
Xenon	-111.9

*Helium is the only element that will not freeze by lowering its temperature at 1 atm. Pressure must be applied to freeze helium.

10.2 The Liquid State

- liquids and liquid solution are vital to our lives
- water is the most important liquid; essential for life, is a medium for food preparation, for transportation, for cooling machines and industrial processes, for recreation, for cleaning, and for a myriad of other uses
- as compared to gases liquids have
 - low compressibility,
 - lack of rigidity, and
 - high density
- when a liquid is poured on a surface it tends to bead as droplets, a phenomenon that depends on the intermolecular forces
 - see Figure 10.6

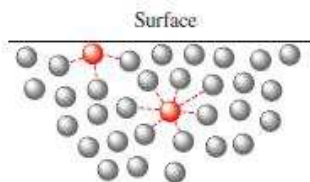


FIGURE 10.6
 A molecule in the interior of a liquid is attracted by the molecules surrounding it, whereas a molecule at the surface of a liquid is attracted only by molecules below it and on each side.

- the resistance of a liquid to increase its surface area is called the surface tension of the liquid; liquid with large intermolecular forces have high surface tensions
- polar liquids exhibit capillary action, the spontaneous rising of a liquid in a narrow tube
- two different types of forces at work;
 - (1) cohesive forces, the intermolecular forces among the molecules of the liquid, and
 - (2) adhesive forces, the forces between the liquid molecules and their container
 - see Figure 10.7



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 is viscosity, a measure of liquid's resistance to flow
- liquids with large intermolecular forces tend to be highly viscous

Structural Model for Liquids

- a typical liquid might best be viewed as containing a large number of regions where the arrangements of the components are similar to those found in the solid, but with more

disorder, and a smaller number of regions where holes are present; the situation is highly dynamic with rapid fluctuations occurring in both types of regions

10.3 An Introduction to Structures and Types of Solids

- two categories of solids
 - (1) crystalline solids, those with a highly regular arrangement of their components, and
 - (2) amorphous solids, those with considerable disorder in their structures
 - see Figure 10.8

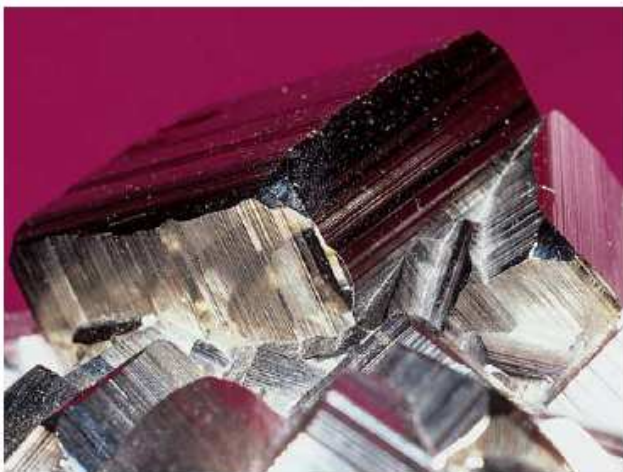


FIGURE 10.8
Two crystalline solids: pyrite (left), amethyst (right).

- the position of the components in a crystalline solid are usually represented by a lattice, a three-dimensional system of points designating the position of the components (atoms, ions, or molecules) that make up the substance
- the smallest repeating unit of the lattice is called the unit cell
 - see Figure 10.9
- there are many important amorphous (noncrystalline) solid; most common is glass, which is best pictured as a solution in which the components are "frozen in place" before they can achieve an ordered arrangement

X-ray Analysis of Solids

- the structures of crystalline solids are most commonly determined by x-ray diffraction
- diffraction occurs when beams of light are scattered from a regular array of points in which the spacings between the components are comparable with the wavelength of the light
- diffraction is due to constructive interference when the waves of parallel beams are in phase and to destructive interference when the waves are out of phase

Types of Crystalline Solids

- many different types of crystalline solids
- recall the differences in sugar (polar covalent compound) and salt (ionic compound)
- have molecular solids, ionic solids, and atomic solids (subgroups metallic solids, network solids, and Group 8A solids)
 - see Figure 10.12
 - see Table 10.3

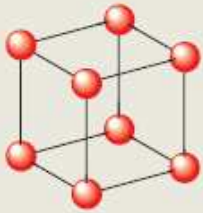
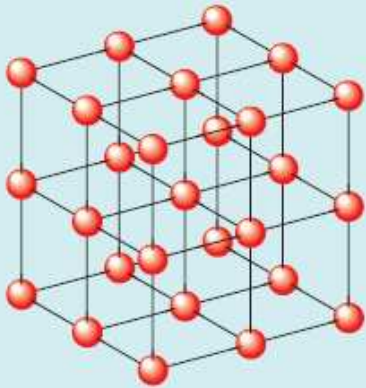
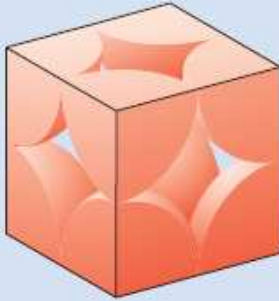
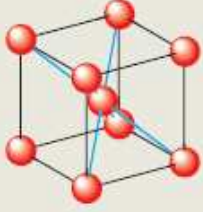
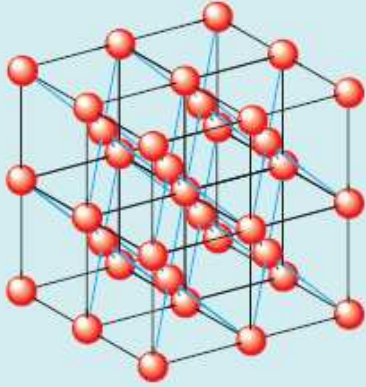
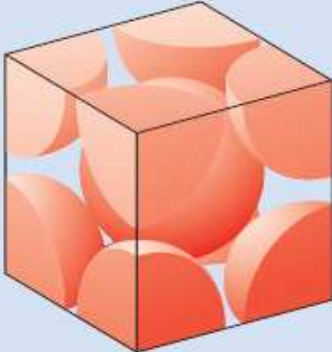
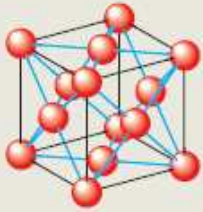
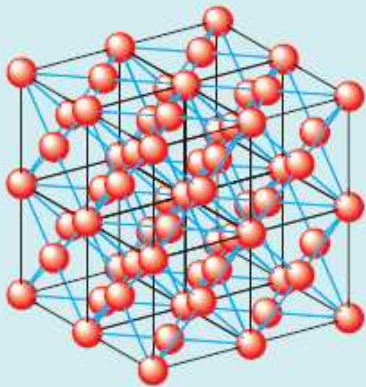
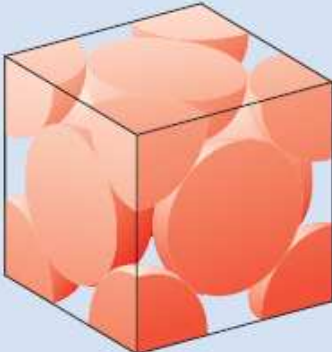
	Unit cell	Lattice	Space-filling unit cell	Example
(a)	 <p>Simple cubic</p>			Polonium metal
(b)	 <p>Body-centered cubic</p>			Uranium metal
(c)	 <p>Face-centered cubic</p>			Gold metal

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.

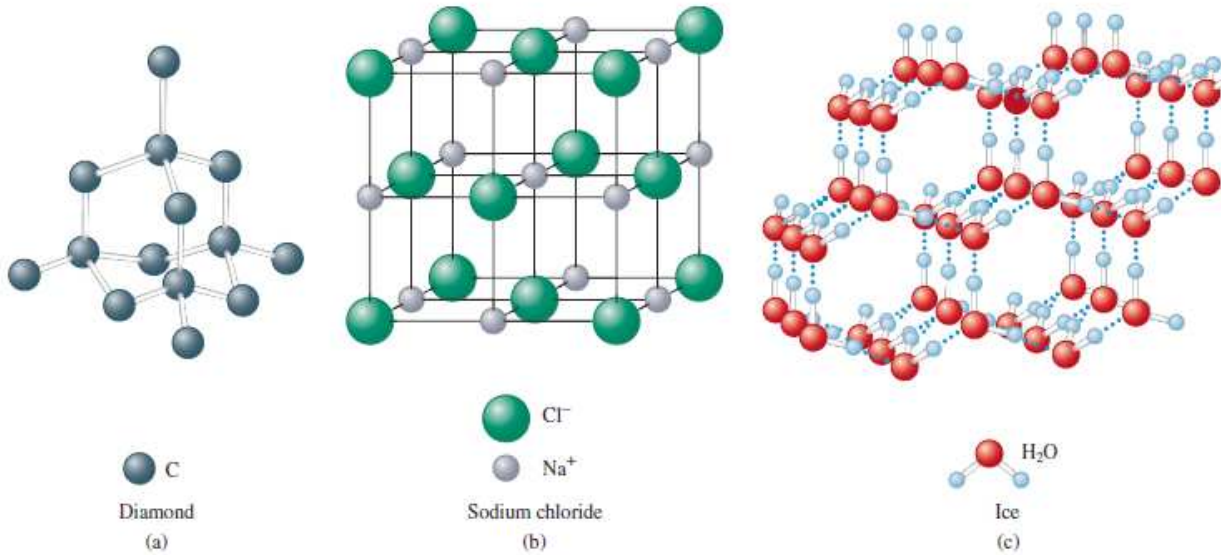


FIGURE 10.12

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			Molecular Solids	Ionic Solids
	Metallic	Network	Group 8A		
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

- metals are characterized by their
 - high thermal conductivity
 - electrical conductivity
 - malleability
 - ductility
 - luster

- a metallic crystal can be pictured as containing spherical atoms packed together and bonded to each other equally in all directions
- the most efficient way of stacking spheres is termed closest packing
- the third layer of atoms can lie directly over the first layer or that no spheres lie over the first layer
 - see Figure 10.13

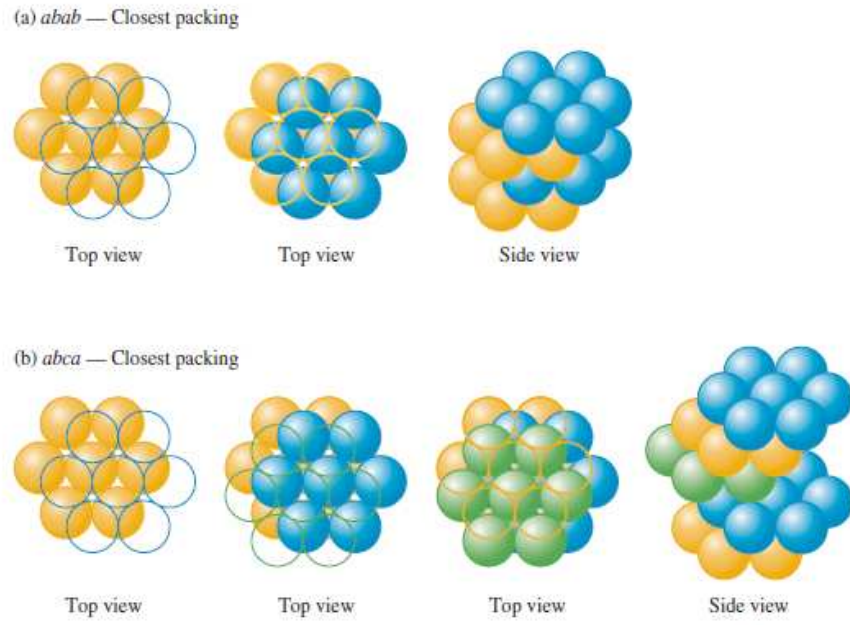


FIGURE 10.13 The closest packing arrangement of uniform spheres. In each layer a given sphere is surrounded by six others, creating six dimples, only three of which can be occupied in the next layer. (a) *aba* packing: The second layer is like the first, but it is displaced so that each sphere in the second layer occupies a dimple in the first layer. The spheres in the third layer occupy dimples in the second layer so that the spheres in the third 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.

- can have an *aba* or *abc* arrangement
- see Figure 10.14; hexagonal closest packed (hcp) structure
- see Figure 10.15; cubic closest packed (ccp) structure; face centered cubic unit cell
- see Figure 10.16

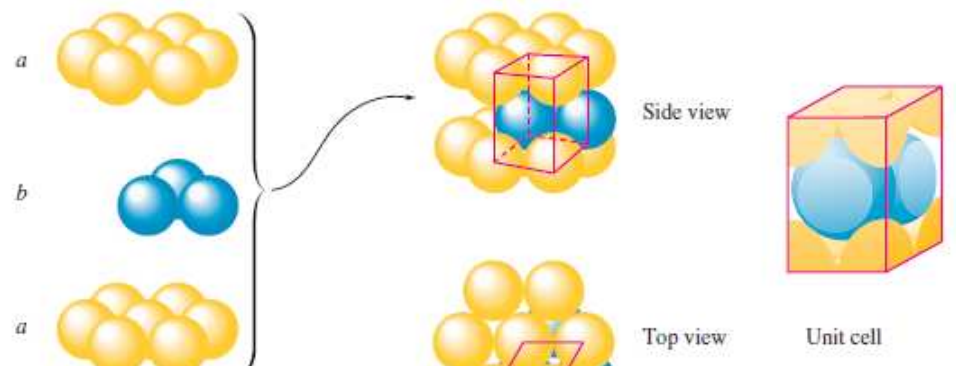


FIGURE 10.14 When spheres are closest packed so that the spheres are stacked in the *aba* arrangement, the unit cell is hexagonal. The unit cell is shown in red.

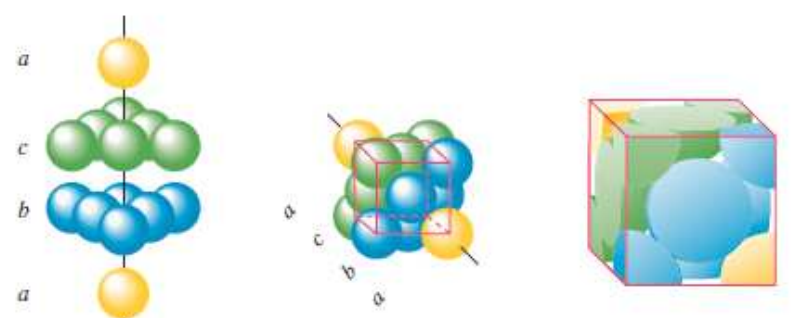


FIGURE 10.15 When spheres are packed in the *abc* arrangement, the unit cell is face-centered cubic. To make the cubic arrangement easier to see, the vertical axis has been tilted as shown.

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

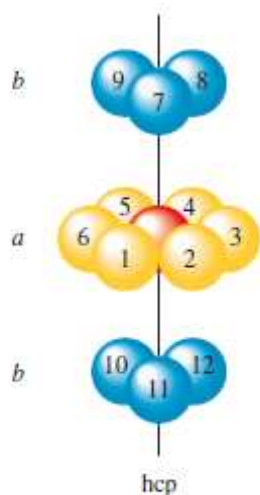


FIGURE 10.16

The indicated sphere has 12 nearest neighbors.

- knowing the net number of spheres (atoms) in a particular unit cell is important for many applications involving solids
 - see Figure 10.17
- aluminum, iron, copper, cobalt, and nickel form cubic closest packed solids
- magnesium and zinc are hexagonal closest packed
- calcium and certain other metals crystallize in either structure
- some metals assume structures that are not closest packed; for example, the alkali metals have structures characterized by a body-centered cubic (bcc) unit cell where the spheres touch along the body diagonal of the cube
- in bcc each sphere has 8 nearest neighbors as compared with 12 in the closest packed structures
- why a metal adopts the structure it does is not well understood

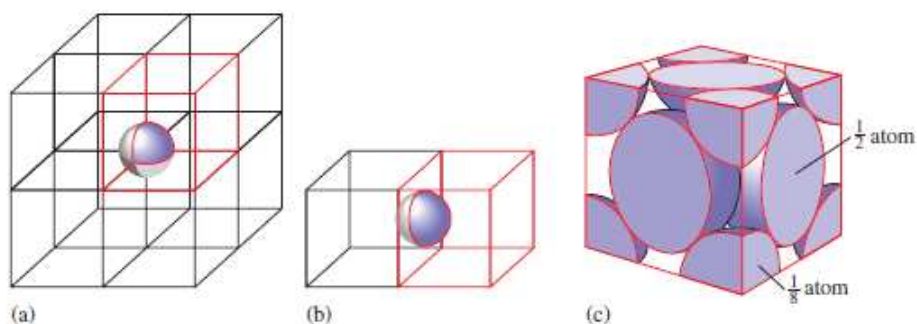


FIGURE 10.17

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 other unit cells (a total of 8). Thus $\frac{1}{8}$ of such a sphere lies within a given unit cell. Since there are 8 corners in a cube, there are 8 of these $\frac{1}{8}$ 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 $\frac{1}{2}$ of each of these types of spheres. There are 6 of these $\frac{1}{2}$ 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).

Bonding Models for Metals

- the properties of metals indicate that bonding in most metals is both strong and non directional
- although it is difficult to separate metal atoms, it is relatively easy to move them, provided the atoms stay in contact with each other
- the simplest picture that explains these observations is the electron sea model; electrons are mobile and the metal ion can be easily moved around as the metal is hammered into a sheet or pulled into a wire
- a related model is the band model or molecular orbital (MO) model
 - see Figure 10.19
 - see Figure 10.20

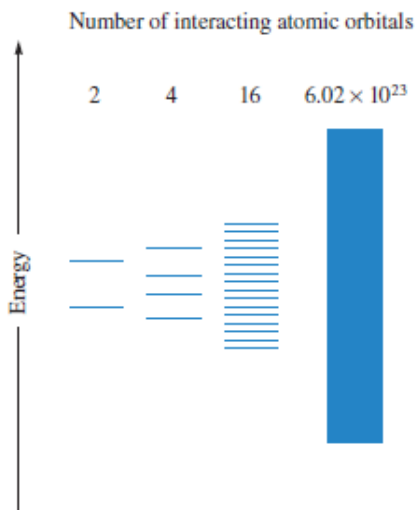


FIGURE 10.19

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.

- when an electric potential is placed across a strip of metal, for current to flow, electrons must be free to move; the band model for are excited into empty ones; the conduction electrons are free to travel throughout the metal crystal as dictated by the potential imposed on the metal
- the molecular orbitals occupied by these conducting electrons are called conduction bands

Metal Alloys

- an alloy is defined as a substance that contains a mixture of elements and has metallic properties
- two types of alloys;
 - (1) substitutional alloy and
 - (2) interstitial alloy
 - see Figure 10.21

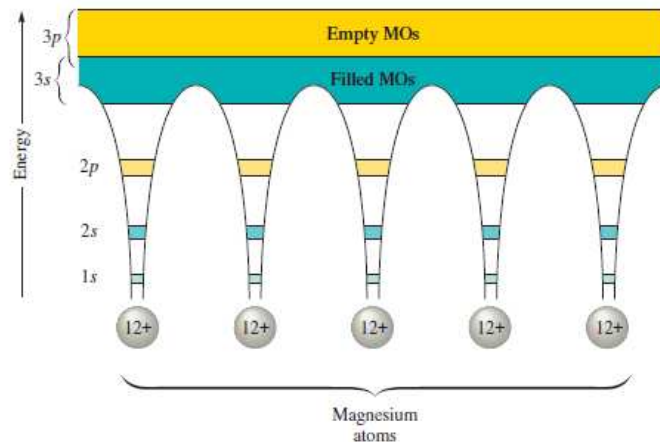


FIGURE 10.20 (left) A representation of the energy levels (bands) in a magnesium crystal. The electrons in the 1s, 2s, and 2p orbitals are close to the nuclei and thus are localized on each magnesium atom as shown. However, the 3s and 3p valence orbitals overlap and mix to form molecular orbitals. Electrons in these energy levels can travel throughout the crystal. (right) Crystals of magnesium grown from a vapor.

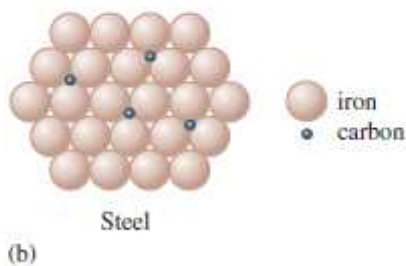
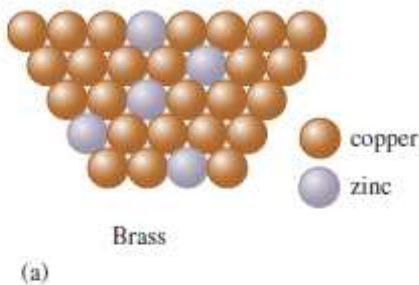


FIGURE 10.21 Two types of alloys.

10.5 Carbon and Silicon: Network Atomic Solids

- many atomic solids contain strong directional covalent bonds to form a solid that may be viewed as a "giant molecule"; these substances are termed network solids
- network solids tend to be brittle and do not conduct heat or electricity
- two common forms of carbon, diamond and graphite, are network solids
 - see Figure 10.22
 - see Figure 10.23

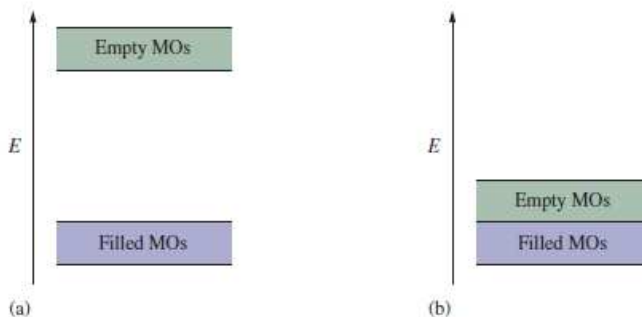
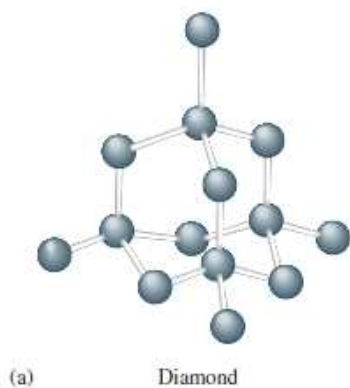
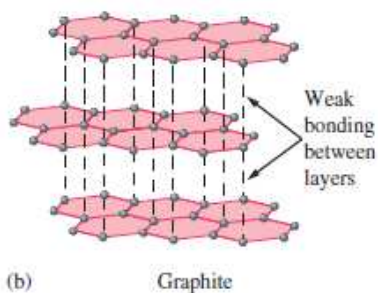


FIGURE 10.23 Partial representation of the molecular orbital energies in (a) diamond and (b) a typical metal.



- graphite is different from diamond;
 - graphite is slippery, black, and a conductor;
 - diamond is hard, basically colorless, and an insulator
- graphite is a good lubricant
- see Figure 10.24

FIGURE 10.22 The structures of diamond and graphite. In each case only a small part of the entire structure is shown.

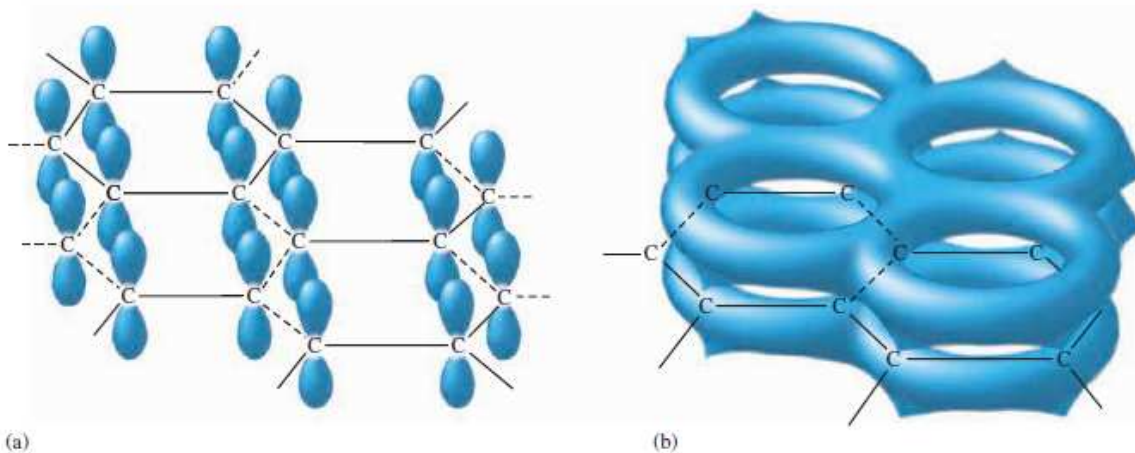
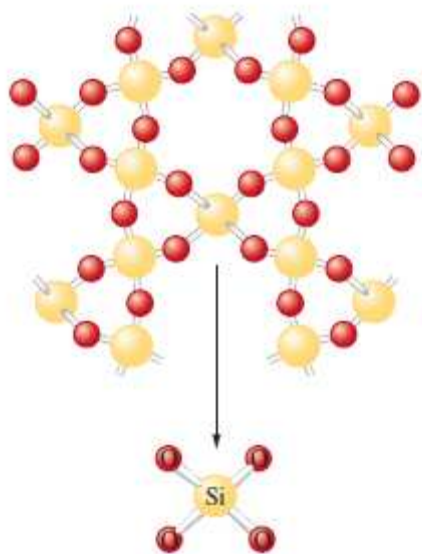


FIGURE 10.24 The *p* orbitals (a) perpendicular to the plane of the carbon ring system in graphite can combine to form (b) an extensive π -bonding network.

- the application of 150,000 atm of pressure at 2800° C converts graphite virtually completely to diamond
- silicon is to geology what carbon is to biology
- the fundamental silicon-oxygen compound is silica which has the empirical formula SiO_2
 - see Figure 10.26



- can also have silicates; like silica, silicates are based on interconnected SiO_4 tetrahedra but 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
 - see Figure 10.27
- when silica is heated above its melting point (about 1600° C) and cooled rapidly an amorphous solid called glass results
 - see Figure 10.28
 - the properties of glass can be varied greatly by varying the additives
 - see Table 10.5

FIGURE 10.26

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

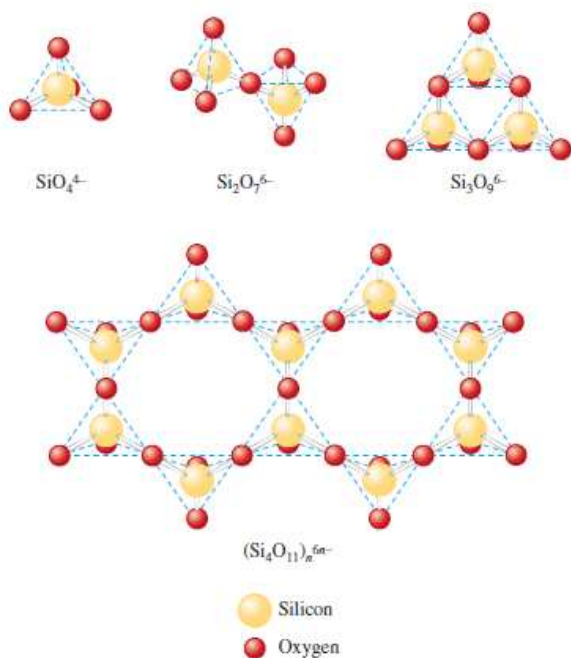


FIGURE 10.27

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

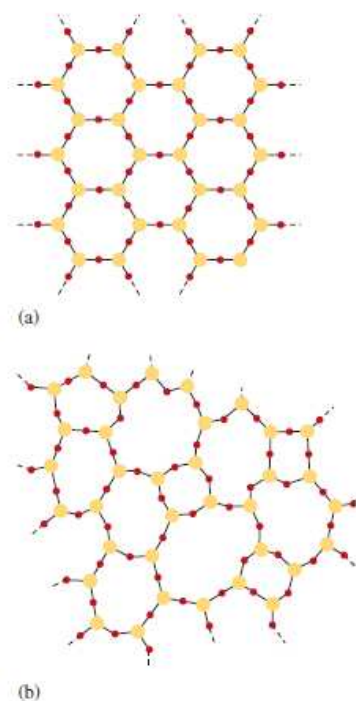


FIGURE 10.28

Two-dimensional representations of (a) a quartz crystal and (b) a quartz glass.

TABLE 10.5 Compositions of Some Common Types of Glass

Type of Glass	Percentages of Various Components						
	SiO ₂	CaO	Na ₂ O	B ₂ O ₃	Al ₂ O ₃	K ₂ O	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 homogeneous, non crystalline "frozen solution" and a ceramic is heterogeneous containing two phases: minute crystals of silicates that are suspended in a glassy cement

Semiconductors

- for pure silicon the gap between filled and empty molecular orbitals is intermediate between those of diamond and metals hence termed semiconductor
- can have n-type and p-type semiconductors
 - see Figure 10.29

10.6 Molecular Solids

- these solids contain discrete molecular units at each lattice position
- common examples are ice, dry ice (solid CO₂), some forms of sulfur that contain S₈ and certain forms of phosphorus that contain P₄
- these substances are characterized by strong covalent bonding within the molecules but relatively weak forces between molecules

10.7 Ionic Solids

- ionic solids are stable, high-melting substances held together by the strong electrostatic forces
- that exist between oppositely charged ions
- typically the larger ions usually the anions are packed in one of the closest packing arrangements (hcp or ccp), and the smaller cations fit into holes among the close packed anions
- the packing is done in a way that maximizes the electrostatic attractions among oppositely charged ion and minimizes the repulsions among ions with like charges
- there are three types of holes in closest packed structures;

