

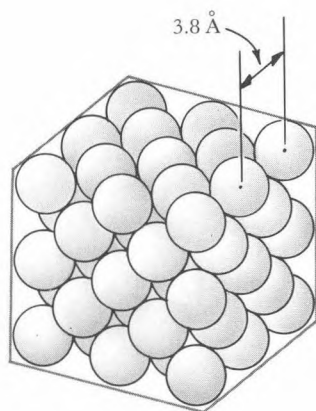
6

Bonding in Solids

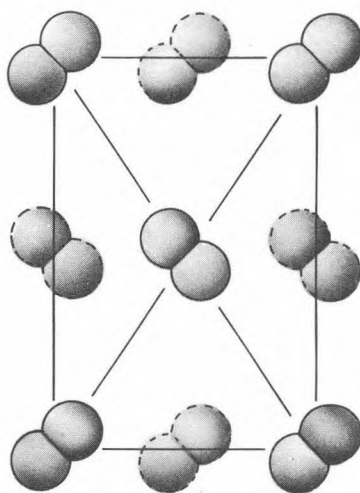
In previous chapters we explored in some detail the bonding between atoms in isolated molecules. In many solids discrete molecules exist, but in many others atoms are bonded together in an infinite array to build a “giant” molecule. In this chapter we will relate the properties of solid substances to the types of bonding interactions between the atoms or molecules present.

6-1 TYPES OF SOLIDS

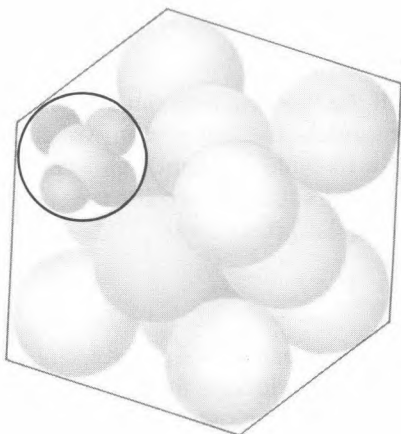
Solids that are built by weak attractive interactions between individual molecules are called *molecular solids*. Examples of molecular solids include iodine crystals, composed of discrete I_2 molecules, and paraffin wax, composed of long-chain alkane molecules. At very low temperatures the noble gases exist as molecular solids that are held together by weak interatomic forces. For example, argon freezes at -189°C to make the close-packed structure shown in Figure 6-1. Examples of nonpolar molecules that crystallize at low temperatures to give molecular solids include Br_2 , which freezes at -7°C to build the structure shown in Figure 6-2. Methane, CH_4 , freezes at -183°C to form the close-packed crystal shown in Figure 6-3.



6-1 The structure of solid argon. Each sphere represents an individual Ar atom, in cubic close packing with 3.8 \AA between atomic centers.

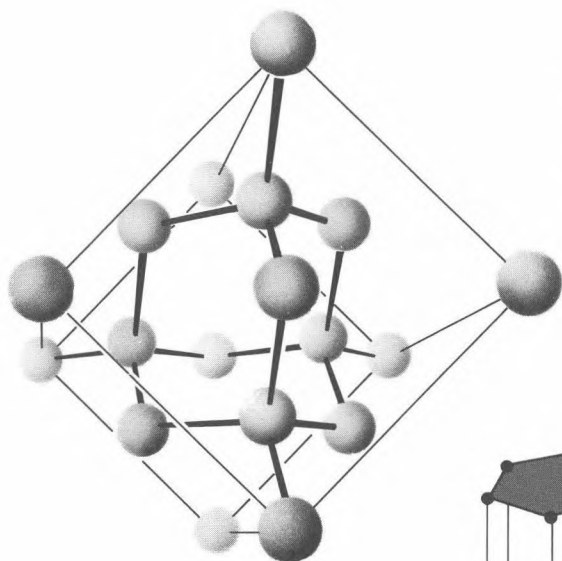


6-2 The structure of crystalline bromine, Br_2 . The solid outlines indicate one layer of packed molecules, and the dashed outlines indicate a layer beneath. The molecules have been shrunk for clarity in this drawing; they are actually in close contact within a layer, and the layers are packed against one another.



6-3

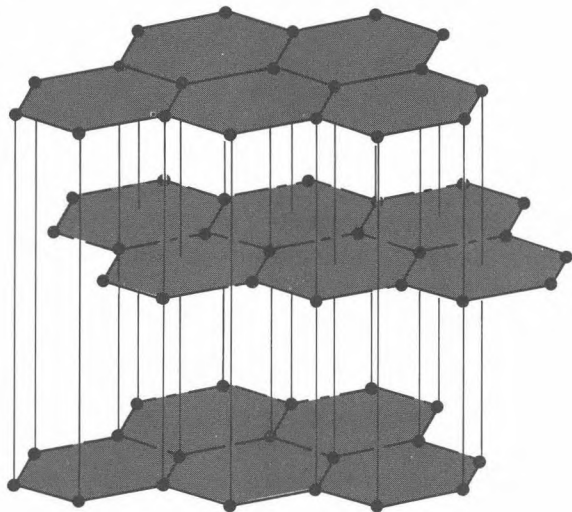
The structure of solid methane, CH_4 . Each large sphere represents a methane molecule, as indicated at the upper left. The methane molecules are arranged in cubic close packing.



(a)

6-4

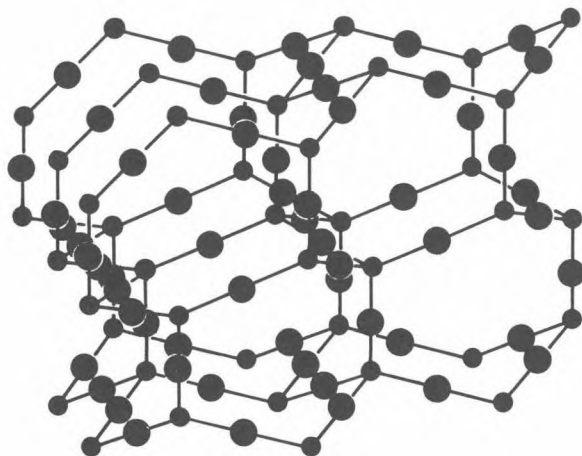
Crystalline carbon. (a) Diamond structure. The coordination number of carbon in diamond is 4. Each atom is surrounded tetrahedrally by four equidistant atoms. The C-C bond distance is 1.54 Å. (b) Graphite structure. This is the more stable structure of carbon. Strong carbon-carbon bonding occurs within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



(b)

6-5

The three-dimensional network of silicate tetrahedra in one crystalline form of silicon dioxide, $(\text{SiO}_2)_n$.



- Silicon atom—each attached to 4 oxygen atoms
- Oxygen atom—each attached to 2 silicon atoms

Nonmetallic network solids consist of infinite arrays of bonded atoms; no discrete molecules can be distinguished. Thus any given piece of a 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. Some of the hardest substances known are nonmetallic network solids.

Diamond, the hardest allotrope of carbon, has the network structure shown in Figure 6-4(a). Diamond sublimates (volatilizes directly to a gas), rather than melts, at 3500°C and above. Graphite, a softer allotrope of carbon, has the layered structure shown in Figure 6-4(b). Silicon dioxide is another high-melting ($>1600^\circ\text{C}$) three-dimensional network solid (Figure 6-5).

One feature that distinguishes network solids from metals is the lower coordination number of atoms in network structures. In the preceding examples the coordination number of C, in diamond, and Si is four, and that of O in $(\text{SiO}_2)_n$ is two. In Section 6-3, we will see that a localized molecular orbital picture of bonding satisfactorily accounts for the properties of diamond.

Metallic solids also consist of infinite arrays of bonded atoms, but in contrast to nonmetals each atom in a metal has a high coordination number: sometimes four or six, but more often eight or twelve (Figure 6-21). The band theory of delocalized molecular orbitals will be developed in Section 6-3 to explain the fact that metals generally are good conductors of electricity.

In the periodic table shown in Figure 6-6 the elemental solids are classified as metallic, network nonmetallic, or molecular. The majority of elements

I	II	III							IV	V	VI	VII	0
			Network nonmetals							Molecular nonmetals			
H 1												He 2	
Li 3	Be 4											Ne 10	
Na 11	Mg 12											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	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	Xe 54
Cs 55	Ba 56	*	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Rn 86
Fr 87	Ra 88	**											

Metals
 Intermediate properties
 Nonmetals

Network nonmetals
 Molecular nonmetals

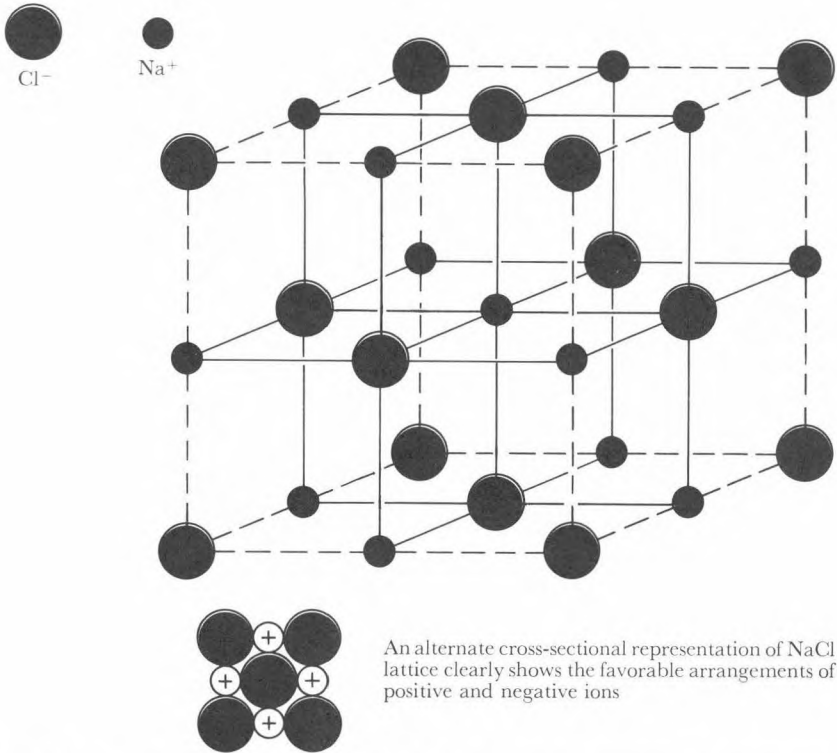
La 57	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
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Ac 89	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103
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6-6 Structural characteristics of elemental solids.



6-7

Representation of the ionic NaCl structure. The bottom figure is a representation of a cross section of the NaCl structure.

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 that have borderline properties. Although germanium crystallizes in a diamondlike structure in which the coordination number of each Ge atom is only four, certain 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 also may 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.

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 (Section 2-8). In solid NaCl the Na^+ and Cl^- ions are arranged to maximize the electrostatic attraction, as shown in Figure 6-7. The coordination number of each Na^+ ion is six, and 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 preceding discussion has distinguished four types of solids—molecular, network nonmetallic, metallic, and ionic. Of these types, by far the weakest bonding is found in molecular solids, in which only *intermolecular* forces hold the crystal together. In the next section we will examine in more detail the nature of these intermolecular forces.

6-2 MOLECULAR SOLIDS

Molecules such as H_2 , N_2 , O_2 , and F_2 form molecular solids because all the valence orbitals are used either for *intramolecular* bonding or are 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.

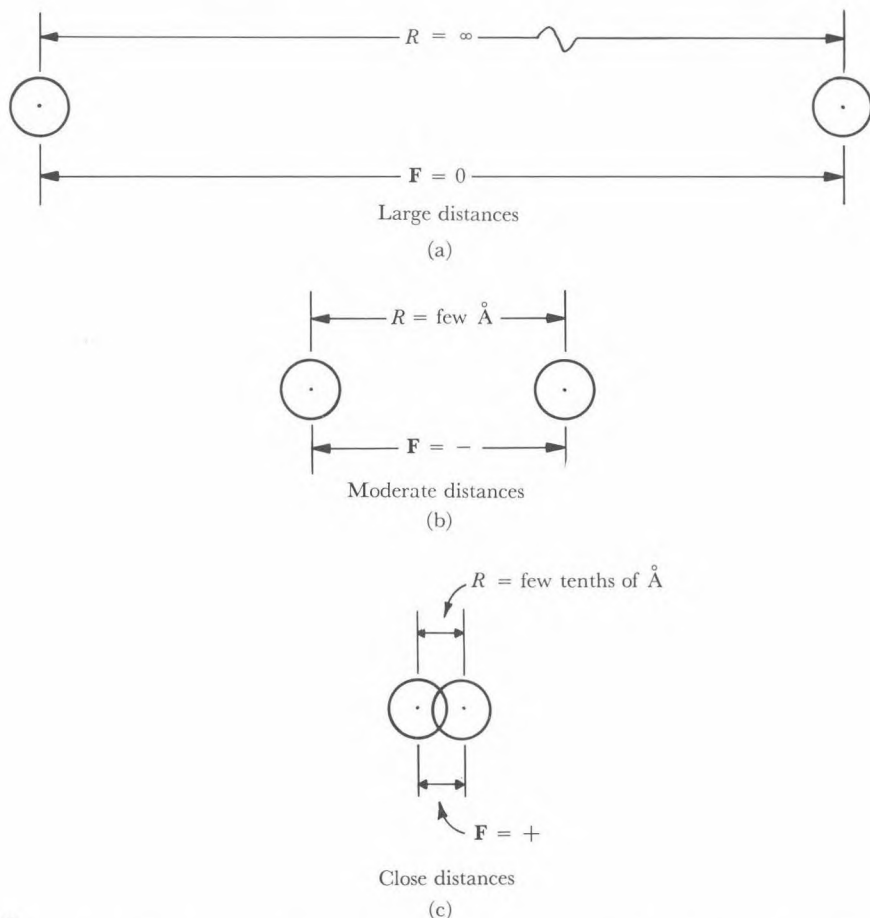
Van der Waals forces

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 6-8. The analytical expression commonly used to describe the energy resulting from this interaction is

$$\text{van der Waals repulsion energy} = be^{-aR} \quad (6-1)$$

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 .

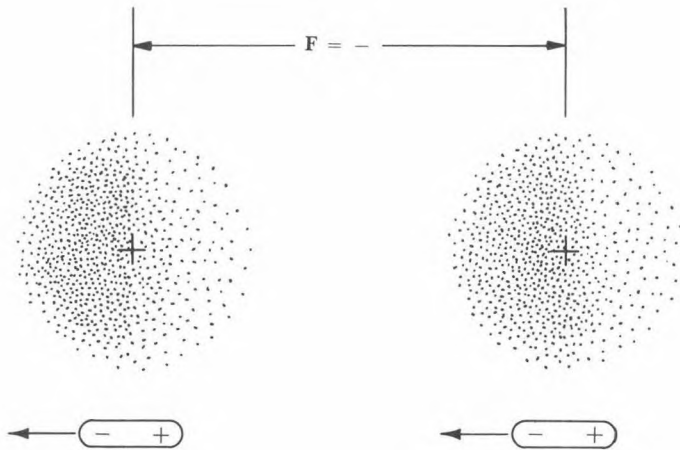
The second force is the attraction that results when electrons in the occupied orbitals of the interacting atoms synchronize their motion to avoid each other as much as possible. For example, as shown in Figure 6-9, electrons in orbitals of atoms belonging to interacting molecules can synchronize their motion to produce an instantaneous dipole-induced dipole attraction. If at any instant the left atom in Figure 6-9 had more of its electron density at the left, as shown, then the atom would be a tiny dipole with a negative left side and a positive right side. This positive side would attract electrons on the right atom in the figure and would change this atom into a dipole with similar orientation.



6-8

Repulsion of electrons in filled orbitals. (a) At very large distances two atoms or molecules behave toward each other 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 6-9) 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.

Therefore these two atoms would 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 will induce a temporary dipole, or asymmetry of electron density, in the left atom. The electron densities are fluctuating continually, yet the net effect is an extremely small but important attraction between atoms. The energy resulting from this attractive force is



Instantaneous polarization of an atom leaves, for a moment, more electron density on the left than on the right, thus creating an “instantaneous dipole”

This “instantaneous dipole” can polarize another atom by attracting more electron density to the left, thereby creating an “induced dipole”

6-9

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.

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:

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

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.

The total potential energy of van der Waals interactions is the sum of the attractive energy of Equation 6-2 and the repulsive energy of Equation 6-1:

$$PE = be^{-aR} - \frac{d}{R^6} \quad (6-3)$$

Table 6-1. Van der Waals energy parameters

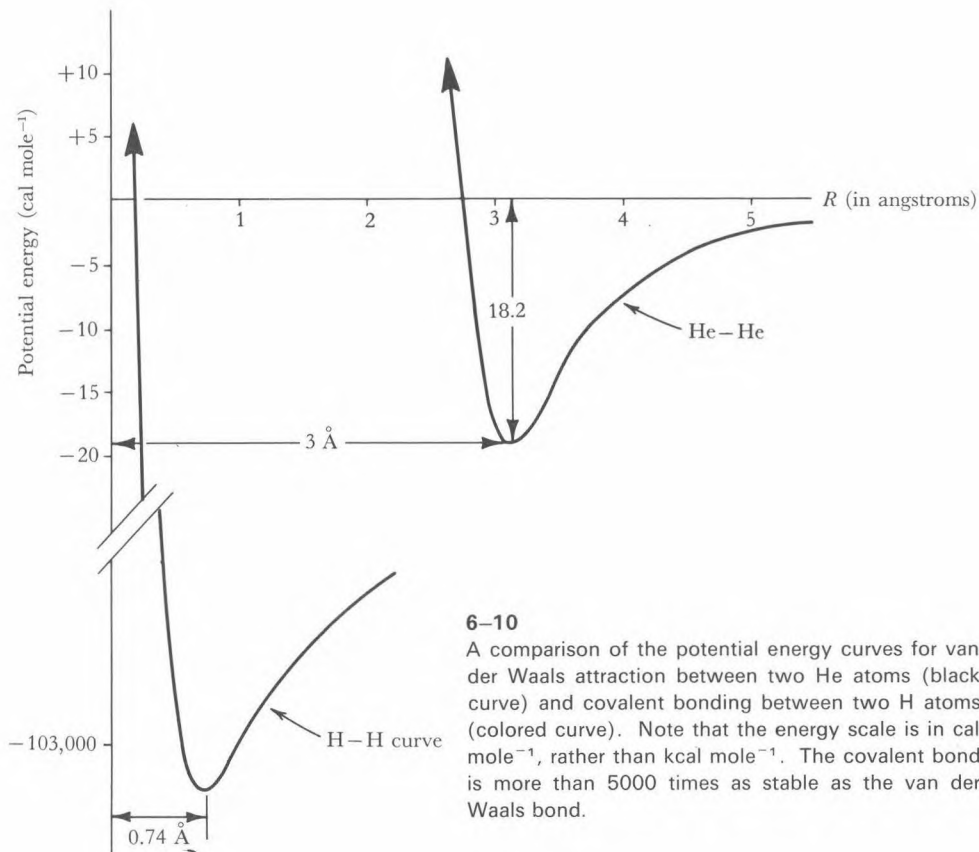
Interaction pair	a (au) ^{-1 a}	b , kcal mole ⁻¹	d , kcal mole ⁻¹ (au) ⁶
He—He	2.10	4.1×10^3	1.5×10^3
He—Ne	2.27	20.7×10^3	2.9×10^3
He—Ar	2.01	30.0×10^3	9.7×10^3
He—Kr	1.85	16.4×10^3	13.7×10^3
He—Xe	1.83	26.6×10^3	21.3×10^3
Ne—Ne	2.44	104.8×10^3	5.7×10^3
Ne—Ar	2.18	151.8×10^3	19.2×10^3
Ne—Kr	2.02	82.8×10^3	26.7×10^3
Ne—Xe	2.00	134.2×10^3	41.5×10^3
Ar—Ar	1.95	219.5×10^3	64.6×10^3
Ar—Kr	1.76	119.8×10^3	90.1×10^3
Ar—Xe	1.74	194.4×10^3	139.3×10^3
Kr—Kr	1.61	65.2×10^3	125.4×10^3
Kr—Xe	1.58	106.0×10^3	194.4×10^3
Xe—Xe	1.55	171.8×10^3	301.1×10^3

^a 1 au = 1 atomic unit = 0.529 Å. The value of R in Equation 6-3 must be expressed in atomic units as well.

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 6-1.

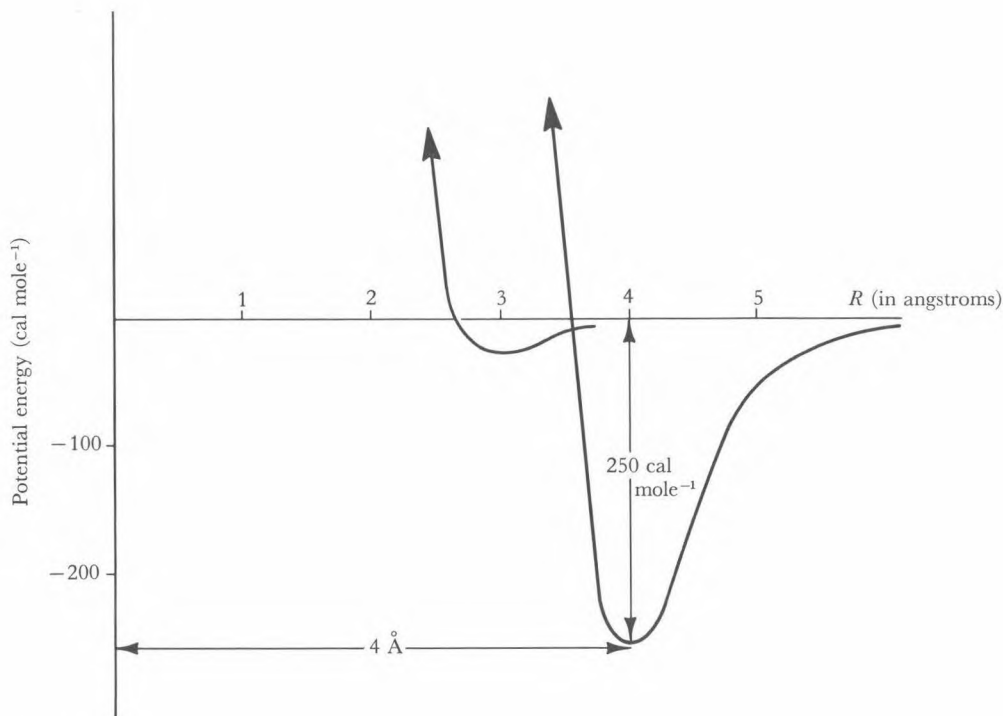
The potential energy curve for van der Waals interactions between helium atoms is illustrated in Figure 6-10. At separations of more than 3.5 Å, the second term in Equation 6-3 predominates. As the atoms move closer together they attract each other more, and the energy of the system decreases. However, at distances closer than 3 Å the strong electron-pair repulsion overwhelms the London attraction, and the potential energy curve in Figure 6-10 rises. A balance between attraction and repulsion exists at 3-Å separation, and the He---He "molecule" is 18.2 cal mole⁻¹ more stable than two isolated atoms.

Figure 6-10 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 H_2 molecule is 0.74 \AA , whereas the equilibrium distance of van der Waals-bonded He atoms is 3 \AA . Moreover, a covalent bond is much stronger than a weak van der Waals interaction. Only $18.2 \text{ cal mole}^{-1}$ is required to separate helium atoms at their equilibrium distance, but $103,000 \text{ cal mole}^{-1}$ is needed to break the covalent bond in H_2 .

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

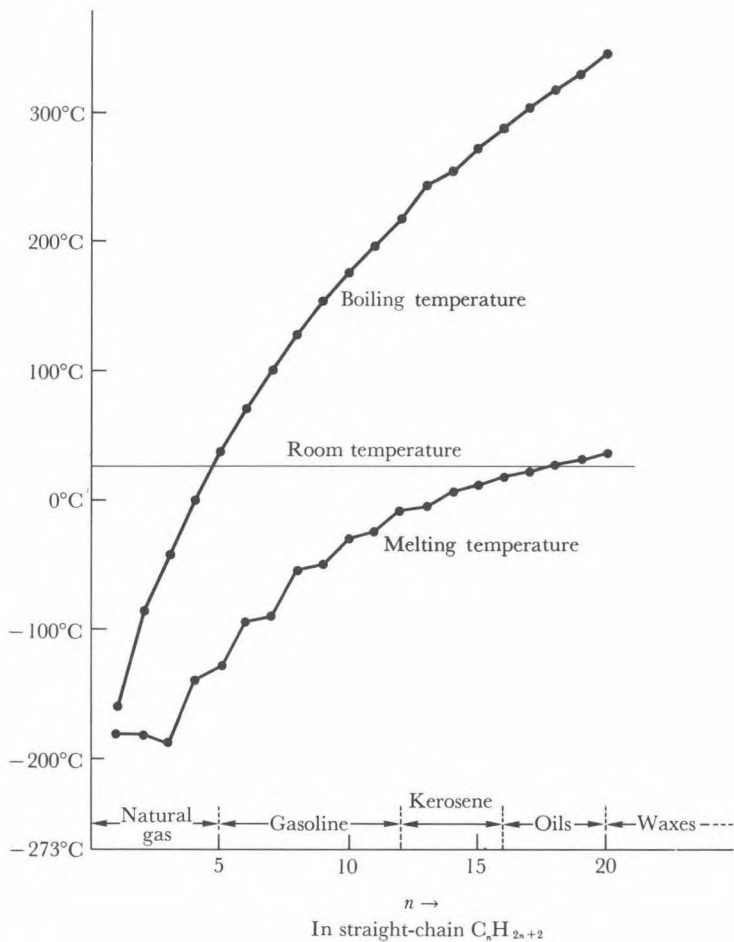


6-11

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.

near absolute zero, solid helium can be produced only at high pressures (29.6 atm at 1.76°K).

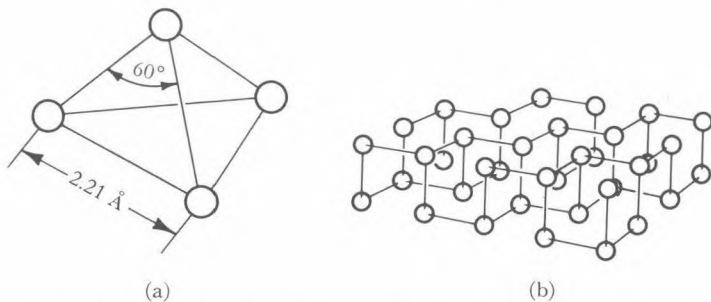
Van der Waals bonds in molecular solids and liquids generally are stronger with increasing size of the atoms and molecules involved. For example, as the atomic number of the noble gases increases, the strength of the van der Waals bonding increases also, as shown by the Ar-Ar potential energy curve in Figure 6-11. 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 solid helium.



6-12

Melting and boiling temperatures of the straight-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 ethane (two carbons) because of the more numerous van der Waals interactions between the two larger molecules.

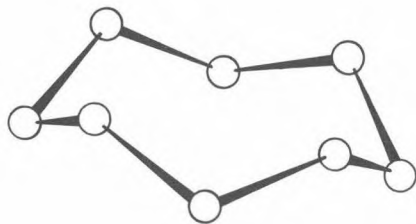
An example of the effect of molecular size on melting and boiling temperatures is provided by a series of straight-chain alkanes, with formulas C_nH_{2n+2} , depicted in Figure 6-12 for $n = 1$ through 20. Part of the increase in melting and boiling temperatures with increasing molecular size and weight 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 ($C_{20}H_{42}$),

**6-13**

Structures of solid phosphorus. (a) White phosphorus consists of discrete P_4 molecules. (b) Black phosphorus, a more stable allotrope of the element, has an infinite network structure.

6-14

Structure of solid sulfur. The S_8 ring structure shown is the form sulfur atoms take in the two principal allotropes of crystalline sulfur—rhombic and monoclinic. Rhombohedral sulfur, a third allotrope that is less stable, consists of S_6 rings. A fourth allotrope, amorphous sulfur, contains helical chains of S atoms.

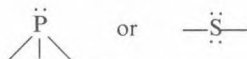


compared with methane, and the greater stability that eicosane therefore can gain from intermolecular van der Waals attractions. The mass effect is similar for both melting and boiling temperatures. However, molecular surface area affects the boiling temperatures more because molecules in the liquid 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.

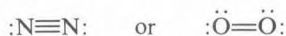
 P_4 and S_8

Phosphorus exists either as a molecular solid that consists of P_4 molecules or as an infinite network structure (Figure 6-13). The four phosphorus atoms in a P_4 molecule define a regular tetrahedron. Crystalline sulfur consists of discrete S_8 molecules, which have the cyclic structure shown in Figure 6-14. The intermolecular van der Waals bonding is much stronger in solid P_4 than in solid N_2 , for example, as indicated by the relatively high melting temperature of solid P_4 (44.1°C), compared to that of N_2 (-210°C). The larger size of the P_4 molecule, and the fact that the outer electrons in P_4 are held much less tightly than in N_2 , are the probable explanations of this phenomenon. A similar comparison can be made between O_2 and S_8 . Solid O_2 melts at -219°C , whereas solid S_8 melts at 119°C .

We could ask why solid phosphorus and solid sulfur are not composed of discrete P_2 and S_2 molecules, since these simple diatomic molecules have all their valence orbitals filled, analogous to N_2 and O_2 . For the larger atoms it appears that structures in which each atom forms only single bonds with other atoms as in



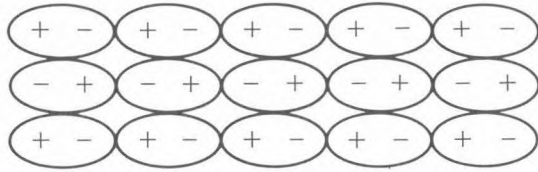
are more stable than structures in which atoms have higher bond orders, hence lower coordination numbers, as in



At large internuclear separations the strength of π bonding between p orbitals on adjacent atoms is small compared with σ bonding, partly because of a much smaller overlap of the two combining $p(\pi)$ valence orbitals. For example, there is good reason to assume that the σ bonds contribute more to the total bond energies in the P_2 and S_2 molecules than they do in the N_2 and O_2 molecules. Thus one less π bond in S_2 than in P_2 results in only a 11.4% decrease in total bond energy (114 kcal mole⁻¹ for P_2 to 101 kcal mole⁻¹ for S_2), whereas from N_2 to O_2 a 48% decrease in bond energy (225 kcal mole⁻¹ for N_2 to 118 kcal mole⁻¹ for O_2) is observed. The relatively weak π bonding in diatomic molecules composed of the larger atoms discourages the formation of structures with higher bond orders. Large atoms of nonmetallic elements tend to form molecular structures that contain only single (σ) bonds.

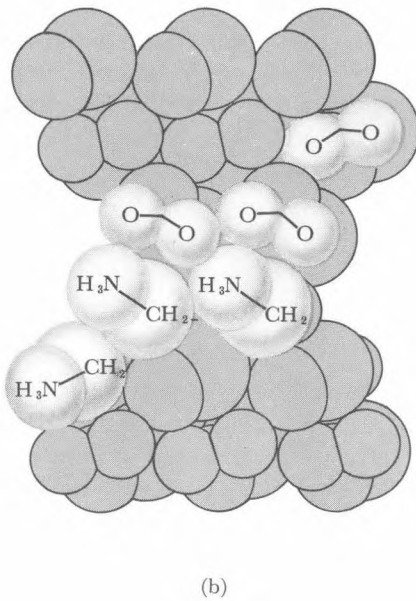
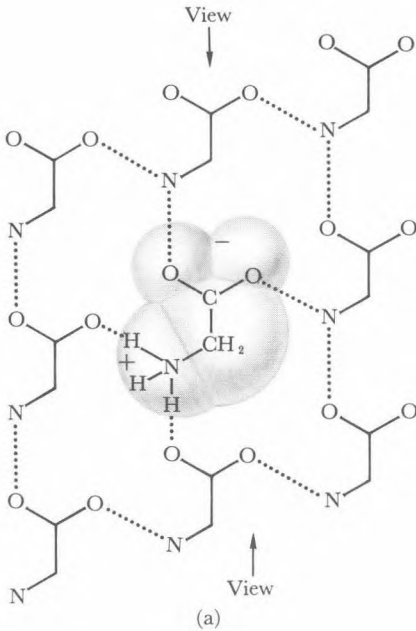
Polar molecules and hydrogen bonds

Polar molecules are stabilized in a molecular solid by the attractive interaction of oppositely charged ends of the molecules (Figure 6-15). This is called *dipole-dipole interaction*. A particularly important kind of polar interaction is the *hydrogen bond*. This is a bond, which is 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 6-16). Ice provides another example of the importance of hydrogen bonding in building intermolecular structures. As shown in Figure 6-17, each oxygen atom of a polar H_2O molecule is tetrahedrally coordinated to four other oxygen atoms in a structure that somewhat 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 water molecules. Such bonds are weak compared with covalent bonds. A typical covalent bond energy is about 100 kcal mole⁻¹, whereas a hydrogen bond between H and O is approximately 5 kcal mole⁻¹. But hydrogen bonds are important for the



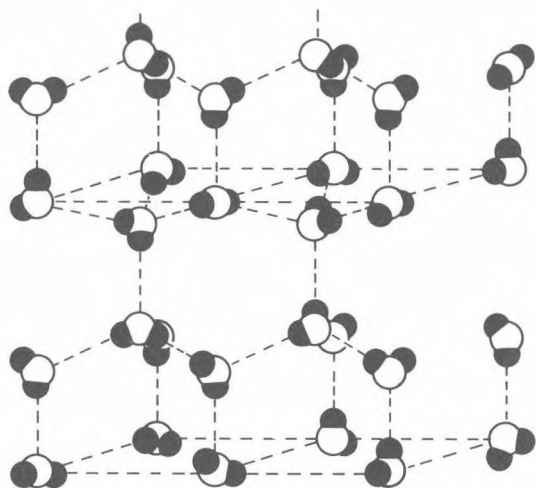
6-15

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



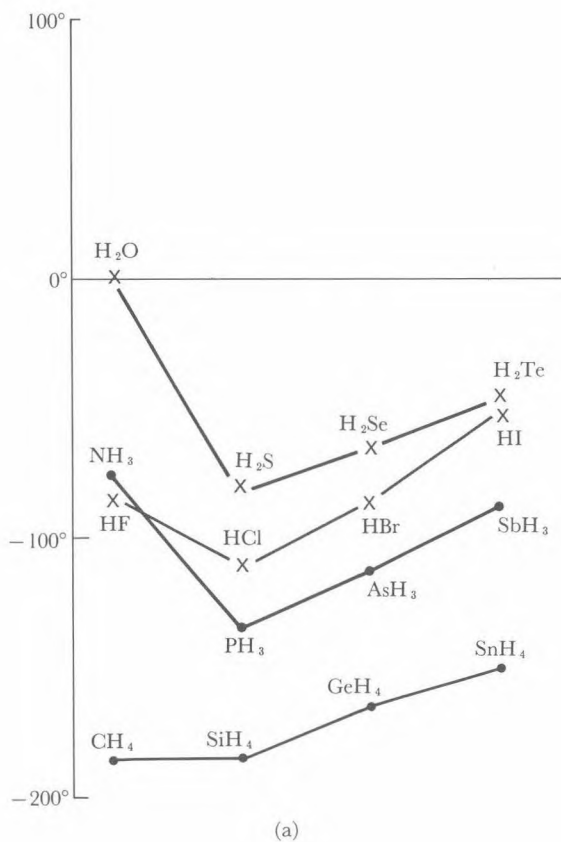
6-16

The bonding in 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 attraction 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).



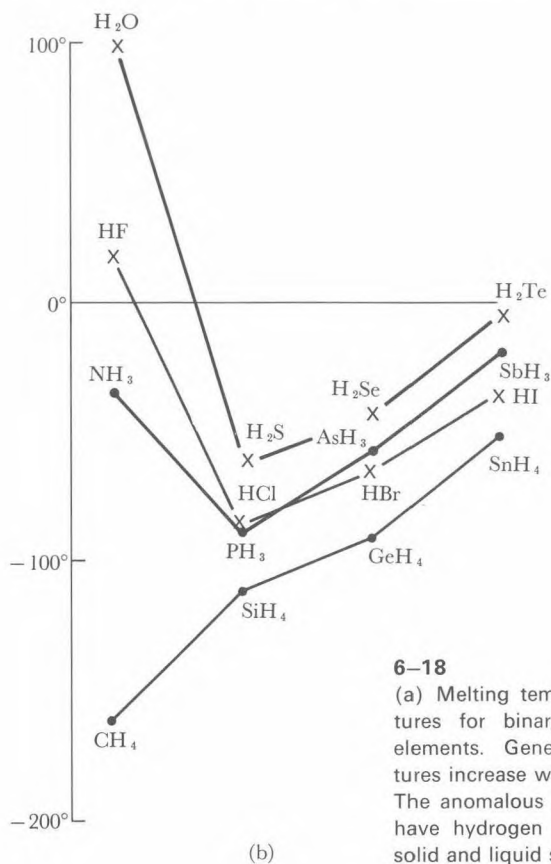
6-17

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.



same reason that van der Waals bonds are: They may be weak but there are many of them.

Hydrogen bonding in water is responsible for many of its most important properties. Because of hydrogen bonds in both the 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 water and for the same reason (Figure 6-18). However, hydrogen bonding in ammonia is less pronounced than 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 less well hydrogen-bonded than is H_2O in spite of 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.



6-18

(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, H_2O , and NH_3 , all have hydrogen bonds between molecules in both solid and liquid states.

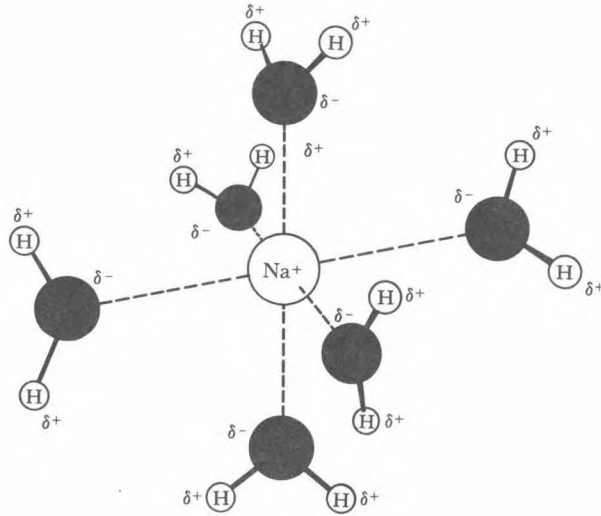
Since hydrogen bonding causes an open network structure in ice (Figure 6-17), ice is less dense than water at the melting temperature. Upon melting, part of this open-cage structure collapses, and the liquid is more compact than the solid. The measured heat of fusion of ice is only $1.4 \text{ kcal mole}^{-1}$, whereas the energy of its hydrogen bonds is 5 kcal mole^{-1} . This indicates that only about 28% 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 raised these clusters break up, and the volume continues to shrink. If the temperature is raised still higher, the expected thermal expansion dominates over the shrinkage caused by the collapse of the cage structures. 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 specific heat than any other common liquid 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 rise than almost any other substance. Correspondingly, as water cools, it gives off more heat to its surroundings than other substances.

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 6-19). 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 end (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.

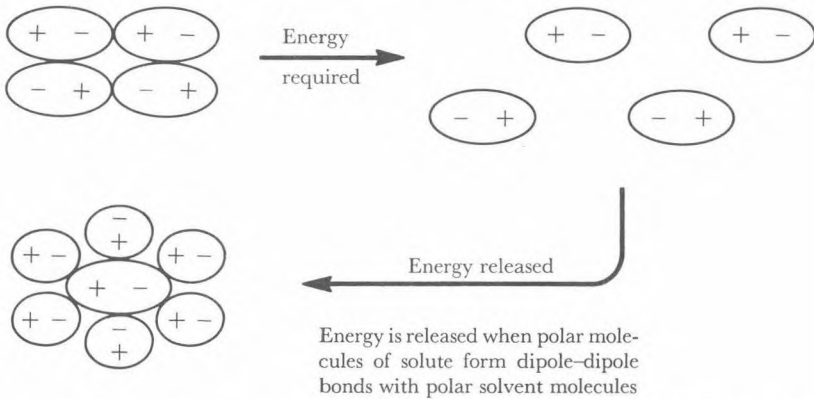
Polar solvents dissolve polar molecular solids because of dipole-dipole interactions. The energy released by the formation of dipole-dipole bonds between a polar solvent and solute molecules is sufficient to break the intermolecular forces in the molecular solids (Figure 6-20). For example, ice is soluble in liquid ammonia but not in benzene because NH_3 is a polar molecule, whereas C_6H_6 is nonpolar.



6-19

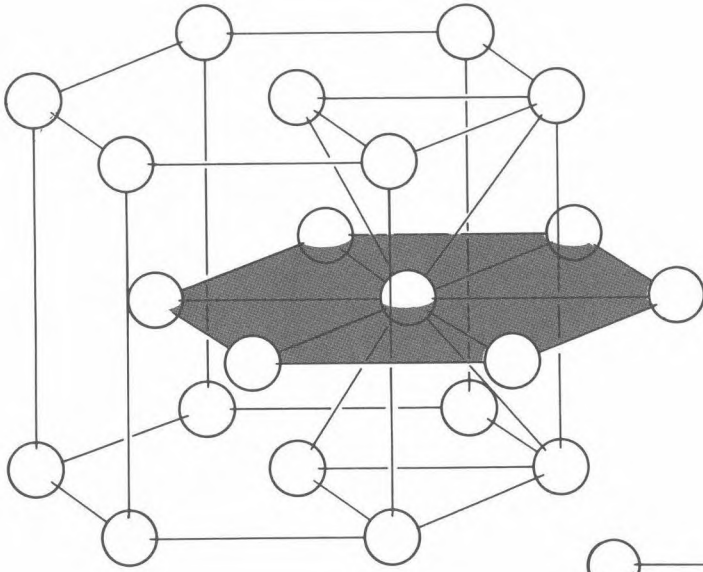
In solution, the hydrated Na^+ ion is surrounded by an octahedron of negative charges, but these negative charges are from the dipolar solvent molecule, H_2O , instead of the Cl^- .

Energy is required to break up a polar molecular solid

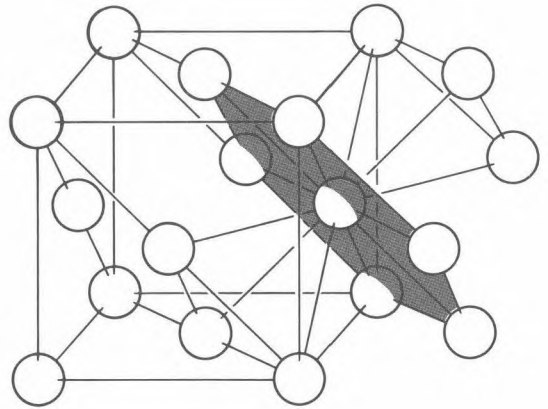


6-20

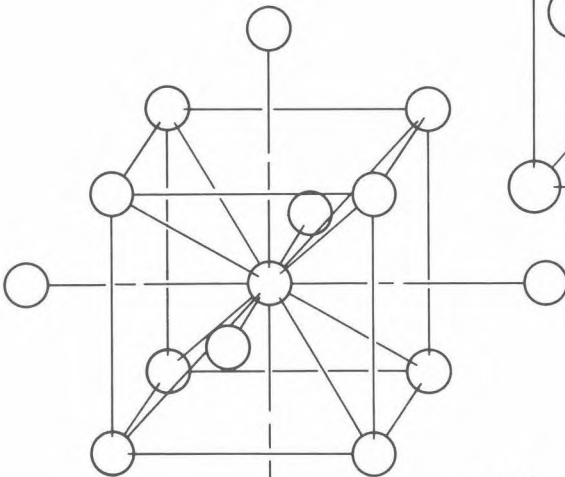
When a crystalline solid composed of polar molecules dissolves, stability is lost when oppositely charged ends of neighboring molecules are removed. This loss is compensated by the stability produced by solvating the polar molecules in solution. A solvent that cannot provide such stabilization cannot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



(a)



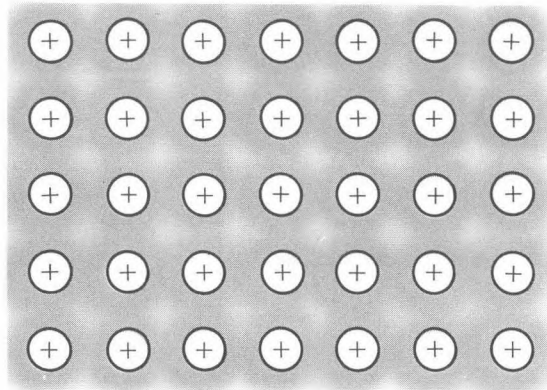
(b)



(c)

6-21

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



6-22

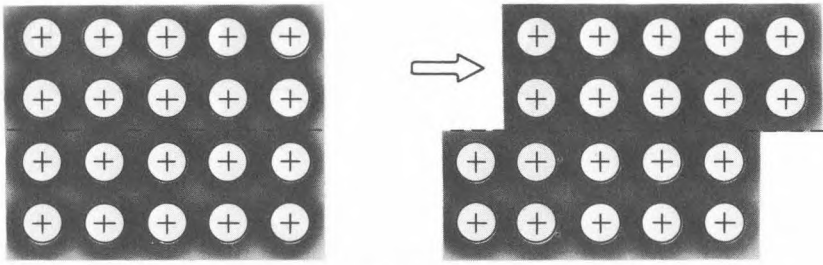
Cross section of a crystal structure of a metal with the sea of electrons. Each circled positive charge represents the nucleus and filled, nonvalence electron shells of a metal atom. The shaded area surrounding the positive metal ions indicates schematically the mobile sea of electrons.

6-3 METALS

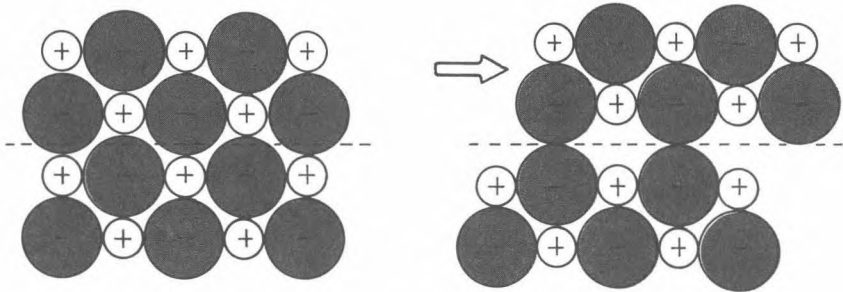
In metals at least eight “nearest-neighbor” atoms surround a particular atom in one of the three common structures shown in Figure 6-21. In both hexagonal and cubic close packing, each sphere touches 12 other spheres, six in a plane, three above, and three below. X-ray analysis reveals that two thirds 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.

The properties of metals suggest that the valence electrons are relatively free to move through the crystal structure. Figure 6-22 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, leaving the nuclei and the filled electron 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 also is 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 each other. This displacement does not result in the



(a)



(b)

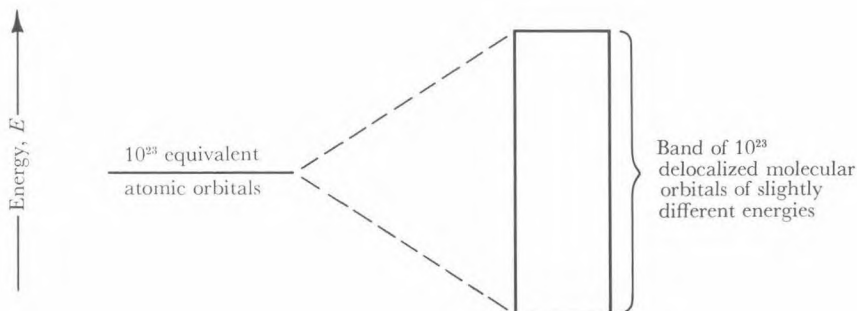
6-23

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

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 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 6-23).

Electronic bands in metals

The delocalized molecular orbital theory provides a more detailed (and more informative) model for metallic bonding. In this model the entire block of



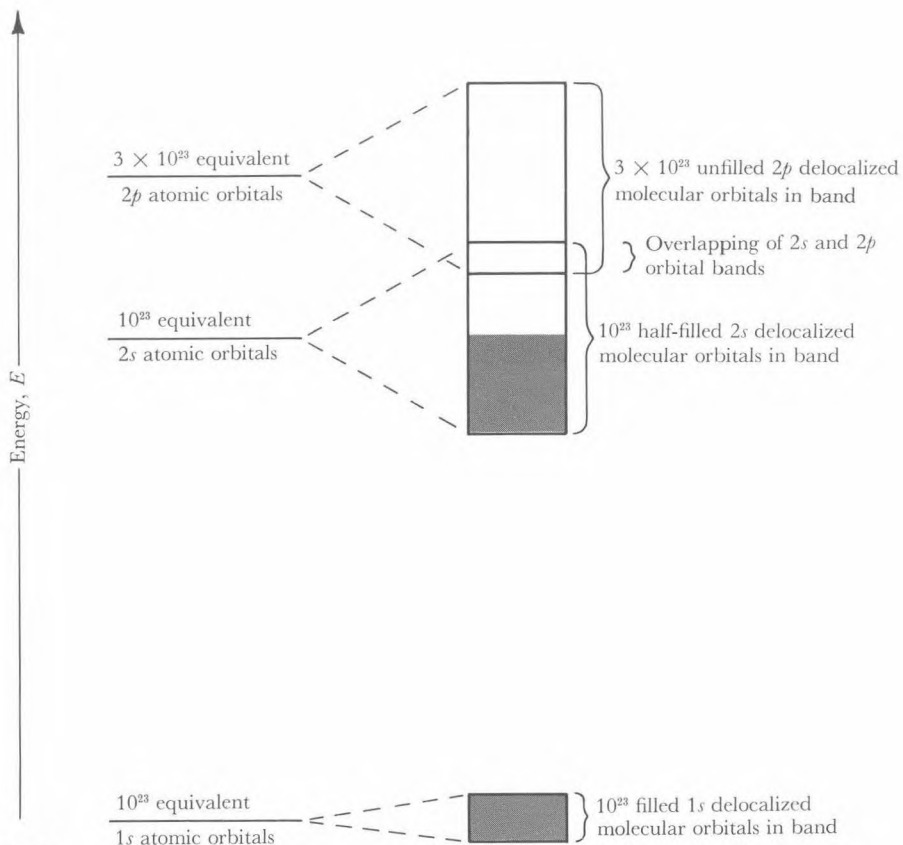
6-24

Just as six atomic p orbitals can combine to produce six delocalized molecular orbitals in benzene, 10^{23} atomic orbitals of a metal can combine to produce 10^{23} metallic orbitals. The metallic orbitals are so closely spaced that they can be treated as a continuous band of energy. The simple band theory of metals can explain many of their properties.

metal is considered as 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 of the order of 10^{23} . Figure 6-24 depicts the combination of approximately 10^{23} equivalent atomic orbitals in a crystal to form 10^{23} delocalized orbitals. All of these orbitals cannot have the same energy if they are delocalized. However, instead of producing an antibonding orbital and a bonding molecular orbital, as a diatomic molecule does, the combination of atomic orbitals produces a band of closely spaced energy levels.

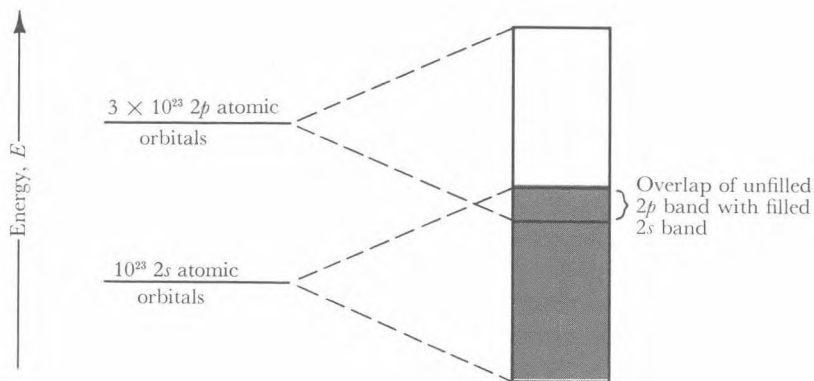
Figure 6-25 illustrates the three bands of energy levels formed by the $1s$, $2s$, and $2p$ orbitals of the simplest metal, lithium. The $1s$ molecular orbitals are filled completely because the $1s$ atomic orbitals in isolated lithium atoms are filled. Thus the $1s$ electrons make no contribution to 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 6-25.

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



6-25

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.



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.

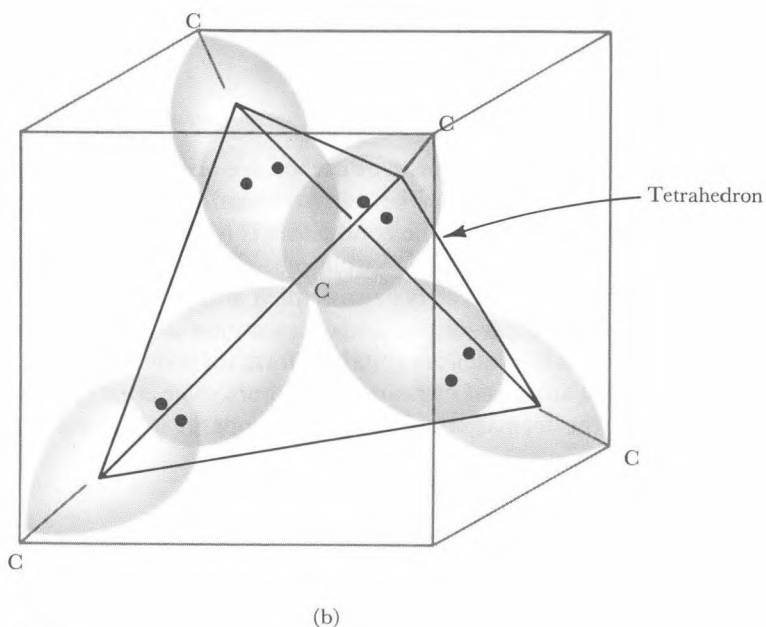
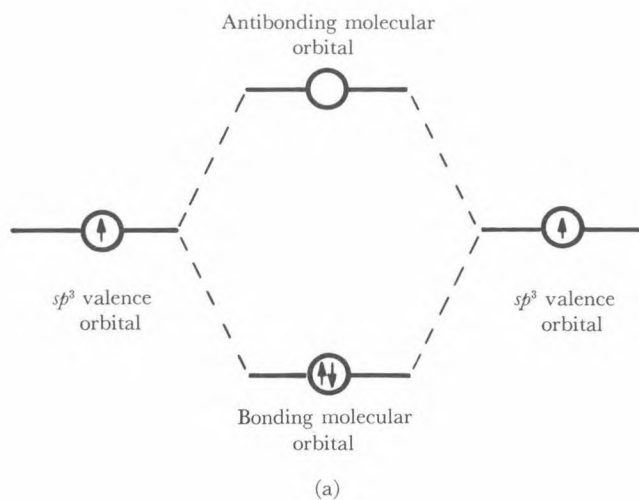
Beryllium is a more complicated example than lithium. An isolated beryllium atom has exactly enough electrons to fill its $2s$ orbital. Accordingly, beryllium metal has enough electrons to fill its $2s$ delocalized band. If the $2p$ band did not overlap the $2s$ (Figure 6-26), beryllium would not conduct 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.

6-4 NONMETALLIC NETWORK SOLIDS

Nonmetallic network materials such as boron or carbon are *insulators*; that is, they do not conduct electrical current. One way to visualize the difference between nonmetallic insulators and metallic conductors is to use approximate localized orbitals to describe the structure of insulators. We can use localized bonds to describe insulators quite accurately because their atomic coordination numbers are relatively low. Because of the low coordination numbers there usually are enough electrons in the valence orbitals to form three or four simple covalent bonds between each atom and its nearest neighbors. The construction of these bonds resembles the formation of localized bonds in a polyatomic molecule.

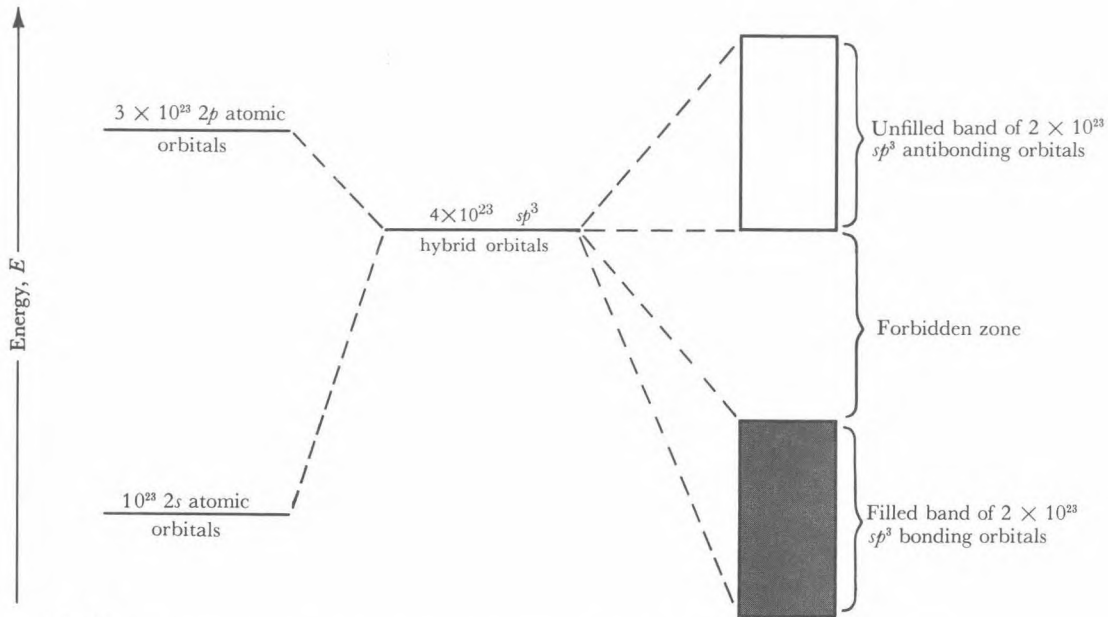
◀ 6-26

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.



6-27

Bonding in diamond crystals. (a) Localized-orbital energy levels in diamond crystals. Each pair of neighboring localized atomic sp^3 orbitals produces a bonding orbital and an antibonding orbital. (b) Schematic representation of the overlap of the four sp^3 hybrid orbitals of a C atom with similar orbitals from four other carbon atoms.



6-28

Delocalized molecular orbital bands in an insulator, formed from equivalent sp^3 localized hybrid orbitals. Note the relatively large zone between the filled band of sp^3 bonding orbitals and the unfilled band of sp^3 antibonding orbitals.

For diamond we begin to construct the bonding model by assigning each carbon atom four localized tetrahedral sp^3 hybrid orbitals. One such orbital from each of two neighboring carbon atoms combine to make one bonding and one antibonding molecular orbital (Figure 6-27). The four valence electrons in each carbon atom are sufficient to fill these bonding orbitals. Thus all electrons in diamond are used for bonding, thereby leaving none to move freely to conduct electricity.

To construct the band model of delocalized orbitals for an insulating network solid such as diamond, we will proceed as follows. Assume 10^{23} carbon atoms. When the 4×10^{23} localized sp^3 orbitals interact with each other, two bands of delocalized orbitals are formed, one from the 2×10^{23} bonding orbitals of Figure 6-27 and one from the 2×10^{23} antibonding orbitals. These are depicted in Figure 6-28, in which the atomic orbitals are drawn at the left to remind you that these orbitals originally came from the $2s$ and $2p$ atomic orbitals. The important fact in this diagram is that the band filled with electrons does not overlap with the next higher energy band, which has completely unfilled orbitals. There is a forbidden energy zone or gap

between what is called the valence band below and the conduction band above. There are 4×10^{23} valence electrons per 10^{23} carbon atoms, enough to fill completely the 2×10^{23} orbitals in the valence band.

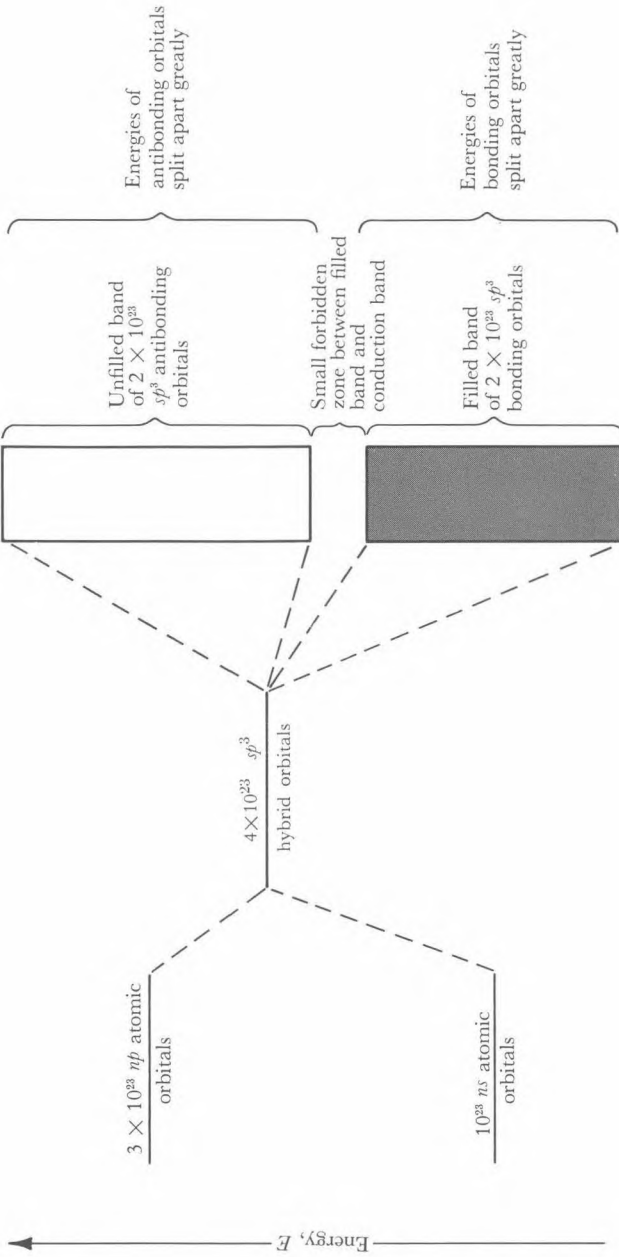
For an insulator to conduct, energy is required that is sufficient to excite electrons in the filled band across this forbidden energy zone into the unfilled molecular orbitals. This energy is the activation energy of the conduction process. Only high temperatures or extremely strong electrical fields will provide enough energy to an appreciable number of electrons for conduction to occur. In diamond the gap between the top of the valence band and the bottom of the conduction band is 5.2 eV, or 120 kcal mole⁻¹.

Semiconductors

The border line between metallic and nonmetallic network structures of elements in the periodic table is not sharp (Figure 6-6). This is shown by the fact that several elemental solids have properties that are intermediate between conductors and insulators. Silicon, germanium, and α -gray tin all have the diamond structure. However, the forbidden energy gap between filled and empty bands for these solids is much smaller than for carbon. Rather than 120 kcal mole⁻¹ for carbon, the gap for silicon is only 25 kcal mole⁻¹. For germanium it is 14 kcal mole⁻¹, and for α -gray tin it is 1.8 kcal mole⁻¹. The metalloids silicon and germanium are called *semiconductors*. Figure 6-29 shows the band diagram for a semiconductor, with a small forbidden energy zone.

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. Although there is a forbidden energy gap in silicon, it 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 0.25 kcal 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 instead of phosphorus 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



6-29

Bands of delocalized orbitals in semiconductors formed from equivalent sp^3 localized hybrid orbitals. The forbidden zone between filled and empty bands is smaller than in an insulator.

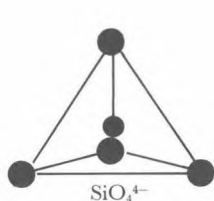
electrons of silicon into these vacant orbitals in the boron atoms, thereby causing the electrons to move through the crystal. To accomplish this conduction an electron from a silicon neighbor drops into the empty boron orbital. Then an electron that is two atoms away can fill the silicon atom's newly 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.

Silicates

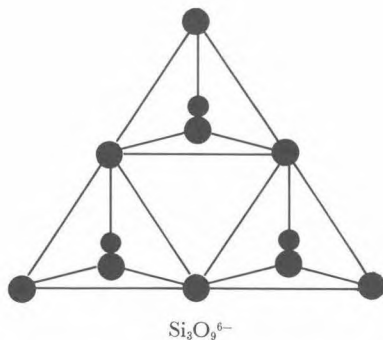
The earth's crust—the upper 20 miles under the continents and as little as three miles under the ocean beds—consists mainly of silicate minerals. The mantle, a layer about 1800 miles thick beneath the crust, probably is composed of dense silicates. The crust is about 48 % oxygen by weight, 26 % silicon, 8 % aluminum, 5 % iron, and 11 % calcium, sodium, potassium, and magnesium combined.

The basic building block in silicates is the orthosilicate ion, SiO_4^{4-} , shown in Figure 6-30. 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 6-31. 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 of 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 6-32. 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 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 therefore are needed to balance the charge.



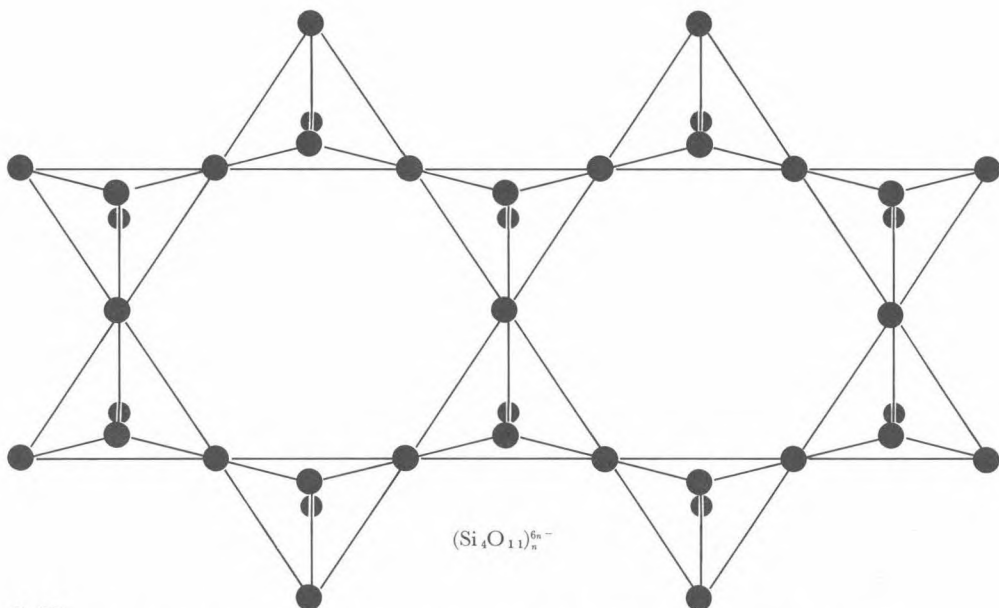
● Silicon
● Oxygen

**6-30**

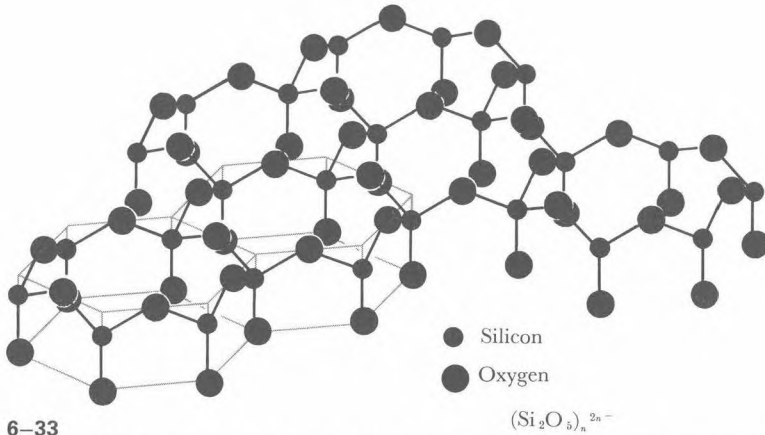
The SiO_4^{4-} tetrahedron, which is the building block of most silicate minerals. The Si atom (black) is covalently bonded to four oxygen atoms (color) at the corners of a tetrahedron. The covalent bonds are not shown. The black lines between oxygen atoms are included only to give form to the tetrahedron.

6-31

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 benitoite, $\text{BaTiSi}_3\text{O}_9$.

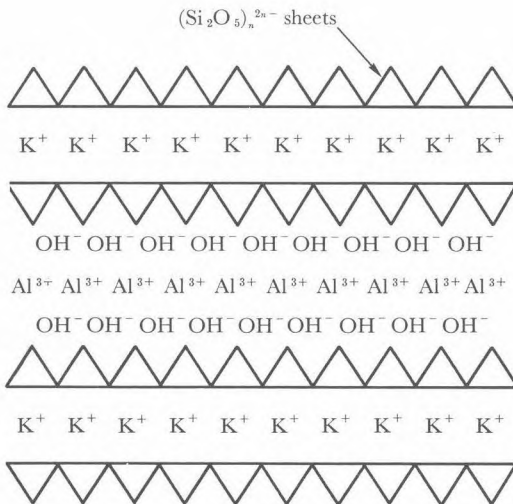
**6-32**

Long double-stranded chains of silicate tetrahedra are in fibrous minerals such as asbestos. A common natural form of asbestos has the empirical formula $\text{Na}_2\text{Fe}_3^{2+}\text{Fe}_2^{3+}(\text{Si}_8\text{O}_{22})(\text{OH})_2$.



6-33

In 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.



6-34

In the mica muscovite, $[\text{K}_2\text{Al}_4\text{Si}_6\text{Al}_2\text{O}_{20}(\text{OH})_4]$, anionic sheets of silicate tetrahedra, as in Figure 6-33, alternate with layers of potassium ions and aluminum ions sandwiched between hydroxide ions. This layer structure gives mica its flaky cleavage properties.

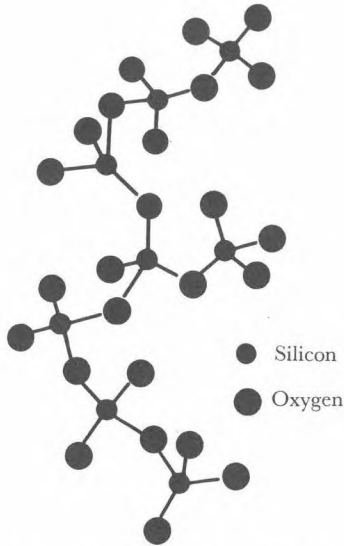
Sheet structures. Continuous broadening of double-stranded silicate chains produces planar sheets of silicate structures (Figure 6-33). Talc, or soapstone, has this structure, in which none of the Si^{4+} is replaced with Al^{3+} . Therefore no additional cations between the sheets are required to balance 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+} in the tetrahedra is replaced by Al^{3+} . Thus an additional positive charge is required for each replacement to balance charges. Mica has the layer structure shown in Figure 6-34. 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 often can absorb large amounts of water and other substances between the silicate layers. This is why clay soils are such useful growth media for plants. This property also is 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 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 prohibits 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+} , are typified by quartz, $(\text{SiO}_2)_n$. In crystalline quartz, all of the tetrahedral structures have Si^{4+} ions, but in other network minerals, up to half the Si^{4+} can be replaced with Al^{3+} . These minerals include the feldspars, with a typical empirical formula KAlSi_3O_8 . Feldspars are nearly as hard as quartz. Basalt, which may be the material of the mantle of the earth, 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 6-35. Common soda-lime glass

**6-35**

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

is made with sand (quartz), 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.

The silicates illustrate all types of bonding in solids: 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, as well as hydrogen bonds between water molecules and the silicate oxygens in clays. If we include nickel catalysts prepared on a clay support, metallic bonding is represented as well.

SUGGESTIONS FOR FURTHER READING

- A. H. Cottrell, "The Nature of Metals," *Scientific American* (September, 1967).
 W. A. Deer, R. A. Howie, and J. Zussman, *Rock Forming Minerals*, Vols. 1-5, Wiley, New York, 1962.
 T. L. Hill, *Matter and Equilibrium*, Benjamin, Menlo Park, Calif., 1966.
 W. J. Moore, *Seven Solid States*, Benjamin, Menlo Park, Calif., 1967.
 N. Mott, "The Solid State," *Scientific American* (September, 1967).
 H. Reiss, "Chemical Properties of Materials," *Scientific American* (September, 1967).
 A. F. Wells, *Structural Inorganic Chemistry*, 3rd ed., Oxford Univ. Press, New York, 1962.

QUESTIONS AND PROBLEMS

1. What types of forces hold molecules together in crystals and liquids?
2. What effect do hydrogen bonds have on the boiling temperatures of liquids? Explain, and give an example.
3. Why are nonmetallic network solids usually quite hard?
4. 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.
5. How do we determine an experimental value for the van der Waals radius of hydrogen? From a theoretical viewpoint, what determines the van der Waals radius?
6. Draw a sketch of the way in which the repulsion part of the van der Waals interaction (Equation 6-1) varies with distance R between atomic centers. Draw a similar sketch for the attraction terms, Equation 6-2. Add these two curves in an approximate way and satisfy yourself that a potential curve such as Figure 6-10 is the result.
7. If van der Waals bonds are extremely weak, why are they discussed at all?
8. In the delocalized molecular orbital theory of metals, in what sense do we say that the entire piece of metal is a large molecule?
9. Why would beryllium be an insulator if the $2s$ and $2p$ molecular-orbital bands did not overlap?
10. What is the structural difference between metals, semiconductors, and insulators?
11. What effect do small amounts of boron or phosphorus have on the conducting properties of silicon?
12. How do hydrogen bonds participate in the structure of ice? What effects do they have on its properties?
13. How do we know that some hydrogen bonding in water persists in the liquid phase?
14. Provide a structural explanation for the fact that quartz is hard, asbestos fibrous and stringy, and mica platelike.
15. Why are clays useful in industrial catalysis?
16. It requires 5.2 eV , or $120 \text{ kcal mole}^{-1}$, 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?
17. Using data given in this chapter, repeat Problem 16 for the semiconductors silicon and germanium.
18. 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 .
19. Construct the potential energy curve for the Kr-Kr van der Waals interaction. How strong is the Kr-Kr van der Waals bond? Estimate the Kr-Kr bond distance in solid krypton.

20. 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 19, 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 90 kcal 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.
21. 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? Which compound should have the higher melting temperature?