

14

Bonding in Solids and Liquids

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- Key Concepts**
- 14-1** Elemental solids. Nonmetallic network solids and metallic solids.
 - 14-2** Ionic solids.
 - 14-3** Molecular solids and liquids. Van der Waals forces: van der Waals repulsion and London energy. Dipole–dipole interactions, hydrogen bonds, and ion–dipole interactions.
 - 14-4** Metallic bonding. Electron sea, electronic bands, and electrical conductivity.
 - 14-5** Nonmetallic network solids. Insulators. Forbidden zone or band gap. Semiconductors.
 - 14-6** Silicate minerals. Silicate tetrahedra. Chain structures and sheet structures. Three-dimensional silicate networks.

Imagine two hundred brilliant violin players playing the same piece with perfectly tuned instruments, but commencing at different places selected at random. The effect would not be pleasing, and even the finest ear could not recognize what was being played. Such music is made for us by the molecules of gases, liquids, and ordinary solids. . . . A crystal, on the other hand, corresponds with the orchestra led by a vigorous conductor when all eyes intently follow his nod, and all hands follow the exact beat. . . . To me, the music of physical law sounds forth in no other department in such full and rich accord as in crystal physics.

W. Voigt

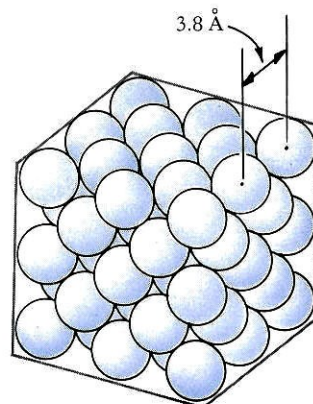
Now that we know how bonding occurs between small numbers of atoms, we can look at bonding in solids and liquids. A simple but quite useful theory of the electrical properties of solids considers the entire solid body as one large molecule and uses delocalized molecular orbitals that extend over the entire solid. This is the **band theory** of metals and insulators.

How are compounds that definitely exist as molecules held together in a solid? Why aren't Br_2 , I_2 , and all organic substances gases at room temperature? What is the force that keeps the hydrocarbon molecules of gasoline in the liquid state? Why is sugar crystalline if no covalent or ionic bonds hold one molecule to another? Molecular solids become comprehensible as soon as we recognize the contributions of the weak forces known as van der Waals attraction and hydrogen bonding.

Five types of chemical bonding—covalent bonding in nonmetals, metallic bonding, ionic attraction, hydrogen bonding, and van der Waals attraction—are sufficient to explain atomic and molecular interactions in solids, liquids, and gases. Each type contributes a different kind of stability to the atoms it binds. In what follows, we shall examine how the types differ.

Figure 14-1

The structure of solid argon. Each sphere represents an individual Ar atom, in cubic close packing (see Figure 14-7) with 3.8 \AA between the atomic centers.



14-1 ELEMENTAL SOLIDS

Solids that are built by weak attractive interactions between individual molecules are called **molecular solids**. At very low temperatures the noble gases (He, Ne, Ar, Kr, Xe, Rn) exist as molecular solids that are held together by weak interatomic forces. For example, Ar freezes at -189°C to make the close-packed structure shown in Figure 14-1. Examples of elemental substances that crystallize to give molecular solids include the halogens; for example, Br_2 freezes at -7°C to build the structure shown in Figure 14-2.

Group VIA atoms such as oxygen and sulfur (s^2p^4) have two vacancies in their valence shells and hence form two electron-pair bonds per atom. Under normal conditions of temperature and pressure, the most stable

Figure 14-2

The structure of crystalline bromine, Br_2 . Spheres with solid outlines represent one layer of packed molecules, and those with dashed outlines represent the layer beneath. The molecules have been shrunk for clarity in this drawing; they are actually in close contact within a layer, and the layers are packed against one another.

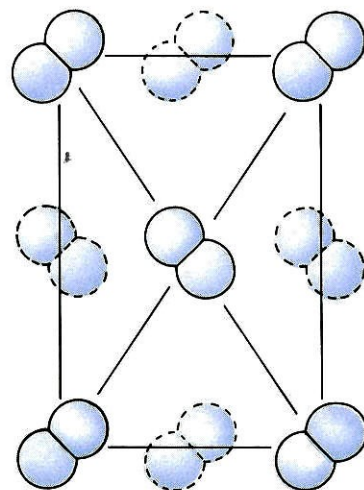
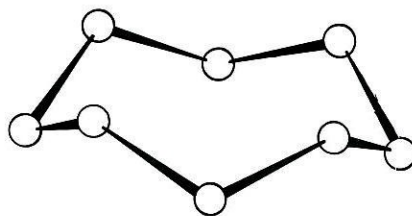


Figure 14-3

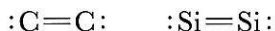
Ring molecule of eight sulfur atoms as found in solid sulfur.



form of elemental oxygen is the diatomic molecule, whereas sulfur exists as a solid, and its two principal allotropes* consist of discrete S_8 rings (Figure 14-3). There are two other allotropes of sulfur, one of which has S_6 rings; the other contains helical chains of S atoms.

Atoms of the Group VA elements have three vacancies in their valence electronic configuration (s^2p^3) and thus are expected to form three electron-pair bonds per atom. The most stable form of elemental nitrogen is the diatomic molecule, whereas the allotrope white phosphorus exists as a solid containing discrete tetrahedral P_4 units (Figure 14-4).

We turn next to the Group IVA elements carbon and silicon, which have the valence electronic configuration s^2p^2 with only two unpaired electrons. We might expect only *two* electron-pair bonds per atom as in the diatomic molecules



However, the C_2 molecule is orbital rich and electron deficient, since it has not achieved an octet around each atom. Each carbon atom prefers to form four electron-pair bonds, as illustrated by the two common allotropes,

*Allotropes of an element possess different interatomic structures and have different physical and chemical properties.

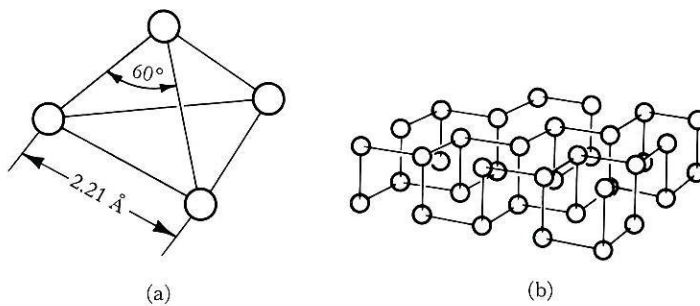
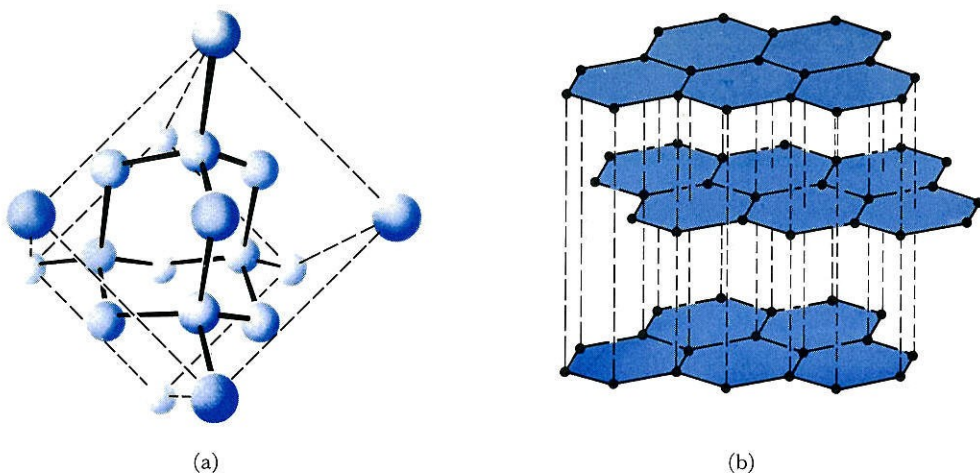


Figure 14-4

Structures of two allotropes of solid phosphorus. (a) White phosphorus consists of discrete P_4 molecules. (b) Black phosphorus, which is more stable, has an infinite network structure.

**Figure 14-5**

Crystalline carbon. (a) Diamond structure. The coordination number of carbon in diamond is 4. Each atom is surrounded tetrahedrally by four equidistant atoms. The C—C bond distance is 1.54 Å. (b) Graphite structure. This is the more stable structure of carbon. Strong carbon—carbon bonding occurs within a layer, and weaker bonding occurs between layers.

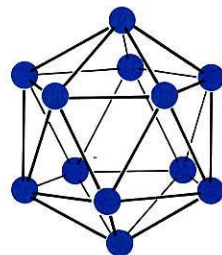
diamond and graphite (Figure 14-5). Similarly, Si_2 is electron deficient, and does not exist as an individual molecule in solid silicon. Rather, the structure of solid silicon is analogous to that of diamond (Figure 14-5a).

Diamond and graphite are called **nonmetallic network solids**, because they consist of infinite arrays of bonded atoms; no discrete molecules can be distinguished. Thus any given piece of network solid may be considered a giant, covalently bonded molecule. Network solids generally are poor conductors of heat and electricity. Strong covalent bonds among neighboring atoms throughout the structure give these solids strength and high melting temperatures. Diamond sublimates (does not melt but volatilizes directly to a gas) at 3500°C and above. Some of the hardest substances known are nonmetallic network solids.

The only Group IIIA element with nonmetallic properties is boron ($2s^22p^1$). There are three principal allotropic forms of elemental boron, and all have network structures based on a B_{12} unit. Each B_{12} unit is icosahedral (Figure 14-6). In the three allotropes the B_{12} icosahedra are linked together

Figure 14-6

Structure of the B_{12} icosahedral unit. In the different crystalline forms (allotropes) of boron, these units are linked together in various ways.



in different ways, but in general the bonds between individual icosahedra are weaker than those within any one icosahedron, where each boron atom is bonded to five others.

Atoms of the metallic elements generally have fewer valence electrons than the number of available orbitals; that is, they are electron deficient. Consequently these atoms tend to share their electron density with several other atoms to achieve a maximum bonding capacity. In most metals at least eight “nearest-neighbor” atoms surround a particular atom in one of three common structures shown in Figure 14-7. In both hexagonal close packing and cubic close packing, each sphere touches 12 other spheres, 6 in a plane, 3 above, and 3 below. It has been shown through x-ray analysis that two-thirds of all metals crystallize in one of these two structures. A majority of the other one-third crystallize as body-centered cubes, in which each atom has only eight nearest neighbors.

Lithium and sodium, which have the s^1 valence electronic configuration, adopt the body-centered cubic structure (Figure 14-7a). Solid beryllium and magnesium (s^2 atoms) both crystallize in the hexagonal close-packed structure (Figure 14-7b). The crystal structure of aluminum (s^2p^1) is cubic close packed (Figure 14-7c).

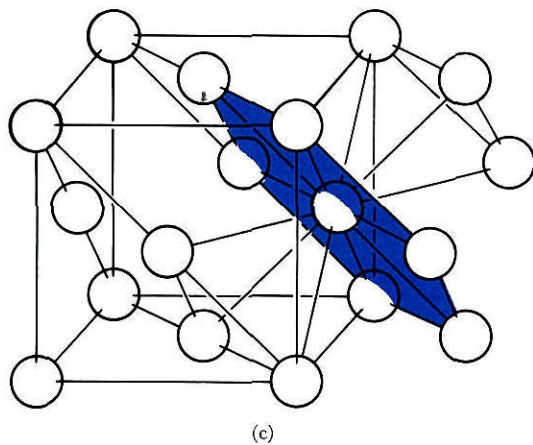
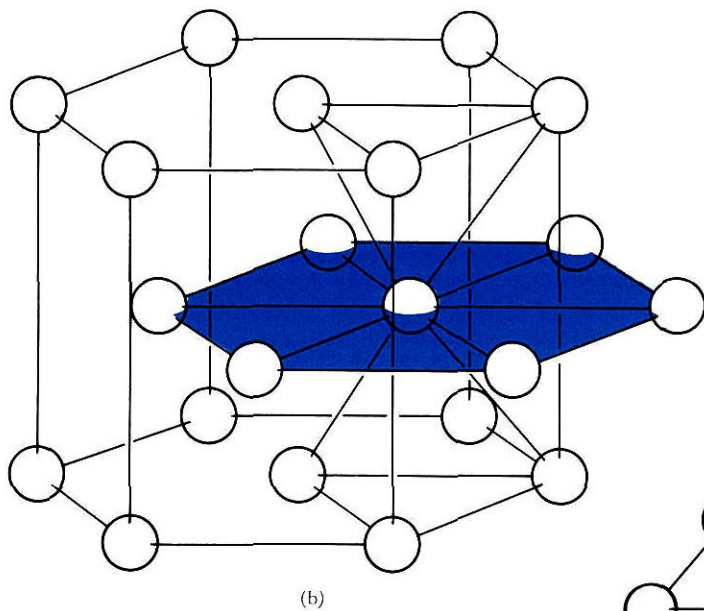
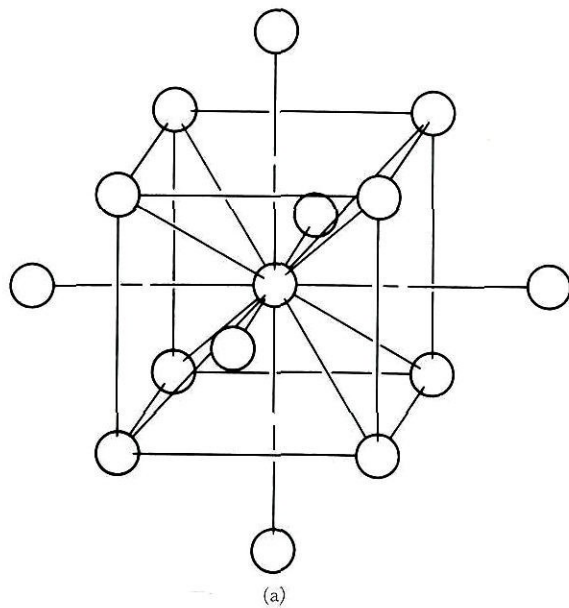
In the periodic table shown in Figure 14-8, the elemental solids are classified as metallic, network nonmetallic, or molecular. In Table 14-1 the correlation between coordination number and structure in elemental solids is presented. The majority of elements crystallize in metallic structures in which each atom has a high coordination number. Included as metals are elements such as tin and bismuth, which crystallize in structures with relatively low atomic coordination numbers but which still have strong metallic properties. The gray area of the periodic table includes elements

Table 14-1**The Correlation between Coordination Number and Structure in Elemental Solids**

Bonding coordination number	Type of solid structure
0	Atomic solids, low melting and boiling points
1	Diatomic molecular solids, low melting and boiling points
2	Rings or chains. Solids with packed ring molecules are less metallic than those with packed chains
3	P_4 tetrahedra or sheets. Solids with packed tetrahedral molecules are less metallic than those with packed sheets
4	Three-dimensional nonmetallic networks
5	B sheet curved in on itself in a B_{12} icosahedron
6 or more	Packed metallic solids

Figure 14-7

Common structures of metals. (a) Body-centered cubic (e.g., Na, V, and Ba); (b) hexagonal close packing (e.g., Mg, Ir, and Cd); (c) cubic close packing, or face-centered cubic (e.g., Al, Cu, and Au).



I	II											III	IV	V	VI	VII	0
H 1																	He 2
Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
Na 11	Mg 12											Al 13	Net work Si 14	P 15	S 16	Cl 17	Ar 18
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Cs 55	Ba 56	La-Lu 57-71	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po? 84	At? 85	Rn 86
Fr 87	Ra 88	Ac- 89-104															

- Metals only
- Intermediate structures
- Monatomic or diatomic molecules

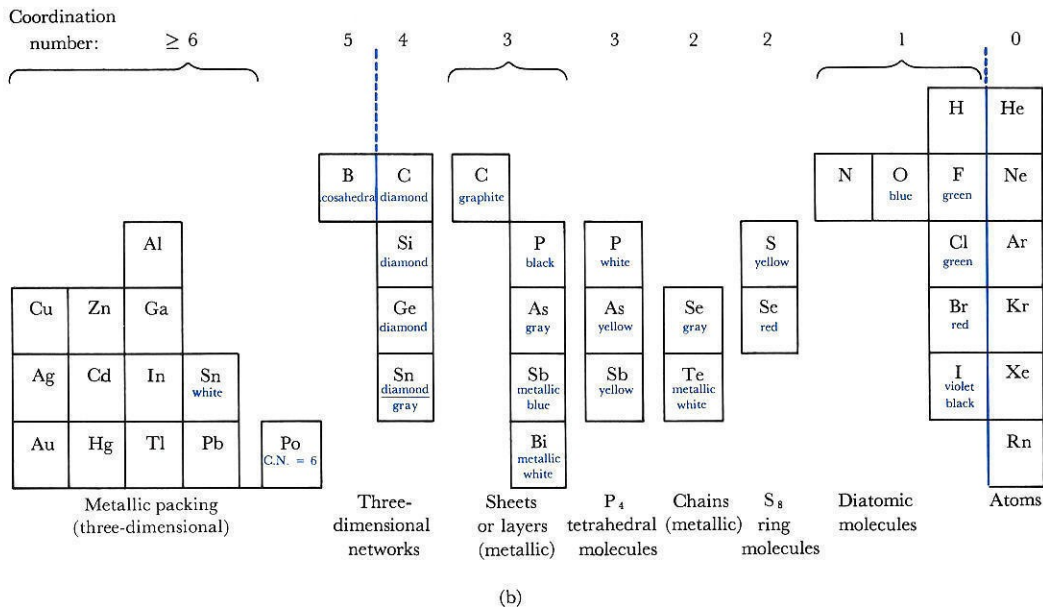


Figure 14-8

Solid structures of the elements. (a) General trends in bonding in solid elements. (b) The types of bonding in the variable zone of the table. The structures of the nonmetals are determined by their coordination numbers, which are 8 minus the group number except when multiple bonds are used as in graphite, N₂, and O₂ (see Table 14-1).

that have borderline properties. Although germanium crystallizes in a diamondlike structure in which the coordination number of each atom is only 4, some of its properties resemble those of metals. This similarity to metals indicates that the valence electrons in germanium are not held as tightly as would be expected in a true nonmetallic network solid. Arsenic, antimony, and selenium exist as either molecular or metallic solids, although the so-called metallic structures have relatively low atomic coordination numbers. We know that tellurium crystallizes in a metallic structure, and it seems reasonable to predict that it may also exist as a molecular solid. From its position in the periodic table we predict intermediate properties for astatine, which has not been studied in detail.

14-2 IONIC SOLIDS

Ionic solids consist of infinite arrays of positive and negative ions that are held together by electrostatic forces. These forces are the same as those that hold a molecule of NaCl together in the vapor phase. In solid NaCl the Na^+ and Cl^- ions are arranged to maximize the electrostatic attraction, as shown in Figure 14-9. The coordination number of each Na^+ ion is 6, and

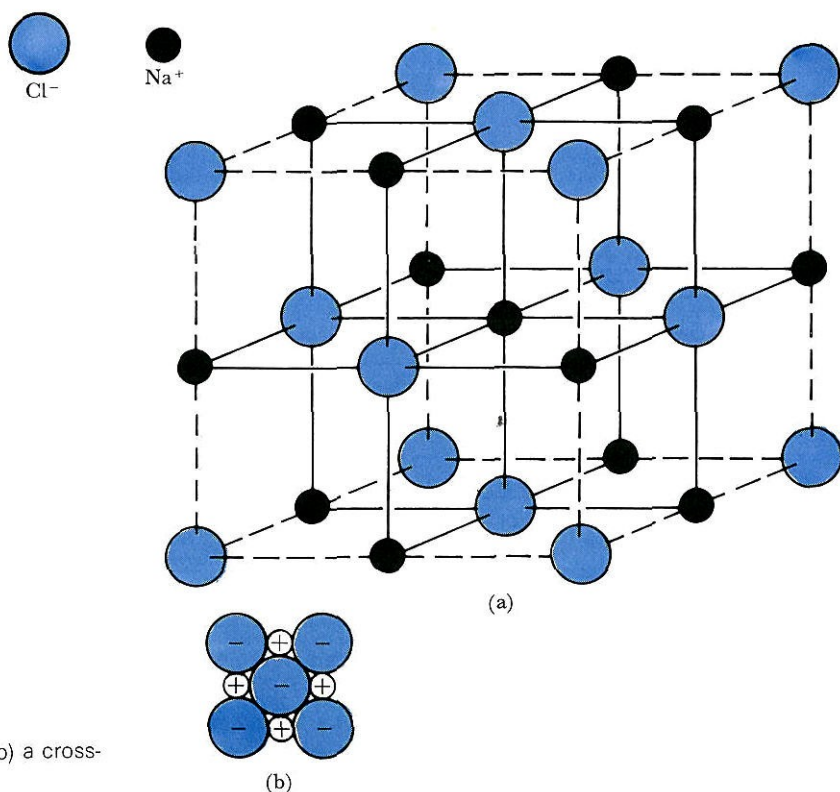


Figure 14-9

(a) The ionic NaCl structure; (b) a cross-sectional view.

each Cl^- ion similarly is surrounded by six Na^+ ions. Because ionic bonds are very strong, much energy is required to break down the structure in solid-to-liquid or liquid-to-gas transitions. Thus ionic compounds have high melting and boiling temperatures.

The crystal structures of several typical ionic solids are shown in Figure 14-10. Cesium chloride crystallizes in a structure in which the cation and

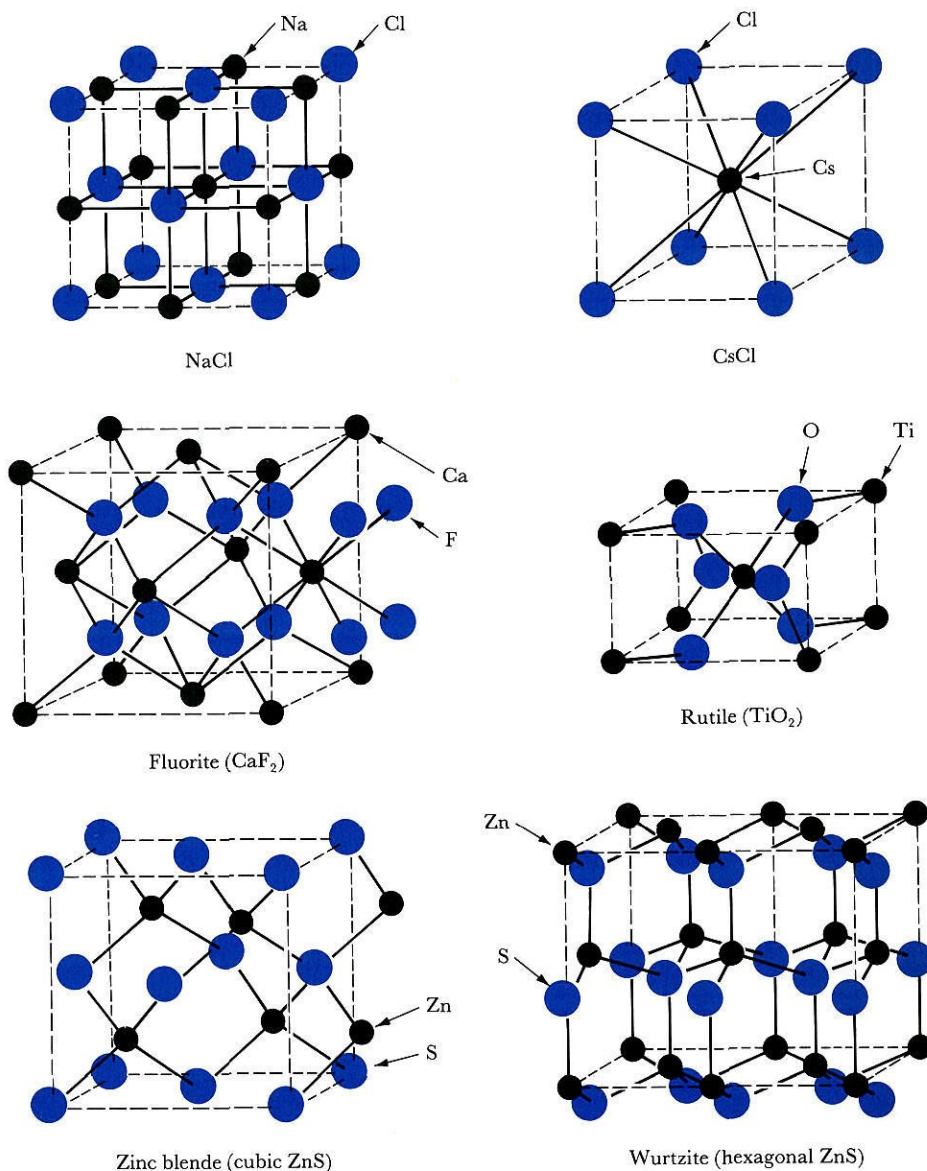


Figure 14-10

Some of the common structural types found for ionic substances.

anion each have a coordination number of 8. Zinc sulfide crystallizes in two distinct structures—the so-called zinc blende and wurtzite structures—in which the cation and anion each have a coordination number of 4. Calcium fluoride crystallizes in the fluorite structure. The coordination numbers are 8 for the cation (eight fluorides surround each calcium) and 4 for the anion. One of the crystalline forms of titanium dioxide is rutile, in which the coordination numbers are 6 for the cation and 3 for the anion.

14-3 MOLECULAR SOLIDS AND LIQUIDS

Molecules such as H_2 , N_2 , O_2 , and F_2 form molecular solids because all the valence orbitals are either used for *intramolecular* bonding or occupied with nonbonding electrons. Thus any intermolecular bonding that holds molecules together in the solid must be weak compared with the strength of the intramolecular bonding in the molecules. The weak forces that contribute to intermolecular bonding are called **van der Waals forces**.

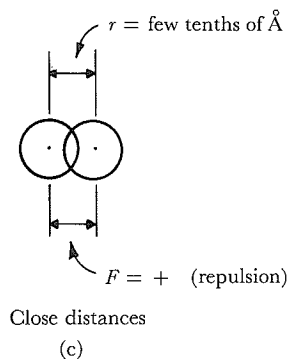
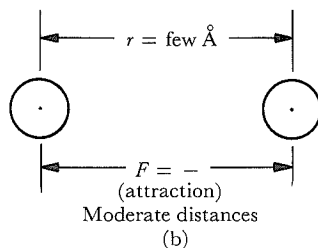
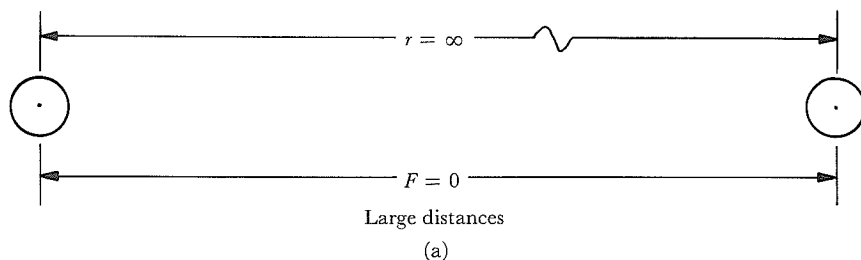
Van der Waals Forces

There are two principal van der Waals forces. The most important force at short range is the repulsion between electrons in the filled orbitals of atoms on neighboring molecules. This electron-pair repulsion is illustrated in Figure 14-11. The analytical expression commonly used to describe the energy resulting from this interaction is

$$\text{van der Waals repulsion energy} = be^{-ar} \quad (14-1)$$

in which b and a are constants for two interacting atoms. Notice that this repulsion term is very small at large values of the interatomic distance, r .

The second van der Waals force is the attraction that results when electrons in the occupied orbitals of the interacting atoms synchronize their motion to avoid one another as much as possible. For example, as shown in Figure 14-12, electrons in orbitals of atoms belonging to interacting molecules can synchronize their motion to produce an instantaneous dipole-induced dipole attraction. If at any instant the atom on the left in Figure 14-12 has more of its electron density at the left (as shown) then the atom becomes a tiny dipole with a negative left side and a positive right side. This positive side attracts electrons of the atom on the right in the figure and changes this atom into a dipole with a similar orientation. Therefore these two atoms attract each other because the positive end of the left atom and the negative end of the right atom are close. Similarly, fluctuation in electron density of the right atom induces a temporary dipole, or asymmetry of electron density, in the left atom. The electron densities fluctuate continually, yet the net effect is an extremely small but important attraction between atoms. The energy resulting from this attractive force

**Figure 14-11**

Repulsion of electrons in filled orbitals. (a) At very large distances two atoms or molecules behave as neutral species and neither repel nor attract one another. The force between them, F , is zero.

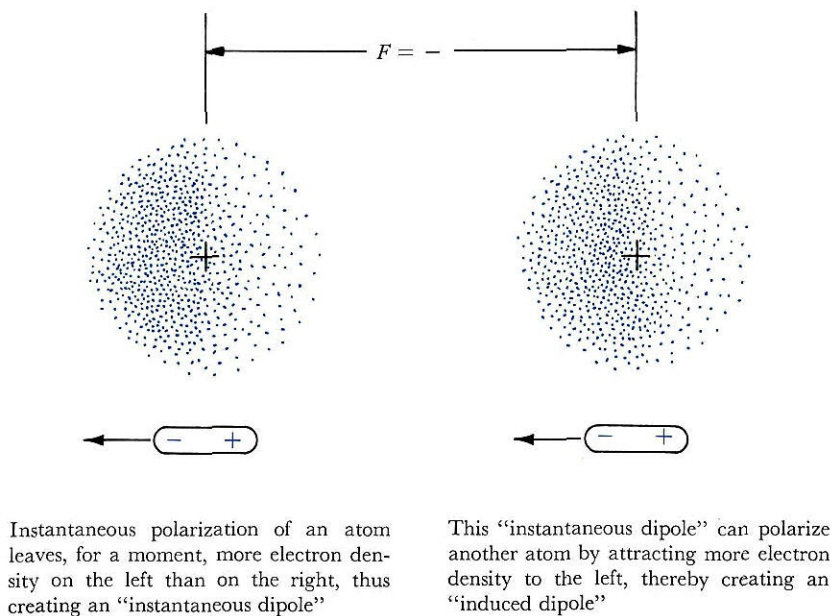
(b) At moderate distances two atoms or molecules have not yet come close enough for repulsion to be appreciable. However, they do attract one another (see Figure 14-12) because of deformations of their electron densities.

(c) At close range, when the electron density around one atom or molecule is large in the same region of space as the electron density around the other atom or molecule (i.e., when the filled orbitals overlap), coulomblike repulsion dominates and the two molecules repel one another.

is known as the **London energy**, after Fritz London, who derived the quantum mechanical theory for this attraction in 1930. The London energy varies inversely with the sixth power of the separation between atoms:

$$\text{London energy} = -\frac{d}{r^6} \quad (14-2)$$

in which d is a constant and r is the distance between atoms. This “inverse sixth” attractive energy decreases rapidly with increasing r , but not nearly as rapidly as the van der Waals repulsion energy. Thus at longer distances the London attraction is more important than the van der Waals repulsion; consequently, a small net attraction results.

**Figure 14-12**

Schematic illustration of the instantaneous dipole–induced dipole interaction that gives rise to a weak attraction. For the brief instant that this figure describes, there is an attractive force, F , between the instantaneous dipole and the induced dipole. The effect is reciprocal: each atom induces a polarization in the other.

The total potential energy (PE) of van der Waals interactions is the sum of the attractive energy of equation 14-2 and the repulsive energy of equation 14-1:

$$PE = be^{-ar} - \frac{d}{r^6} \quad (14-3)$$

The total van der Waals potential energy can be compared quantitatively with ordinary covalent bond energies by examining systems for which the curves of potential energy versus interatomic distance r are known accurately. We can calculate values for the constants a , b , and d from experimental data on the deviation of real gases from ideal gas behavior. Some of these values for interactions of noble gases are listed in Table 14-2.

The potential-energy curve for van der Waals interactions between helium atoms is illustrated in Figure 14-13. At separations of more than 3.5 Å, the second term in equation 14-3 predominates. As the atoms move closer, they attract each other more, and the energy of the system decreases. However, at distances less than 3 Å the strong electron-pair repulsion overwhelms the London attraction, and the potential-energy curve in Figure 14-13 rises. A balance between attraction and repulsion exists at a

Table 14-2
Van der Waals Energy Parameters

Interaction pair	a (a.u.) ^{-1a}	b (kJ mole ⁻¹)	d [kJ mole ⁻¹ (a.u.) ⁶]
He—He	2.10	17.1×10^3	6.3×10^3
He—Ne	2.27	86.6×10^3	12.1×10^3
He—Ar	2.01	125.5×10^3	40.6×10^3
He—Kr	1.85	68.6×10^3	57.3×10^3
He—Xe	1.83	111.3×10^3	89.1×10^3
Ne—Ne	2.44	438.5×10^3	23.8×10^3
Ne—Ar	2.18	635.1×10^3	80.3×10^3
Ne—Kr	2.02	346.4×10^3	111.7×10^3
Ne—Xe	2.00	561.5×10^3	173.6×10^3
Ar—Ar	1.95	918.4×10^3	270.3×10^3
Ar—Kr	1.76	501.2×10^3	377.0×10^3
Ar—Xe	1.74	813.4×10^3	582.8×10^3
Kr—Kr	1.61	272.8×10^3	524.7×10^3
Kr—Xe	1.58	443.5×10^3	813.4×10^3
Xe—Xe	1.55	718.8×10^3	1259.8×10^3

^a 1 a.u. = 1 atomic unit = 0.529 Å. The value of r in equation 14-3 must be expressed in atomic units as well.

separation of 3 Å and the He—He “molecule” is 76.1 J mole⁻¹ more stable than two isolated atoms.

Figure 14-13 also shows the marked contrast between van der Waals attraction and covalent bonding. In the H₂ molecule strong electron–proton attractions in the bonding molecular orbital cause the potential energy to decrease as the H atoms approach one another, and it is proton–proton repulsion that makes the energy increase sharply if the atoms are pushed too closely together. This proton–proton repulsion operates at smaller distances than the electronic repulsion between the two He atoms. The H—H bond length in the H₂ molecule is 0.74 Å, whereas the equilibrium distance of van der Waals–bonded He atoms is 3 Å. Moreover, a covalent bond is much stronger than a weak van der Waals interaction. Only 76.1 J mole⁻¹ are required to separate helium atoms at their equilibrium distance, but 431,000 J mole⁻¹ are needed to break the covalent bond in H₂.

Molecular solids, in which only van der Waals intermolecular bonding exists, generally melt at low temperatures. This is because relatively little energy of thermal motion is needed to overcome the energy of van der Waals bonding. The liquid and solid phases of helium, which result from weak van der Waals “bonds,” exist only at temperatures below 4.6 K. Even at temperatures near absolute zero, solid helium can be produced only at high pressures (29.6 atm at 1.76 K).

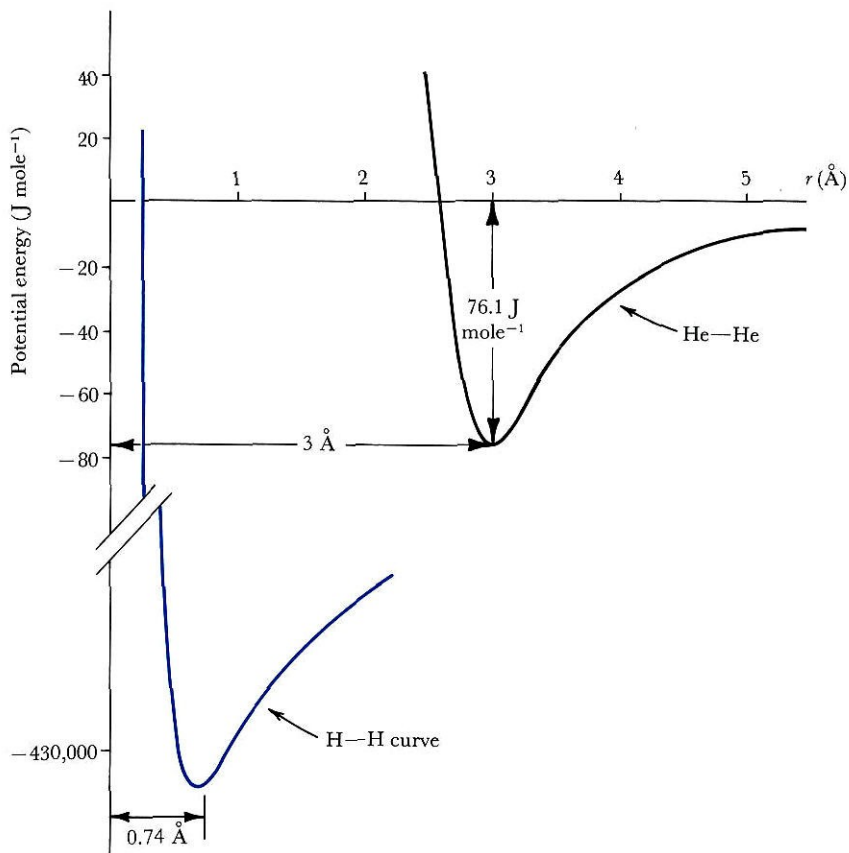


Figure 14-13

A comparison of the potential-energy curves for van der Waals attraction between two He atoms (black curve) and covalent bonding between two H atoms (colored curve). Notice that the energy scale is in joules rather than kilojoules per mole. The covalent bond is more than 5000 times as stable as the van der Waals bond.

Van der Waals bonds in molecular solids and liquids generally are stronger with increasing size of the atoms and molecules involved. For example, as the atomic number of the noble gases increases, the strength of the van der Waals bonding also increases, as shown by the argon–argon potential-energy curve in Figure 14-14. The attraction between the heavier atoms is stronger, presumably because the outer electrons are held more loosely, and larger instantaneous dipoles and induced dipoles are possible. Because of this stronger van der Waals bonding, solid argon melts at -184°C , or 89 K, which is considerably higher than the melting point for solid helium.

An example of the effect of molecular size on melting and boiling temperatures is provided by a series of continuous-chain alkanes, with formulas $\text{C}_n\text{H}_{2n+2}$, depicted in Figure 14-15 for $n = 1$ through 20. Part of

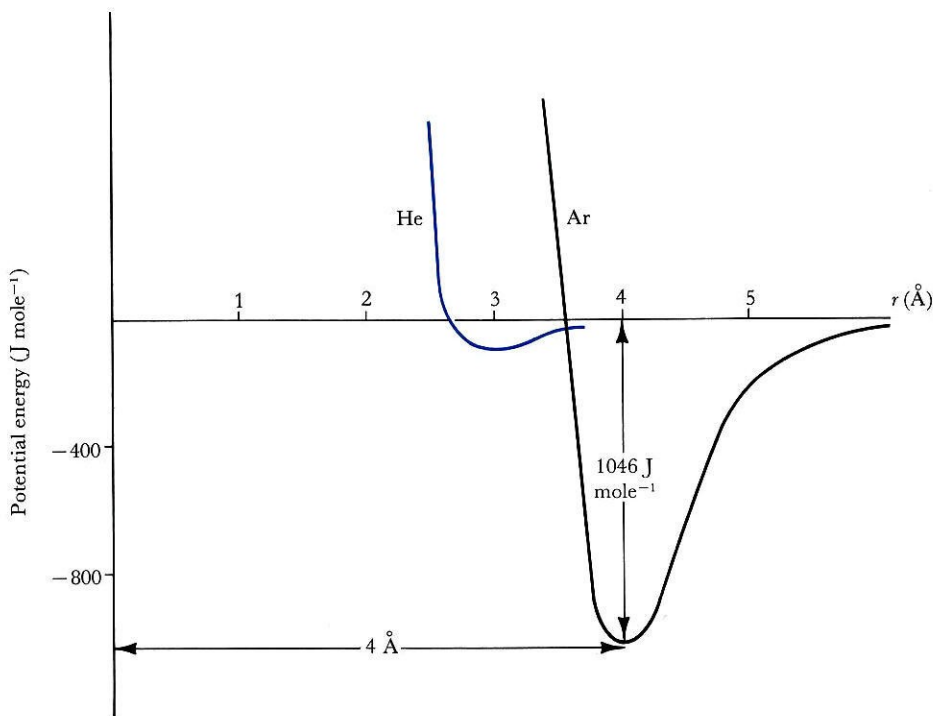


Figure 14-14

A comparison of the potential-energy curves for van der Waals attraction between two Ar atoms (black curve) and two He atoms (colored curve). The larger Ar atoms are more tightly held, although the bond energy is still one four-hundredth that of a H—H bond.

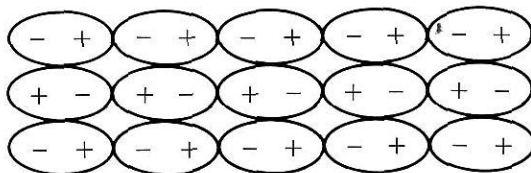
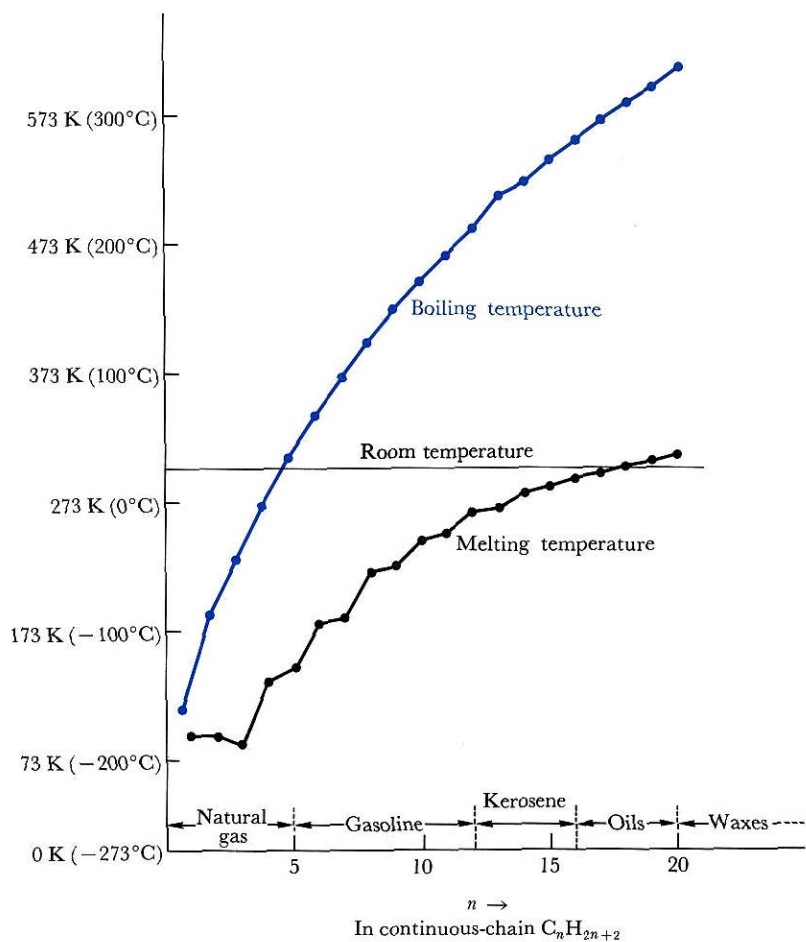
the increase in melting and boiling temperatures with increasing molecular size and weight arises from the greater energy needed to move a heavy molecule. However, another important factor is the large surface area of a molecule such as eicosane ($C_{20}H_{42}$), compared with methane, and the greater stability that eicosane can therefore gain from intermolecular van der Waals attractions. The mass effect is similar for both melting and boiling temperatures. However, molecular surface area affects the boiling temperatures more because molecules in the liquid phase are still close enough to exert van der Waals attractions. In fact, without these attractions, which are broken during vaporization, the liquid state could not exist.

Polar Molecules and Hydrogen Bonds

Polar molecules are stabilized in a molecular solid by the attractive interaction of oppositely charged ends of the molecules (Figure 14-16). This is

Figure 14-15

Melting and boiling temperatures of the continuous-chain hydrocarbons as a function of the length of the carbon chain. More energy is required to separate two molecules of eicosane (20 carbons) than two molecules of ethane (2 carbons) because of the more numerous van der Waals interactions between the two larger molecules.

**Figure 14-16**

Diagrammatic representation of the packing of polar molecules into a crystalline solid. Packing occurs so partial charges of opposite sign are in close proximity.

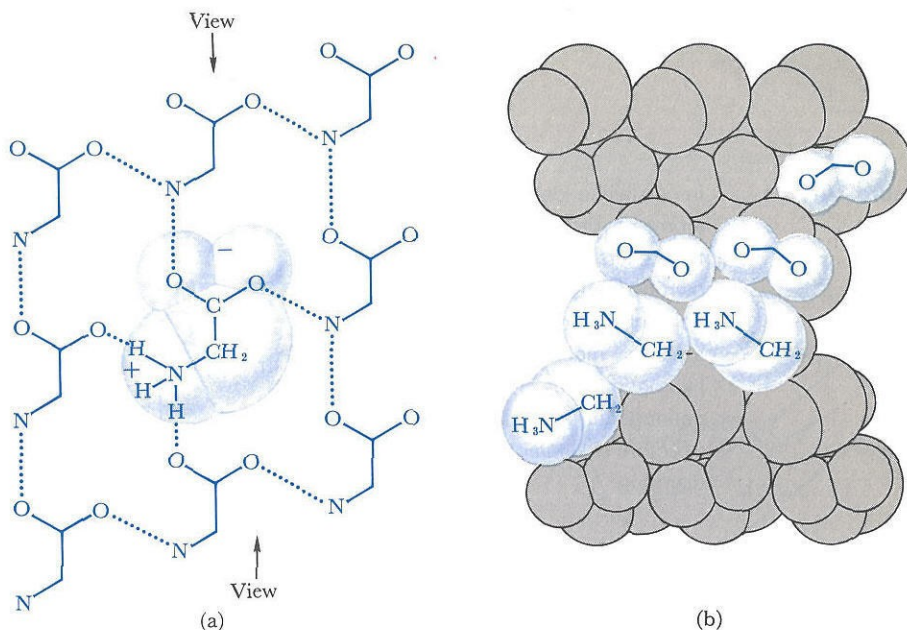


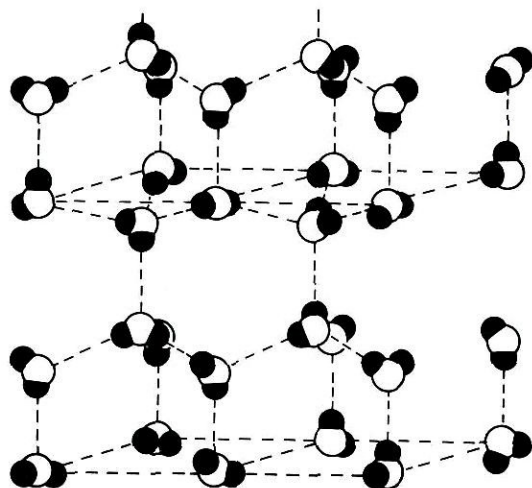
Figure 14-17

The bonding in the sheet structure of solid glycine, $^+\text{H}_3\text{N}-\text{CH}_2-\text{COO}^-$. (a) Molecules in a layer are packed tightly and are held together by van der Waals attractions and by hydrogen bonds (dotted). (b) The layers are stacked on top of one another and held together by van der Waals attractions. With this perspective the layers are on edge, and in a horizontal position. The view of the layers in (b) is marked by arrows in (a).

called **dipole–dipole interaction**. A particularly important kind of polar interaction is the **hydrogen bond**. This is a bond, primarily electrostatic, between a positively charged hydrogen atom and a small, electronegative atom, usually N, O, or F. For example, glycine molecules are held in a sheet structure by van der Waals forces and hydrogen bonds (Figure 14-17). Ice provides another example of the importance of hydrogen bonding in building intermolecular structures. As shown in Figure 14-18, each oxygen atom of a polar H_2O molecule is tetrahedrally coordinated to four other oxygen atoms in a structure that resembles the diamond structure. Each oxygen atom is bound to its four neighbor oxygen atoms by hydrogen bonds. In two of these hydrogen bonds the central H_2O molecule supplies the hydrogen atoms; in the other two bonds the hydrogen atoms come from neighboring H_2O molecules. Such bonds are weak compared with covalent bonds. A typical covalent bond energy is about 400 kJ mole^{-1} , whereas a hydrogen bond between H and O is approximately 20 kJ mole^{-1} . But hydrogen bonds are important for the same reason that van der Waals bonds are: They may be weak but there are many of them.

Figure 14-18

In crystalline ice each oxygen atom is hydrogen bonded to two others by means of its own hydrogen atoms, and bonded to two more oxygen atoms by means of their hydrogen atoms. The coordination is tetrahedral and the structure is similar to that of diamond.



Hydrogen bonding in water is responsible for many of its most important properties. Because of hydrogen bonds in both solid and liquid phases the melting and boiling temperatures of water are unexpectedly high when compared with those of H_2S , H_2Se , and H_2Te , which are hydrogen compounds of elements also in Group VIA of the periodic table. Solid and liquid ammonia and hydrogen fluoride show anomalous behavior similar to that of water and for the same reason (Figure 14-19). However, hydrogen bonding is less pronounced in ammonia than it is in water for two reasons: N is less electronegative than O, and NH_3 has only one lone pair of electrons to attract the H from a neighboring molecule. In contrast, HF is not as well hydrogen-bonded as H_2O , despite the greater electronegativity of F and the presence of three lone pairs. This is because HF has only one hydrogen atom to use in making such bonds.

Since hydrogen bonding causes an open network structure in ice (Figure 14-18), ice is less dense than water at the melting temperature. Upon melting, part of this open-cage structure collapses, and the liquid is more compact than the solid. The measured heat of fusion of ice is only 5.9 kJ mole^{-1} , whereas the energy of its hydrogen bonds is 20 kJ mole^{-1} . This indicates that only about 30% of the hydrogen bonds of ice are broken when it melts. Water is not composed of isolated, unbonded molecules of H_2O ; rather, it has regions or clusters of hydrogen-bonded molecules. That is, part of the hydrogen-bonded structure of the solid persists in the liquid. As the temperature is increased these clusters break up, and the volume continues to shrink. If the temperature is increased still more, the expected thermal expansion begins to take place. Consequently, liquid water has a minimum molar volume, or a maximum density, at 4°C .

Because the hydrogen-bonded H_2O clusters are broken slowly as heat is added, water has a higher heat capacity than any other common liquid

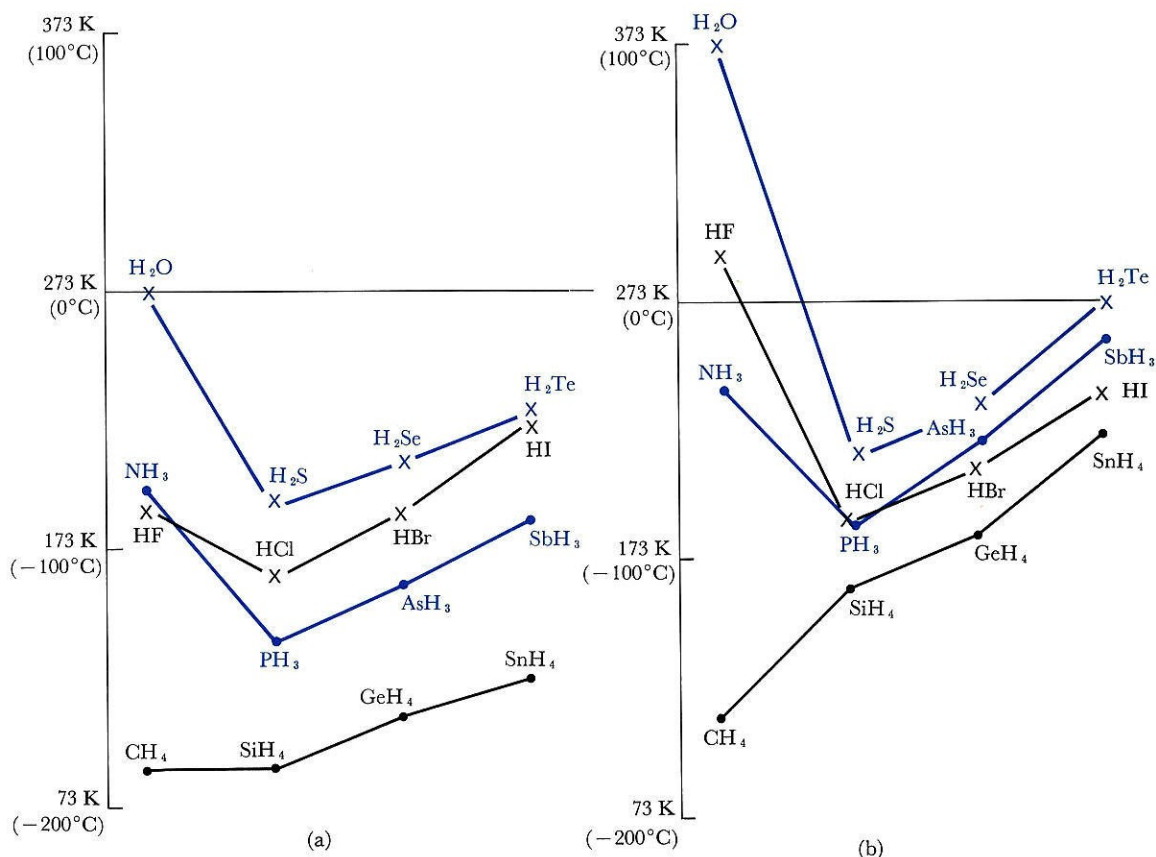


Figure 14-19

(a) Melting temperatures and (b) boiling temperatures for binary hydrogen compounds of some elements. Generally, melting and boiling temperatures increase with molecular weight within a group. The anomalous compounds HF, H₂O, and NH₃ have hydrogen bonds between molecules in both solid and liquid states.

except ammonia. Water also has an unusually high heat of fusion and heat of vaporization. All three of these properties give water the capability to act as a large thermostat, which confines the temperature on the earth within moderate limits. Ice absorbs a large amount of heat when it melts, and water absorbs more heat per unit of temperature increase than almost any other substance. Correspondingly, as water cools, it gives off more heat to its surroundings than other substances.

Coastal regions never experience the extremes of heat and cold that are typical of continental regions like the American Great Plains and the steppes of Central Asia and Siberia. It is unlikely that life could evolve and develop to a high level on planets where the extremes of temperature were not moderated by a high-specific-heat liquid such as H₂O.

Hydrogen bonds are even more important to life than the water structure suggests. They are one of the principal means of holding protein molecules together, as we shall see in Chapter 21. Without such bonds between carbonyl oxygen atoms and amine hydrogen atoms, no polypeptide chain would fold properly to make its protein.

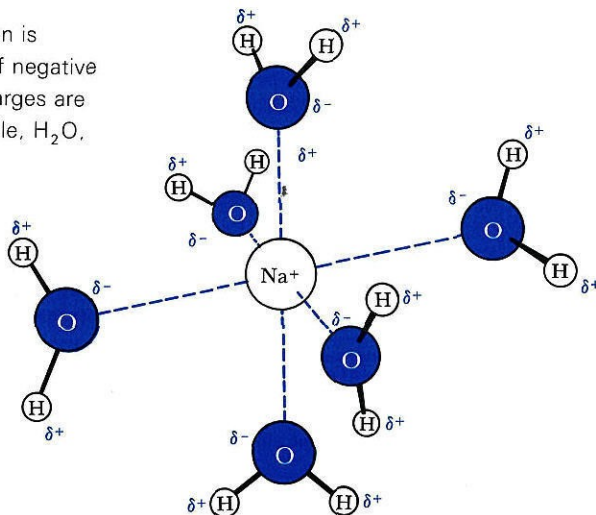
Polar Molecules as Solvents

The polar nature of liquid water makes it an excellent solvent for ionic solids such as NaCl. Water can dissolve NaCl and separate the oppositely charged Na^+ and Cl^- ions because the energy required to separate the ions is provided by the formation of hydrated ions (Figure 14-20). Each Na^+ ion in solution still has an octahedron of negative charges around it, but instead of being Cl^- ions they are the negative poles of the oxygen atoms of the water molecules. The Cl^- ions also are hydrated, but it is the positive ends (H) of the water molecules that approach the Cl^- ions. A nonpolar solvent such as gasoline, a liquid composed of hydrocarbon molecules, cannot form such *ion-dipole bonds* with Na^+ and Cl^- . Consequently NaCl and other salts are insoluble in gasoline.

Polar solvents dissolve polar molecular solids because of dipole-dipole interactions. The energy released by the formation of dipole-dipole bonds between a polar solvent and solute molecules is sufficient to break the intermolecular forces in the molecular solids (Figure 14-21). For example, ice is soluble in liquid ammonia but not in benzene because NH_3 is a polar molecule, whereas C_6H_6 is nonpolar.

Figure 14-20

In solution, the hydrated Na^+ ion is surrounded by an octahedron of negative charges, but these negative charges are from the dipolar solvent molecule, H_2O , instead of from Cl^- .



Energy is required to break up a solid molecular lattice

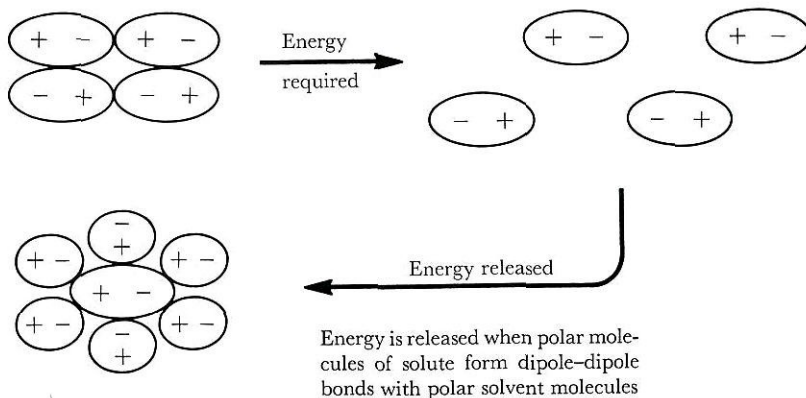


Figure 14-21

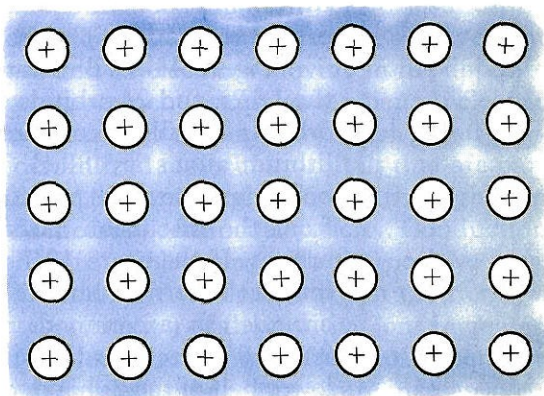
When a crystalline solid composed of polar molecules dissolves, stability is lost when oppositely charged ends of neighboring molecules are removed. This loss is compensated by the stability produced by solvating the polar molecules in solution. A solvent that cannot provide such stabilization cannot dissolve the solid.

14-4 METALS

The high thermal and electrical conductivities of metals suggest that the valence electrons are relatively free to move through the crystal structure. Figure 14-22 illustrates one model in which the electrons form a sea of negative charges that holds the atoms tightly together. The circled positive charges represent the positively charged ions remaining when valence electrons are stripped away, thereby leaving the nuclei and the filled electron

Figure 14-22

Cross section of a crystal structure of a metal with the sea of electrons. Each circled positive charge represents the nucleus and filled, non-valence electron shells of a metal atom. The shaded area surrounding the positive metal ions represents the mobile sea of electrons.



shells. Since metals generally have high melting temperatures and high densities, especially in comparison with molecular solids, the "electron sea" must strongly bind the positive ions in the crystal.

The simple electron-sea model for metallic bonding is also consistent with two other commonly observed properties of metals: malleability and ductility. A malleable material can be hammered easily into sheets; a ductile material can be drawn into thin wires. For metals to be shaped and drawn without fracturing, the atoms in the planes of the crystal structure must be displaced easily with respect to one another. This displacement does not result in the development of strong repulsive forces in metals because the mobile sea of electrons provides a constant buffer, or shield, between the positive ions. This situation is in direct contrast to that of ionic crystals, in which the binding forces are due almost entirely to electrostatic attractions between oppositely charged ions. In an ionic crystal, valence electrons are bound firmly to the atomic nuclei. Displacement of layers of ions in such a crystal brings ions of like charge together and causes strong repulsions that can lead to crystal fracture (Figure 14-23).

Electronic Bands in Metals

The molecular orbital theory provides an adequate model for metallic bonding. According to this model, the entire block of metal is considered to be a giant molecule. All the atomic orbitals of a particular type in the crystal interact to form a set of delocalized orbitals that extend throughout the entire block. For a particular crystal, assume that the number of valence orbitals is on the order of 10^{23} . To visualize the interaction of such a large number of valence orbitals, consider the hypothetical sequence of linear lithium molecules Li_2 , Li_3 , and Li_4 in which the important valence orbitals are $2s$ orbitals. Figure 14-24 shows the buildup of molecular orbitals for these three molecules. Notice that because of the delocalization of the molecular orbitals, none of the electrons is required to reside in an antibonding orbital. The spacing between the orbitals also becomes smaller. In the limit of 10^{23} equivalent atoms, the combination of atomic orbitals produces a band of closely spaced energy levels.

Figure 14-25 illustrates the three bands of energy levels formed by the $1s$, $2s$, and $2p$ orbitals of the simplest metal, lithium. The $1s$ molecular orbitals are filled completely because the $1s$ atomic orbitals in isolated lithium atoms are filled. Thus the $1s$ electrons make no contribution to bonding. They are part of the positive ion cores and can be eliminated from the discussion. Atomic lithium has one valence electron in a $2s$ orbital. If there are 10^{23} atoms in a lithium crystal, the 10^{23} $2s$ orbitals interact to form a band of 10^{23} delocalized orbitals. As usual, each of these orbitals can accommodate two electrons, so the capacity of the band is 2×10^{23} electrons. Lithium metal has enough electrons to fill only the lower half of the $2s$ band, as illustrated in Figure 14-25.

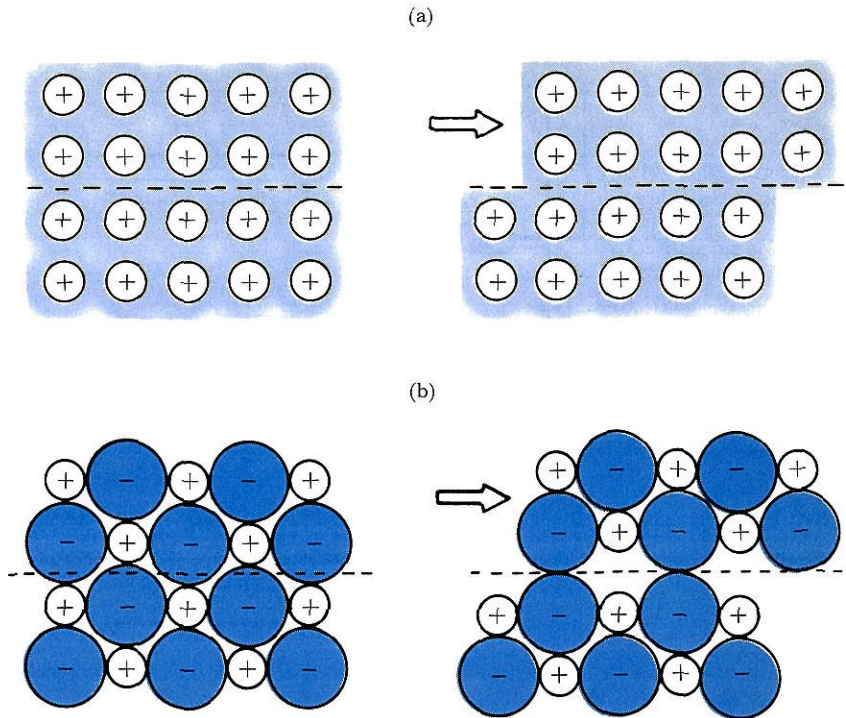


Figure 14-23

(a) Shift of metallic crystal along a plane results in no strong repulsive forces. (b) Shift of an ionic crystal along a plane results in strong repulsive forces and crystal distortion.

The presence of a partially filled band of delocalized orbitals accounts for bonding and electrical conduction in metals. Electrons in the lower filled orbital band move throughout the crystal in a random fashion such that their motion results in no *net* separation of electrons and positive ions in the metal. For a metal to conduct an electric current, electrons must be excited to unfilled delocalized orbitals in such a way that their movement in one direction is not exactly canceled by electrons moving in the opposite direction. Such concerted electron movement occurs only when an electric potential difference is applied between two regions of a metal. Then electrons are excited to the unfilled delocalized molecular orbitals that are part of the same band (the $2s$ band for lithium) and just slightly higher in energy. Therefore we can expect a metal to conduct electricity. Conduction is restricted by the frequent collisions of electrons with the positive ions, which have kinetic energy and thus vibrate randomly within their crystal sites. As the temperature increases, vibration of the positive ions increases, and collisions with the conduction electrons are more frequent. Therefore electrical conductivity in metals decreases as the temperature increases.

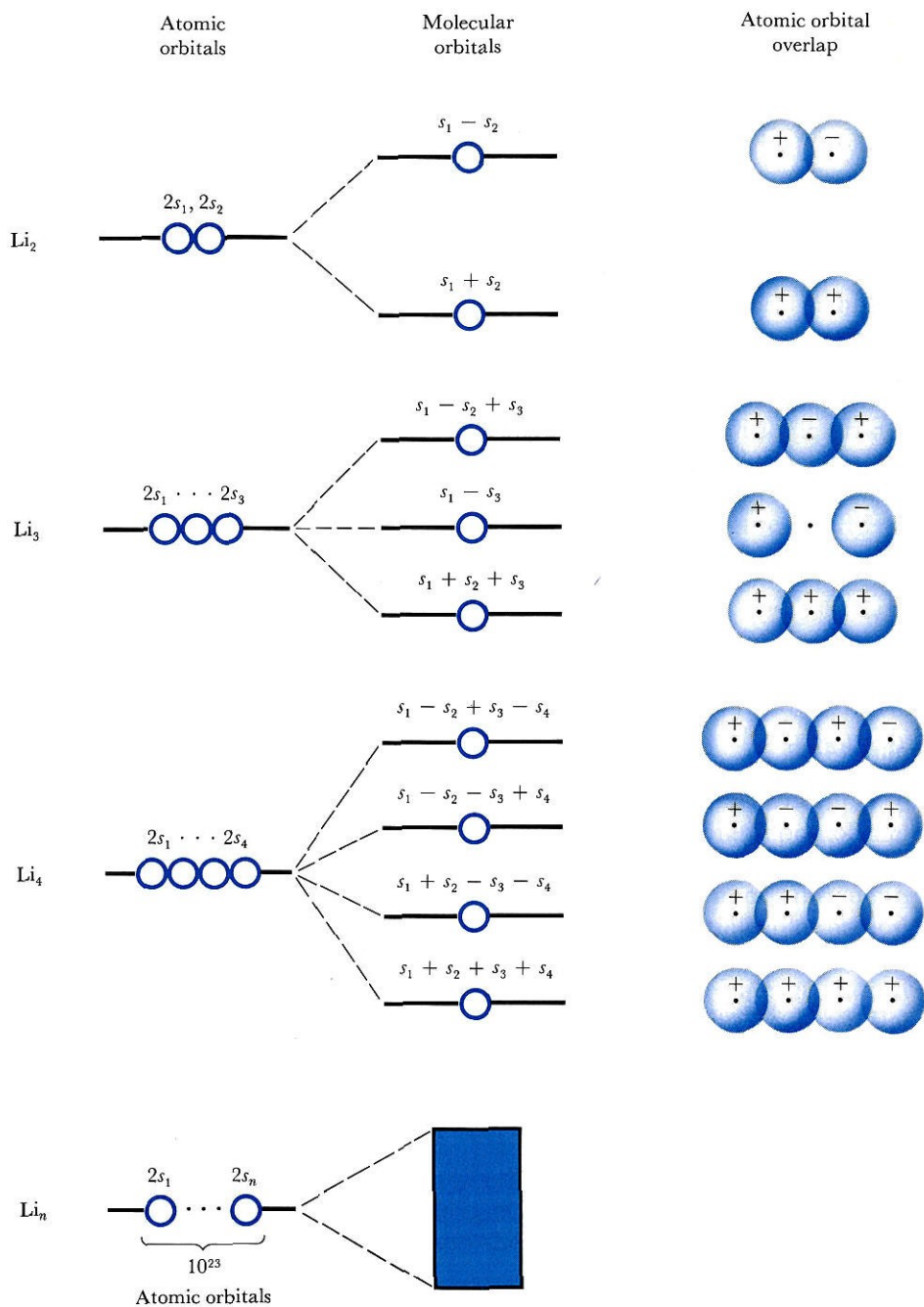


Figure 14-24

Molecular orbital development of the band theory of metals.

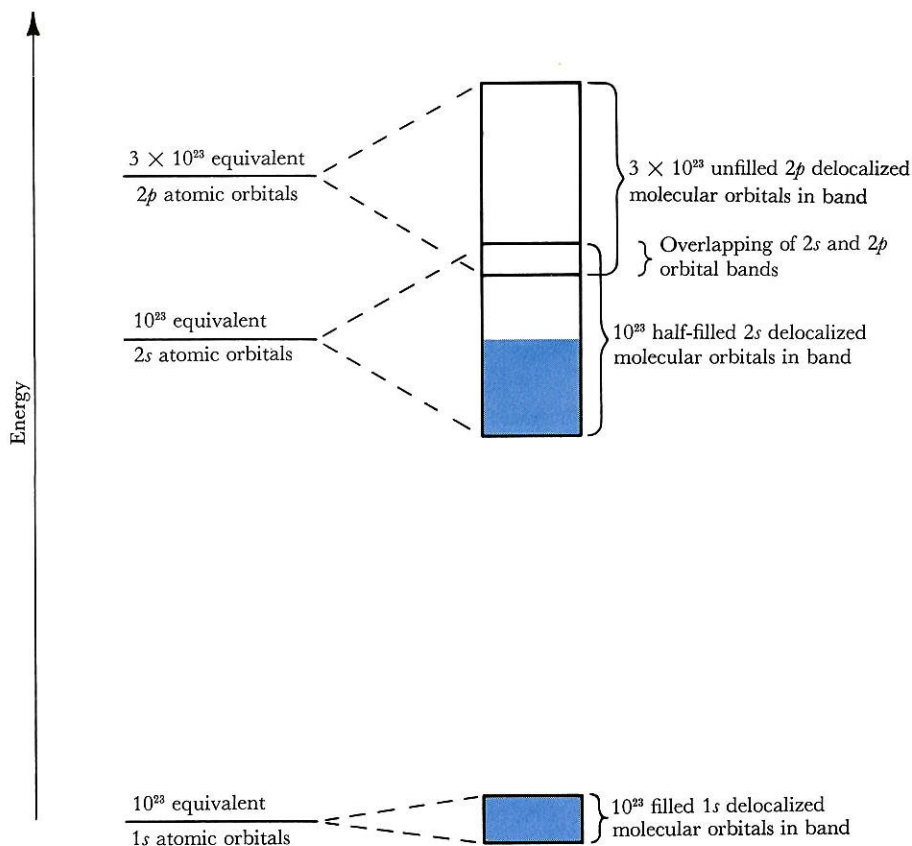


Figure 14-25

Delocalized-molecular-orbital bands in lithium. The original $2s$ and $2p$ atomic orbitals are so close in energy that the molecular orbital bands overlap. Lithium has one electron in every $2s$ atomic orbital, hence only half as many electrons as can be accommodated in the $2s$ atomic orbitals or in the delocalized-molecular-orbital band. There are unfilled energy states an infinitesimal distance above the highest-energy filled state, so an infinitesimal energy is required to excite an electron and send it moving through the metal. Thus lithium is a conductor.

Beryllium is a more complicated example of a metal than lithium is. An isolated beryllium atom has exactly enough electrons to fill its $2s$ orbital. Accordingly, beryllium metal has enough electrons to fill its $2s$ delocalized band. If the $2p$ band did not overlap the $2s$ (Figure 14-26), beryllium would not conduct well because an energy equal to the gap between bands would be required before electrons could move through the solid. However, the two bands do overlap and beryllium has unoccupied delocalized orbitals that are an infinitesimal distance above the most energetic filled orbitals. Consequently, beryllium is a metallic conductor.

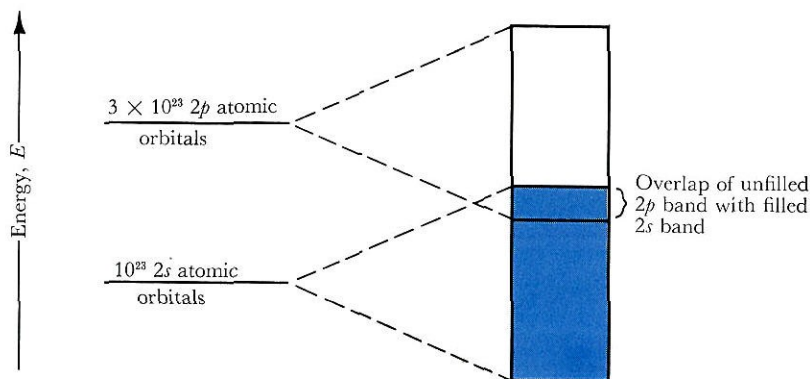


Figure 14-26

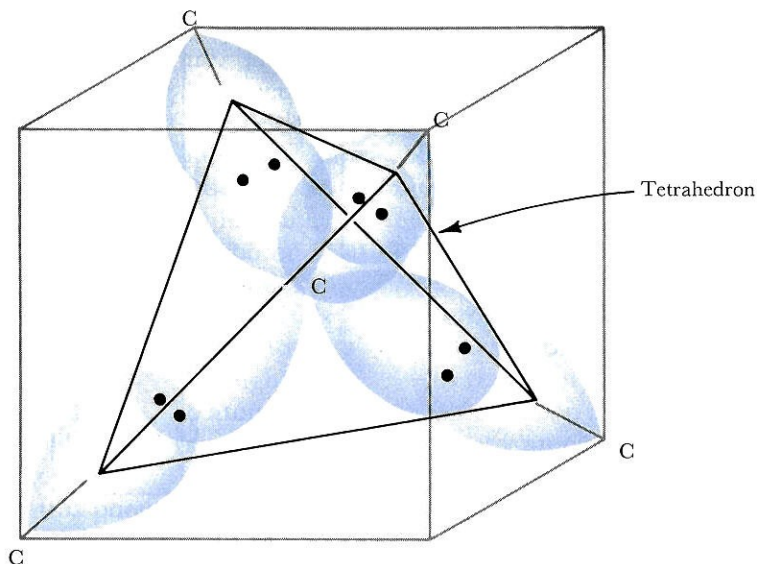
Band-filling diagram for beryllium. A Be atom has enough electrons (two) to fill its 2s orbital, so Be metal has enough electrons to fill its 2s delocalized-molecular-orbital band. If the 2s and 2p bands did not overlap, Be would be an insulator because an appreciable amount of energy would be required to make electrons flow in the solid. But with the band overlap shown here, an infinitesimal amount of energy excites electrons to the 2p band orbitals and electrons flow.

14-5 NONMETALLIC NETWORK SOLIDS

Nonmetallic network materials such as carbon or silicon are **insulators**, that is, they do not conduct electrical current. There is no simple way to apply the molecular orbital model to a discussion of the bonding in nonmetallic network solids. Suffice it to say that in nonmetallic network solids it is usually possible to “count” electrons in the Lewis electron-dot sense and show that the octet is achieved. This is because the atoms in nonmetallic network solids usually have at least as many valence electrons as the number of valence orbitals. Consequently, low coordination numbers are preferred, and simple electron-pair bonds can be formed between each atom and its nearest neighbors. Because of the low coordination numbers, the potential energy is not constant throughout the crystal; rather, it is greatly lowered in the internuclear region and the electrons are not free to move throughout the crystal as they are in the case of the metals.

For example, in diamond each carbon atom has a coordination number of 4. The hybrid orbital model adequately describes the bonding by assigning to each carbon atom four localized tetrahedral sp^3 hybrid orbitals (Figure 14-27). The four valence electrons in each carbon atom are sufficient to fill these bonding orbitals. Thus all electrons in diamond are used for bonding, leaving none to move freely to conduct electricity.

The effect of coordination number on the electronic bands of a solid can be illustrated with respect to carbon. Calculations have shown that the electronic bands for carbon would be delocalized *if* carbon crystallized in a

**Figure 14-27**

Schematic representation of the overlap of the four sp^3 hybrid orbitals of a carbon atom with similar orbitals from four other carbon atoms in diamond crystals.

structure with a high coordination number such as is found for the metals (Figure 14-28a). Consequently carbon would be an electrical conductor. Experimentally it is found that carbon has a coordination number of 4, and this causes the extended bands shown in Figure 14-28a to split into a filled band corresponding to bonding orbitals, and an unfilled band of anti-bonding orbitals. A “forbidden zone” or “band gap” separates the bands (Figure 14-28b).

For an insulator to conduct, it needs sufficient energy to excite the electrons in the filled band to move across the band gap into the unfilled molecular orbitals. This energy is the activation energy of the conduction process. Only high temperatures or extremely strong electrical fields will provide enough energy to an appreciable number of electrons for conduction to occur. In diamond the band gap (between the top of the filled or valence band and the bottom of the unfilled or conduction band) is 5.2 eV, or 502 kJ mole⁻¹.

Semiconductors

The borderline between metallic and nonmetallic network structures of elements in the periodic table is not sharp (Figure 14-8). This is shown by the fact that several elemental solids have properties that are intermediate

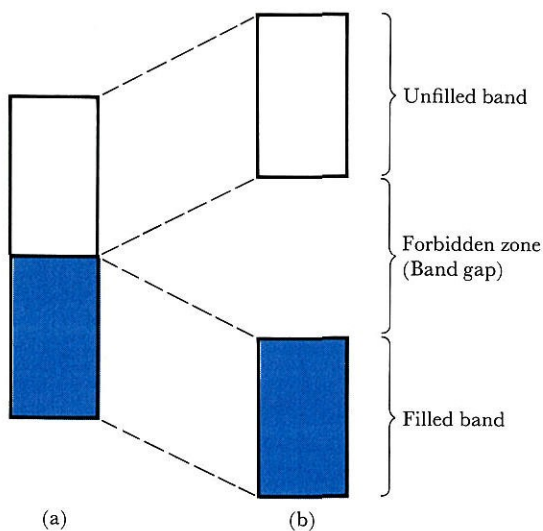


Figure 14-28

Two calculated band structures of crystalline carbon. The structure in (a) is based on the assumption that carbon crystallizes in the body-centered cubic structure with each carbon atom surrounded by eight other carbon atoms; the structure in (b) is based on the assumption that carbon crystallizes in the known diamond structure wherein each carbon atom is surrounded by four other carbon atoms. In (a) carbon would behave as an electrical conductor; in (b) carbon would behave as an insulator, which is observed experimentally for diamond.

between conductors and insulators. Silicon, germanium, and α -gray tin all have the diamond structure. However, the band gap between filled and empty bands for these solids is much smaller than it is for carbon. The gap for silicon is only 105 kJ mole^{-1} . (As we have seen, it is 502 kJ mole^{-1} for carbon.) For germanium it is 59 kJ mole^{-1} , and for α -gray tin it is 7.5 kJ mole^{-1} . The metalloids silicon and germanium are called **semiconductors**.

A semiconductor can carry a current if the relatively small energy required to excite electrons from the lower filled valence band to the upper empty conduction band is provided. Since the number of excited electrons increases as the temperature increases, the conductance of the semiconductor increases with temperature. This behavior is exactly the opposite of that of metals.

Conduction in materials such as silicon and germanium can be enhanced by adding small amounts of certain impurities. The band gap in silicon can be narrowed effectively if impurities such as boron or phosphorus are added to silicon crystals. Small amounts of boron or phosphorus (a few parts per million) can be incorporated into the silicon structure when the crystal is grown. Phosphorus has five valence electrons and thus has an extra

free electron even after four electrons have been used in the covalent bonds of the silicon structure. This fifth electron can be moved away from a phosphorus atom by an electric field; hence we say phosphorus is an electron donor. Only $1.05 \text{ kJ mole}^{-1}$ is required to free the donated electrons, thereby making a conductor out of silicon to which a small amount of phosphorus has been added. The opposite effect occurs if boron is added to silicon. Atomic boron has one too few electrons for complete covalent bonding. Thus for each boron atom in the silicon crystal there is a single vacancy in a bonding orbital. It is possible to excite the valence electrons of silicon into these vacant orbitals in the boron atoms, thereby causing the electrons to move through the crystal. To accomplish this conduction an electron from a silicon neighbor drops into the empty boron orbital. Then an electron that is two atoms away can fill the silicon atom's newly created vacancy. The result is a cascade effect, whereby an electron from each of a row of atoms moves one place to the neighboring atom. Physicists prefer to describe this phenomenon as a hole moving in the opposite direction. No matter which description is used, it is a fact that less energy is required to make a material such as silicon conduct if the crystal contains small amounts of either an electron donor such as phosphorus or an electron acceptor such as boron.

14-6 THE FRAMEWORK OF THE PLANET: SILICATE MINERALS

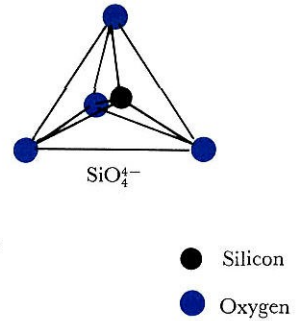
The core of our planet is believed to be mainly iron and nickel, with a radius of approximately 2200 miles. This core gives earth its magnetic field, which the moon and our neighbor planets, Mars and Venus, apparently lack. The earth's core is at a high pressure and temperature, and is probably fluid. An old theory of the origin of our planet presumed that it formed when hot gases collected and cooled. By this theory, the core is a relic of the first hot period; it has not solidified because of the insulating effect of the outer layers.

The current view is that the earth grew by cold accretion of solid debris and dust. After a certain critical mass was reached, heat from the interior could not be lost to the surroundings as rapidly as it was generated by natural radioactivity and pressure, and the center of the planet liquefied. This could occur only in a planet above a critical size, which presumably explains the absence of a molten core and a strong magnetic field in Mars and the moon. The phenomenon is similar to that of critical mass in uranium fission. Below a certain mass of ^{235}U the metal loses too many neutrons to the outside to sustain a chain reaction, so nuclear explosion occurs only in pieces of ^{235}U above this critical size.

For 1800 miles above the core of the earth extends the *mantle*, a layer

Figure 14-29

The SiO_4^{4-} tetrahedron, which is the building block of most silicate minerals. The Si atom (black) is covalently bonded to four oxygen atoms at the corners of a tetrahedron (color). The black lines between oxygen atoms are included only to give form to the tetrahedron.



probably composed of a dense silicate material similar to basalt. The upper 20 miles under the continents, or as little as three miles under the ocean beds, is the *crust*, the only part about which we have any real chemical knowledge. On top of this crust—itsself only 1.5% of the volume of the planet—is spread the thin layer containing virtually all the matter with which we are concerned.

The crust is 48% oxygen by weight, in the form of the various silicate minerals. It is also 26% silicon, 8% aluminum, 5% iron, and 2% to 5% calcium, sodium, potassium, and magnesium. Remarkably enough, these silicate minerals are more than 90% oxygen by volume. Most of the crust is some form of the mixture of silicate minerals known as *granite*.

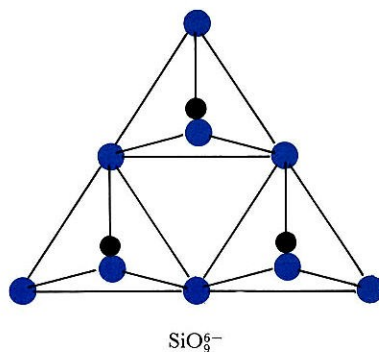
The basic building block in silicates is the orthosilicate ion, SiO_4^{4-} , shown in Figure 14-29. Each silicon atom is covalently bonded to four oxygen atoms at the corners of a tetrahedron. The SiO_4^{4-} anion occurs in simple minerals such as zircon (ZrSiO_4), garnet, and topaz. Two tetrahedra can share a corner oxygen atom to form a discrete $\text{Si}_2\text{O}_7^{6-}$ anion, or three tetrahedra can form a ring, shown in Figure 14-30. Benitoite, $\text{BaTiSi}_3\text{O}_9$, is the best known example of this uncommon kind of silicate. Beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, a common source of beryllium, has anions composed of rings of six tetrahedra with six shared oxygen atoms.

Chain Structures

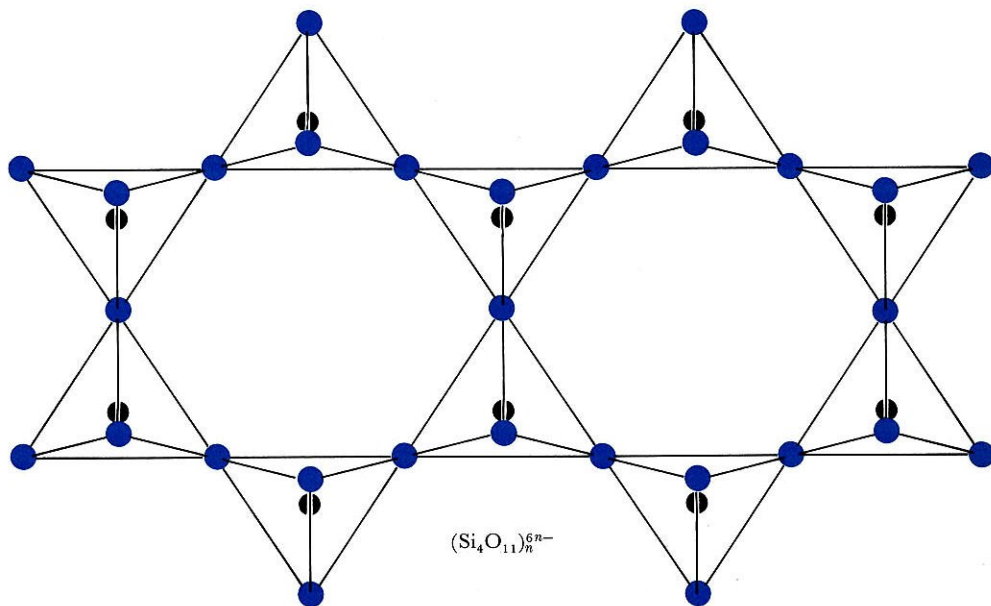
All the silicates mentioned so far are made from discrete anions. A second class is made of endless strands or chains of linked tetrahedra. Some minerals have single silicate strands with the formula $(\text{SiO}_3)_n^{2n-}$. A form of asbestos has the double-stranded structure shown in Figure 14-31. The double-stranded chains are held together by electrostatic forces between themselves and the Na^+ , Fe^{2+} , and Fe^{3+} cations packed around them. The chains can be pulled apart with much less effort than is required to snap the covalent bonds within a chain. Therefore, asbestos has a stringy, fibrous texture. Aluminum ions can replace as many as one quarter of the silicon ions in the tetrahedra. However, each replacement requires one more positive charge

Figure 14-30

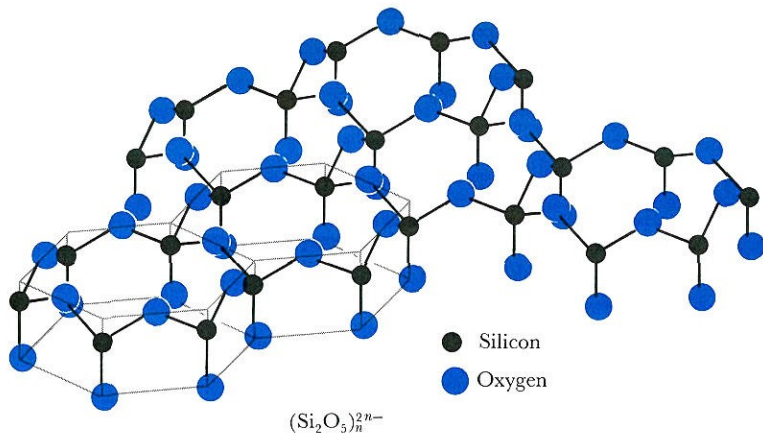
A ring of three tetrahedra, with three oxygen atoms shared between pairs of tetrahedra, has the formula $\text{Si}_3\text{O}_9^{6-}$. This structure occurs as the anion in soft, crumbly rocks such as benitoite, $\text{BaTiSi}_3\text{O}_9$.



from another cation (such as K^+) to balance the charge on the silicate oxygen atoms. The physical properties of the silicate minerals are influenced strongly by how many Al^{3+} ions replace Si^{4+} ions, and by how many extra cations are therefore needed to balance the charge.

**Figure 14-31**

Long double-stranded chains of silicate tetrahedra are in fibrous minerals such as asbestos.

**Figure 14-32**

In talc, mica, and the clay minerals, silicate tetrahedra each share three of their corner oxygen atoms to make endless sheets. All of the unshared oxygen atoms point down in this drawing on the same side of the sheet.

Sheet Structures

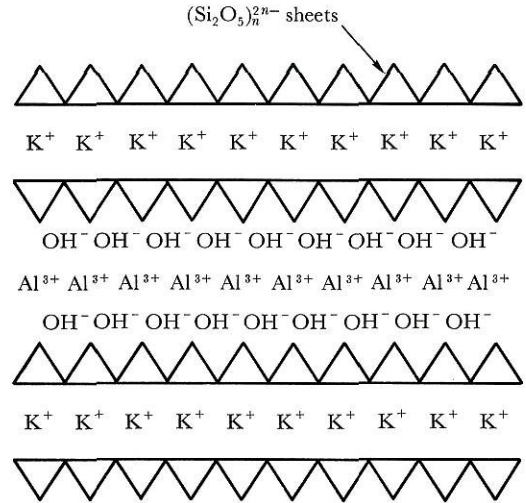
Continuous broadening of double-stranded silicate chains produces planar sheets of silicate structures (Figure 14-32). Talc, or soapstone, has this structure, in which none of the Si^{4+} is replaced with Al^{3+} . Therefore, no additional cations between the sheets are required to balance charges. The silicate sheets in talc are held together primarily by van der Waals forces. Because of these weak forces the layers slide past one another relatively easily, and produce the slippery feel that is characteristic of talcum powder.

Mica resembles talc, but one quarter of the Si^{4+} ions in the tetrahedra are replaced by Al^{3+} ions. Thus an additional positive charge is required for each replacement to balance charges. Mica has the layer structure shown in Figure 14-33. The layers of cations (Al^{3+} serves as a cation between layers as well as a substitute in the silicate tetrahedra) hold the silicate sheets together electrostatically with much greater strength than in talc. Thus mica is not slippery to the touch and is not a good lubricant. However, it cleaves easily, thereby splitting into sheets parallel to the silicate layers. Little effort is required to flake off a chip of mica, but much more strength is needed to bend the flake across the middle and break it.

The clay minerals are silicates with sheet structures such as in mica. These layer structures have enormous “inner surfaces,” and can often absorb large amounts of water and other substances between the silicate layers. This is why clay soils are such useful growth media for plants. It is also why clays are used as beds for metal catalysts. The common catalyst platinum black is finely divided platinum metal obtained by precipitation from solution. The catalytic activity of platinum black is enhanced by the large amount of exposed metal surface. The same effect can be achieved

Figure 14-33

In a form of mica called muscovite, $K_2Al_4Si_6Al_2O_{20}(OH)_4$, anionic sheets of silicate tetrahedra (Figure 14-32) alternate with layers of potassium ions and aluminum ions sandwiched between hydroxide ions. This layer structure gives mica its flaky cleavage properties.

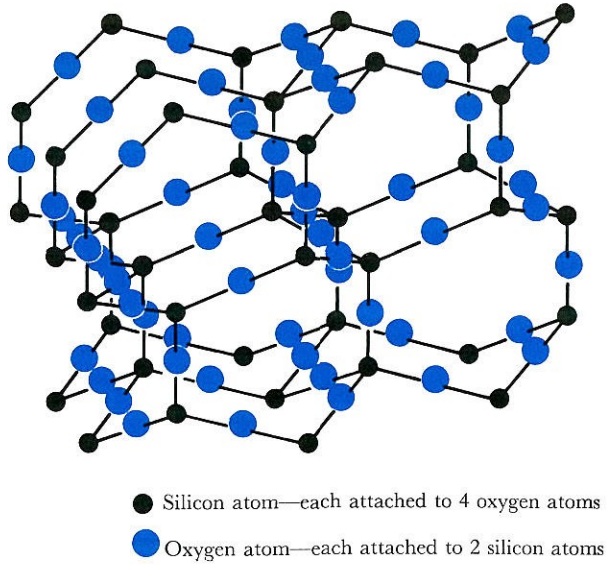


by precipitating a metal to be used as a catalyst (Pt, Ni, or Co) onto clays. The metal atoms coat the interior walls of the silicate sheets, and the clay structure prevents the metal from consolidating into a useless mass. J. D. Bernal has suggested that the first catalyzed reactions in the early stages of the evolution of life, before biological catalysts (enzymes) existed, may have occurred on the surfaces of clay minerals.

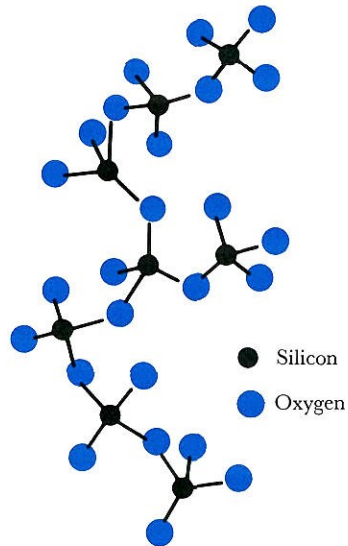
Three-Dimensional Networks

The three-dimensional silicate networks, in which all four oxygen atoms of SiO_4^{4-} are shared with other Si^{4+} ions, are typified by quartz, $(SiO_2)_n$, shown in Figure 14-34. In quartz, all the tetrahedral structures have Si^{4+} ions, but in other network minerals, up to half the Si^{4+} ions can be replaced with Al^{3+} ions. These minerals include the feldspars, for which a typical empirical formula is $KAlSi_3O_8$. Feldspars are nearly as hard as quartz. Basalt is a compact mineral related to feldspar. Granite, the chief component of the earth's crust, is a mixture of crystallites of mica, feldspar, and quartz.

Glasses are amorphous, disordered, noncrystalline aggregates with linked silicate chains of the sort depicted in Figure 14-35. Common soda-lime glass is made with sand (SiO_2), limestone ($CaCO_3$), and sodium carbonate (Na_2CO_3) or sodium sulfate (Na_2SO_4), which are melted together and allowed to cool. Other glasses with special properties are made by using other metal carbonates and oxides. Pyrex glass has boron as well as silicon and some aluminum in its silicate framework. Glasses are not true solids, but are extremely viscous liquids. If you examine the panes of glass in a very old New England home, you can sometimes see that the bottom of the

**Figure 14-34**

The three-dimensional network of silicate tetrahedra in quartz, SiO_2 .

**Figure 14-35**

Glasses are amorphous, disordered chains of silicate tetrahedra that are fused with metal oxides or carbonates such as Na_2CO_3 or CaCO_3 .

pane is slightly thicker than the top because of two centuries of slow, viscous flow of the glass.

Summary

The types of bonding in solids that we have seen are summarized in Table 14-3. **Ionic** or **electrostatic bonds** and electron-pair **covalent bonds** both have bond energies of approximately 400 kJ mole^{-1} . **Metallic bonds** are variable, but are of comparable strength. **Hydrogen bonds** are much weaker: The bond between O and H is about 20 kJ mole^{-1} . **Van der Waals attractions** are weaker yet; from a few tenths to 2 kJ mole^{-1} . Hydrogen

Table 14-3

Types of Bonding in Solids

	Molecular	Nonmetallic network	Metallic	Ionic
Structural unit:	Molecule	Atom	Atom	Ion
Principal bonding between units:	Weak van der Waals and, in polar molecules, a stronger dipole—dipole bond	Strong covalent bonds	Delocalized electron sea through a system of metallic positive ion centers	Strong ionic bonding (electrostatic)
Properties:	Soft Low melting point Insulator	Hard High melting point Insulator or semiconductor	Wide range of hardness Wide range of melting points Conductor	Hard High melting point Insulator
Usually occurs in:	Nonmetals at right of periodic table and compounds predominantly composed of nonmetals	Nonmetals in center of periodic table	Metals in left half of periodic table	Compounds of metals and nonmetals
Examples	O_2 , C_6H_6 , H_2O , Br_2	Diamond, Si, ZnS, SiO_2	Na, Zn, Au, brass, bronze	KI, Na_2CO_3 , LiH

bonds and van der Waals attractions assume a greater importance than their strength would suggest because of the large number of such bonds that can form.

Hydrogen bonding results from the attractive interaction between a positive hydrogen atom and an electronegative atom so small that the proton can approach it closely. Oxygen and fluorine can participate in such hydrogen bonds, as can nitrogen to a lesser degree, but chlorine is usually too large. Hydrogen bonds are responsible for many of the familiar properties of water and ice.

Both metals and covalent network solids can be interpreted by using delocalized molecular orbitals, in which the “molecule” extends over the entire piece of matter under study. This band theory accounts for many of the observed properties of conductors, semiconductors, and insulators.

The basic subunit of the silicates, a SiO_4^{4-} tetrahedron, can be organized into rings, chains, sheets, and three-dimensional networks. Aluminum can replace some silicon, but other cations must be added to balance the charge, thereby increasing the electrostatic contribution to holding the solid together. The silicates illustrate four of the five types of bonding that have been discussed in this chapter: covalent bonding between Si and O in the tetrahedra, van der Waals forces between silicate sheets in talc, ionic attractions between charged sheets and chains, and hydrogen bonds between water molecules and the silicate oxygen atoms in clays. If we include Ni catalysts prepared on a clay support, the fifth type of bonding (metallic) is represented as well.

Self-Study Questions

1. What types of forces hold molecules together in crystals and liquids?
2. Why do the halogen molecules form molecular solids?
3. Why do carbon and silicon form network solids?
4. What is the main structural unit in elemental boron?
5. Why are nonmetallic network solids usually quite hard?
6. What physical effect is responsible for the attraction in van der Waals interactions? What is responsible for the repulsion in such interactions? Compare the origin of attraction and repulsion in van der Waals interactions with that in ionic and covalent bonds.
7. Which molecule would you predict to have the higher boiling point, H_2 or CH_4 ? Why?
8. If van der Waals bonds are extremely weak, why are they discussed at all?
9. What effect do hydrogen bonds have on the boiling temperatures of liquids?

10. How do hydrogen bonds participate in the structure of ice? What effects do they have on its properties?
11. How do we know that some hydrogen bonding in water persists in the liquid phase?
12. Why are ionic solids soluble in polar solvents? Why are they insoluble in nonpolar solvents?
13. What is the coordination number of a metallic atom in a cubic close-packed structure? A hexagonal close-packed structure? A body-centered cubic structure?
14. Why are metals found on the left side of the periodic table?
15. In the delocalized-molecular-orbital theory of metals, in what sense do we say that the entire piece of metal is a large molecule?
16. Where does the "band" of energy levels come from in the delocalized-molecular-orbital theory of electronic structure of metals?
17. Why would beryllium be an insulator if the $2s$ and $2p$ molecular orbital bands did not overlap?
18. What is the structural difference between metals, semiconductors, and insulators?
19. What effect do small amounts of boron or phosphorus have on the conducting properties of silicon?
20. What is the difference between white phosphorus and black phosphorus?
21. Why is diamond an insulator? What properties would carbon have if it were to crystallize in a body-centered cubic structure?
22. Which has the largest gap between the valence band and the conduction band: an insulator, a metal, or a semiconductor? Which has the smallest?
23. What is the basic building block of silicate minerals?
24. How does mica differ structurally from talc?
25. Why are clays useful in industrial catalysis?
26. How do glasses differ from quartz?

Problems

Van der Waals interactions

1. Explain the trend in the melting temperatures of the following tetrahedral molecules: CF_4 , 90 K; CCl_4 , 250 K; CBr_4 , 350 K; CI_4 , 440 K.
2. Make a sketch of the way in which the repulsion part of the van der Waals interaction (equation 14-1) varies with distance r between atomic centers. Make a similar sketch for the attraction terms, equation 14-2. Add these two curves in an approximate way and satisfy yourself that a potential-energy curve such as Figure 14-13 is the result.

3. Construct the potential-energy curve for the van der Waals interaction between two Kr atoms. How strong is the van der Waals bond? Estimate the Kr—Kr bond distance in solid krypton.
4. The molecule RbBr is held together primarily by an ionic bond. The distance between Rb^+ and Br^- in the molecule is 2.945 Å. The closed electron shells of Rb^+ and Br^- both have the configuration of the noble gas Kr. From the energy curve constructed for Problem 4, estimate the van der Waals energy between Rb^+ and Br^- , assuming that the energy is the same as for a pair of Kr atoms separated by a distance of 2.945 Å. Is the repulsive part, or the attractive part, of the interaction dominant? How important is the van der Waals energy compared to the overall bond energy of 377 kJ mole⁻¹ in RbBr? Examine the Kr—Kr van der Waals energy for distances of 2 Å and 1 Å and then explain what prevents Rb^+ and Br^- ions from approaching each other too closely in an ionic solid.

Solid structures

5. The internuclear distances in gas-phase ionic molecules are considerably smaller than those in the corresponding crystals. For example, the internuclear distance in $\text{NaCl}(g)$ is 2.36 Å, whereas in $\text{NaCl}(s)$ the shortest internuclear distance is 2.81 Å. Examine the $\text{NaCl}(s)$ structure in Figure 14-9 and explain why this should be so.
6. Solid carbon dioxide behaves as a molecular solid (it is easily compressible and sublimates at 195 K), whereas solid silicon dioxide (quartz, Figure 14-34) is a non-metallic network solid (it is very hard and has a melting point of 1883 K). Rationalize this difference in behavior

in terms of the relative σ and π bonding in the molecular species CO_2 and SiO_2 .

7. Compare the structures for diamond and graphite shown in Figure 14-5.
 - a) What type of model (metallic, non-metallic covalent, or van der Waals) best describes the bonding within a layer of the graphite structure?
 - b) What type of model best describes the bonding between layers in the graphite structure?
 - c) Explain why graphite, unlike diamond, is very soft, whereas like diamond it has a very high melting point.
 - d) Draw a Lewis structure for a fragment of one graphite layer.
 - e) Graphite is a relatively good electrical conductor. Use the Lewis structure obtained in part d to rationalize the conductivity of graphite. Which type of electrons (σ or π) do you suspect are mobile and therefore able to conduct electrical current?
8. Replacement of the zinc and sulfur atoms by carbon atoms in the wurtzite structure of zinc sulfide (Figure 14-10) results in the diamond structure (Figure 14-5). Optical and electrical measurements on samples of ZnS show that it has a band gap of approximately 3.6 eV. Discuss the nature of ZnS in terms of the three models: nonmetallic network, ionic, and metallic, all of which have been applied to describe this solid.
9. Provide a structural explanation for the fact that quartz is hard, asbestos fibrous and stringy, and mica platelike.
10. What type of solid will BF_3 and NF_3 molecules build? What kinds of intermolecular interactions are likely to be important in each case?

11. Which should have the higher melting temperature, BF_3 or NF_3 ?

Band gaps

12. It requires 5.2 eV, or 502 kJ mole⁻¹, to excite electrons in a diamond crystal from the valence band to the conduction

band. What frequency of light is needed to bring about this excitation? What wavelength? What wave number? What part of the electromagnetic spectrum does this correspond to?

13. Using data given in this chapter, repeat Problem 12 for the semiconductors silicon and germanium.

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