CHAPTER 2
Introduction to Materials: Review of Chemical Bonding

PREVIEW

In all solids, atoms are held together by bonds. They provide strength and related electrical and thermal properties to the solids. For example, strong bonds lead to high melting temperatures, high moduli of elasticity, shorter interatomic distances, lower thermal expansion coefficients.

In this chapter, we shall draw upon the concepts introduced in general chemistry. We will need to examine the role of the valence electrons in the primary bonds—*ionic*, *covalent*, and *metallic*—in sufficient detail so we may anticipate their effect on interatomic distances and atomic coordination. These bonds also provide a basis for categorizing materials as metals, polymers (plastics), and ceramics.

Van Vlack, "Elements of Materials Science"

CONTENTS

The Review and Study section of this chapter includes *generalizations regarding properties* in addition to a list of key terms and concepts, discussion topics, and study problems.

STUDY OBJECTIVES

1 To review those parts of your general chemistry that pertain to bonds between atoms.

2 To understand key terms and concepts, so that you may follow later topics more readily.

3 To know the characteristics of the three major types of primary bonds (but to appreciate that actual bonds usually involve contributions from more than one of these bond types).

4 To develop a qualitative picture of how the forces and energies of bonds vary with interatomic distances (as presented in Fig. 2–5.2) to give us a basis for interatomic distance, modulus of elasticity, thermal expansion, etc., in later chapters.

5 To understand various factors that affect atom size. You should be able to rationalize size differences in Table 2–5.1.

6 To know the characteristics of the three major types of materials (but to appreciate that many materials will have intermediate characteristics).

7 To develop some generalizations regarding properties as they relate to bond type.

2–1 INDIVIDUAL ATOMS AND IONS

The atom is the basic unit of internal structure for our studies of materials. The initial concepts involving individual atoms are familiar to most of the readers. They include *atomic number*, *atomic mass*, and the relationships in the *periodic table*. We shall also give attention to the energy levels that are established by the electrons of the atoms.

Atomic mass unit Since atoms are extremely small in comparison to our day-to-day concepts of mass, it is convenient to use the *atomic mass unit* as the basis for many calculations. The amu is defined as one twelfth of the atomic mass of carbon-12, the most common isotope of carbon. There are $0.6022\ldots \times 10^{24}$ amu per g. We will use this conversion factor (called *Avogadro's number N*) in various ways. Since natural carbon contains approximately one percent C^{13} along with 98.9% C^{12}, the average atomic mass of a carbon atom is 12.011 . . . amu. This is the value presented in the *periodic table* (Fig. 2–1.1) and in tables of selected elements (Appendix B). Those atomic masses encountered most commonly by the reader include

H	1.0079 . . . amu (or 1.0079 g/(0.602 × 10^{24} atoms))
C	12.011 . . .
O	15.9994 . . .
Cl	35.453 . . .
Fe	55.847 . . .

These values may be rounded off to 1, 12, 16, 35.5, and 55.8 amu, respectively, for all but the most precise of our calculations.

The *atomic number* indicates the number of electrons associated with each neutral atom (and the number of protons in the nucleus). Each element is unique with respect to its atomic number. Appendix B lists selected elements, from hydrogen, with an atomic number of one, to uranium (92). It is the electrons, particularly the outermost ones, that affect most of the properties of engineering interest: (1) they determine the chemical properties; (2) they establish the nature of the interatomic bonding, and therefore the mechanical and strength characteristics; (3) they control the size of the atom and affect the electrical conductivity of materials; and (4) they influence the optical characteristics. Consequently, we shall pay specific attention to the distribution and energy levels of the electrons around the nucleus of the atom.

Periodic table The *periodicity of elements* is emphasized in chemistry courses. We shall not repeat those characteristics here except to observe that the periodic table (Fig. 2–1.1) arranges the atoms of sequentially higher atomic numbers so that the vertical columns, called *groups*, possess atoms of similar chemical and electronic characteristics. In brief, those elements at the far left of the periodic table are readily ionized to give positive ions, *cations*. Those in the upper right corner of the periodic table more readily share or accept electrons. They are *electronegative*.

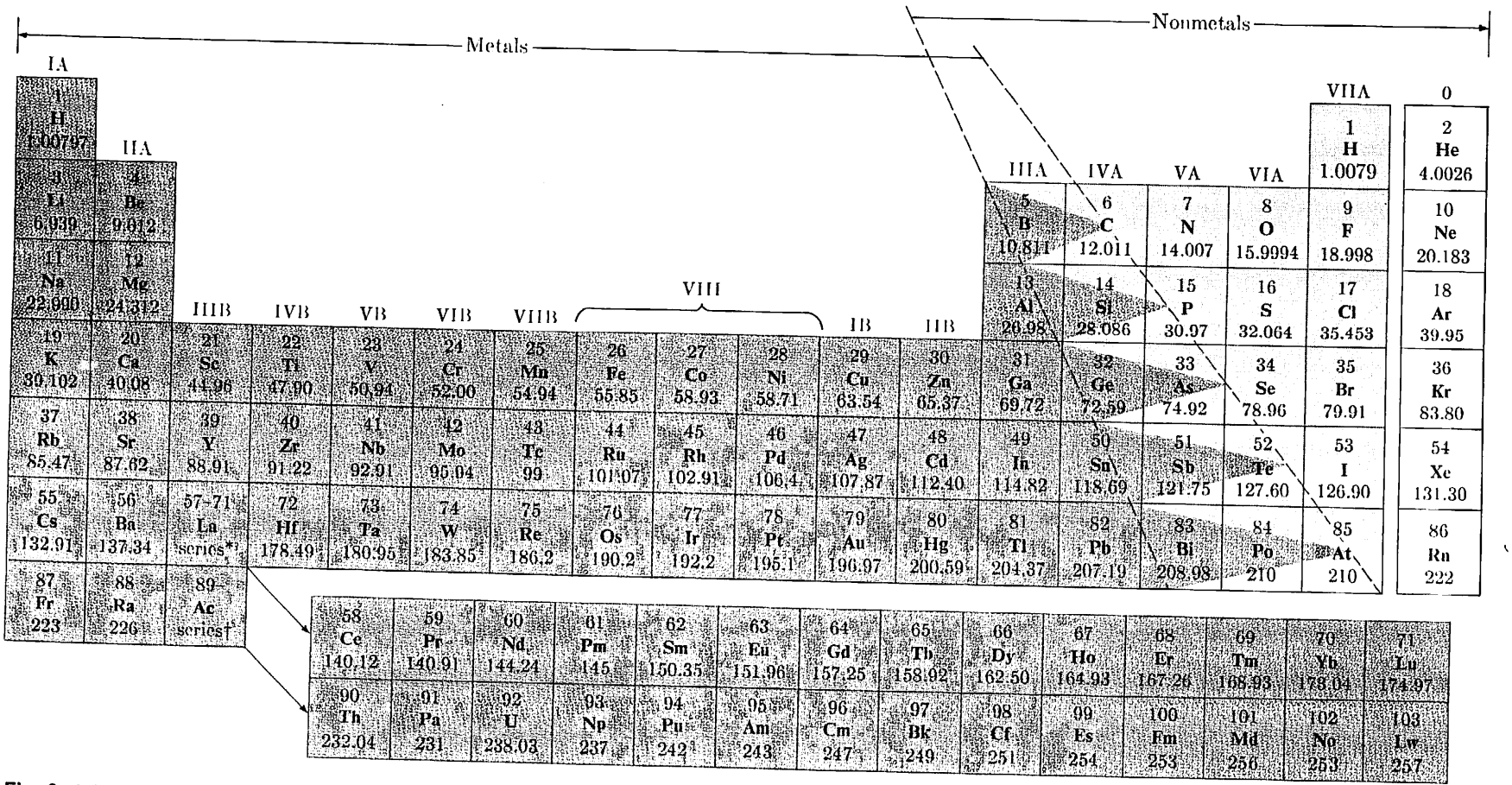

Fig. 2–1.1 Periodic table of the elements, showing the atomic number and atomic mass (in amu). There are 0.6×10^{24} amu per gram; therefore the atomic masses are grams per 0.6×10^{24} atoms. Metals readily release their outermost electrons. Nonmetals readily accept or share additional electrons.

Electrons Since electrons are components of all atoms, their negative electrical charge is commonly regarded as unity. In physical units, this charge is equal to 0.16×10^{-18} A·s per electron (or 0.16×10^{-18} coul/electron).

The electrons that accompany an atom are subject to very rigorous rules of behavior because they have the characteristics of standing waves during their movements in the neighborhood of the atomic nuclei. Again the reader is referred to introductory chemistry texts; however, let us summarize several features here. With individual atoms, electrons have specific energy states—*orbitals.* As shown in Fig. 2–1.2, the available electron energy states around a hydrogen atom can be very definitely identified.* To us, the important consequence is that there are large ranges of intermediate energies *not* available for the electrons. They are forbidden because the corresponding frequencies do not permit standing waves. Unless excited by external means, the one electron of a hydrogen atom will occupy the lowest orbital of Fig. 2–1.2.

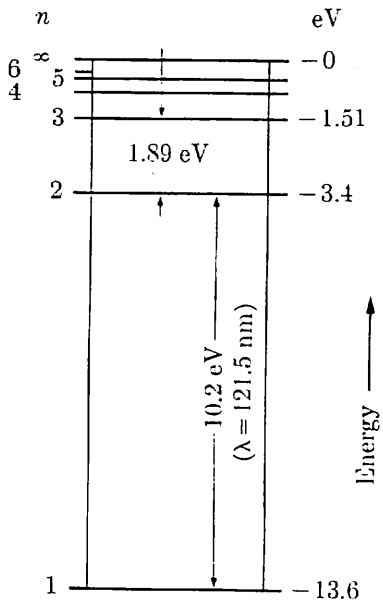

Fig. 2–1.2 Energy levels for electrons (hydrogen). The electron of hydrogen normally resides in the lowest energy level. (At this level, it would take 13.6 eV, or 2.2×10^{-18} J, to separate the electron from the nucleus.) Electrons can be given additional energy, but only at specific levels. Gaps exist between these levels. These are forbidden energies.

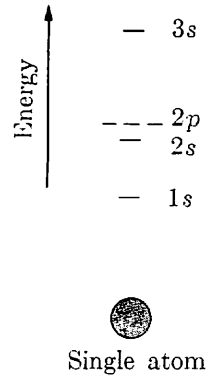

Fig. 2–1.3 Energy levels for electrons (sodium). Since a sodium atom possesses eleven electrons, and only two electrons may occupy each level (orbital), several orbitals must be occupied. Gaps exist between them. It takes 5.1 eV (0.82×10^{-18} J) to remove the uppermost (valence) electron from sodium.

Figure 2–1.3 shows schematically the energies of the lowest orbitals for sodium. Each orbital can contain no more than two electrons. These must be of opposite spins. Again, there are forbidden energy gaps between the orbitals that are unavailable for electron occupancy.

* This is done by spectrographic experiments.

In our considerations, the topmost occupied orbital will have special significance since it contains the *valence electrons*. These electrons may be removed by a relatively small electric field, to give us the positive *cations* mentioned a few paragraphs ago. The energy requirements are called the *ionization energies*. In the next section we will see that these outermost or valence electrons are *delocalized* in metallic solids and free to move throughout the metal rather than remaining bound to individual atoms. This provides the basis for electrical and thermal conductivity.

When the valence orbitals are not filled, the atom may accept a limited number of extra electrons within these unfilled energy states, to become a negative ion, *anion*. These electronegative atoms with unfilled valence orbitals may also share electrons. This becomes important in covalent bonding and will be reviewed in the next section.

Example 2–1.1 Sterling silver contains approximately 7.5 w/o* copper and 92.5 w/o silver. What are the a/o* copper and a/o silver?

Solution: Basis: 10,000 amu alloy = 9250 amu Ag + 750 amu Cu.

$$\text{Ag:}\quad 9250 \text{ amu Ag}/(107.87 \text{ amu Ag/atom}) = 85.75 \text{ atoms} = 88 \text{ a/o}$$

$$\text{Cu:}\quad 750 \text{ amu Cu}/(63.54 \text{ amu Cu/atom}) = \underline{11.80 \text{ atoms}} = 12 \text{ a/o.} \quad \blacktriangleleft$$
$$97.55$$

Example 2–1.2 The mass of small diamond is 3.1 mg. (a) How many C^{13} atoms are present if carbon contains 1.1 a/o of that isotope? (b) What is the weight percent of that isotope?

Solution

a)
$$\frac{0.0031 \text{ g}}{(12.011 \text{ g}/0.6022 \times 10^{24} \text{ atoms})} = 1.55 \times 10^{20} \text{ C atoms;}$$

$$(1.55 \times 10^{20})(0.011) = 1.7 \times 10^{18} \text{ C}^{13} \text{ atoms.}$$

b) Basis: 3.1 mg.

$$\frac{\text{Mass}_{13}}{\text{Mass}_{\text{total}}} = \frac{(1.7 \times 10^{18})(13 \text{ amu})}{(1.55 \times 10^{20})(12.011 \text{ amu})} = 1.2 \text{ w/o.}$$

Comment. Since the mass of the C^{13} is greater than the average atom, the weight percent will be greater than the atom percent. ◀

Example 2–1.3 From Appendix B, indicate the orbital arrangements for a single iron atom, and for Fe^{2+} and Fe^{3+} ions.

Solution: The argon core is $1s^2 2s^2 2p^6 3s^2 3p^6$; therefore,

$$\text{Fe: } 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2. \qquad (2\text{–}1.1)$$

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* Weight percent, w/o; atom percent, a/o; linear percent, l/o; volume percent, v/o; mole percent, m/o; etc. In condensed phases (*solids and liquids*) weight percent is implied unless specifically stated otherwise. In *gases*, v/o or m/o are implied unless specifically stated otherwise.

During ionization, the 4*s* electrons are removed first: therefore:

$$Fe^{2+}: 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6; \tag{2–1.2}$$

$$Fe^{3+}: 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5. \blacktriangleleft \tag{2–1.3}$$

Example 2–1.4 Ten grams of nickel are to be electroplated on a steel surface with an area of 0.8953 m^2. The electrolyte contains Ni^{2+} ions. (a) How thick will the nickel plate be? (b) What amperage is required if this is to be accomplished in 50 minutes?

Solution

a) $$10 \text{ g}/(8.9 \times 10^6 \text{g/m}^3)(0.8953 \text{ m}^2) = 1.25 \times 10^{-6} \text{ m (or } 1.25 \ \mu m).$$

b) $$\left[\frac{10 \text{ g Ni}}{58.71 \text{ g Ni}/0.6 \times 10^{24} \text{ atoms}}\right]\left[\frac{(2 \text{ el/atom})(0.16 \times 10^{-18} \text{ A·s/el})}{(3000 \text{ s})}\right] = 10.9 \text{ amperes.}$$

Comment. By now, the student should be alert to the data available in the Appendices. ◀

2–2 STRONG BONDING FORCES (PRIMARY BONDS)

Since most products are designed with solid materials, it is desirable to understand the attractions that hold the atoms together. The importance of these attractions may be illustrated with a piece of copper wire, in which each gram contains ($0.602 \times 10^{24}/63.54$) atoms. Based on the density of copper, each cubic centimeter contains 8.9 times this number, i.e., 8.4×10^{22} atoms/cm^3 (or $8.4 \times 10^{28}/m^3$). Under these conditions, the forces of attraction that bond the atoms together are strong. If this were not true, they would easily separate, the metal would deform under small loads, and atomic vibrations associated with thermal energy would gasify the atoms at low temperatures. As in the case of this wire, the engineering properties of any material depend on the interatomic forces which are present.

Interatomic attractions are caused by the electronic structure of atoms. The noble (inert or chemically inactive) gases, such as He, Ne, Ar, have only limited interactions with other atoms because they have a very stable arrangement of eight electrons (2 for He) in their outer, or valence, electron orbitals. Furthermore, they have no net charge as a result of an unbalanced number of protons and electrons. Most other elements, unlike the noble gases, must achieve the relatively stable configuration of having eight electrons available for their outer orbitals through one of the following procedures: (1) receiving extra electrons, (2) releasing electrons, or (3) sharing electrons. The first two of these processes produce ions with a net negative or positive charge and thus provide the ions with coulombic attractions to other ions of unlike charge. The third process obviously requires an intimate association between atoms in order for the sharing of electrons to be operative. Where applicable, the above three processes produce strong or primary bonds. Energies approximating 500 kJ/mole (i.e., 500,000 joules per 0.602×10^{24} bonds) are required to rupture these bonds. Other weaker or secondary bonds (less than 40 kJ/mole) are also always present, but gain importance when they are the only forces present (Section 2–4).

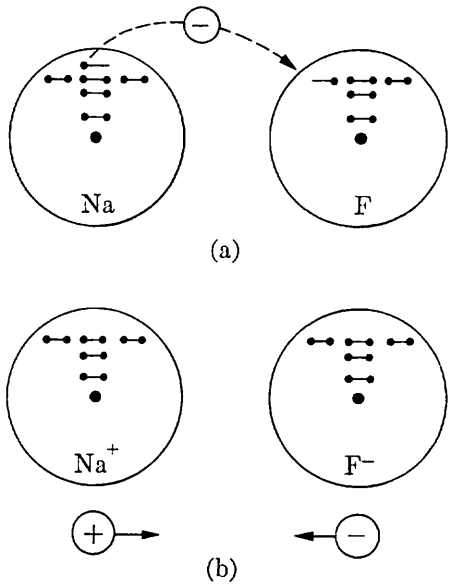

Fig. 2–2.1 Ionization. (a) Electron transfer from the outer orbital of sodium to fluorine. (b) The resulting positive and negative ions are mutually attracted, by coulombic forces, to form an ionic bond.

Ionic bonds The interatomic bond that is easiest to describe is the ionic bond, which results from the mutual attraction of positive and negative charges. Atoms of elements such as sodium and calcium, with one and two electrons in their valence orbitals, respectively, easily release these outer electrons and become positively charged ions. Likewise, chlorine and oxygen atoms readily add to their valence orbitals until they have eight electrons by accepting one or two electrons and thus becoming negatively charged ions. Since there is always a *coulombic attraction* between negatively and positively charged materials, a bond is developed between neighboring ions of unlike charges as shown schematically in Fig. 2–2.1.

A negative charge possesses an attraction for *all* positively charged particles and a positive charge for *all* negatively charged particles. Consequently, sodium ions surround themselves with as many negative chlorine ions as possible, and chlorine ions surround themselves with the maximum number of positive sodium ions, the attraction being equal in all directions (Fig. 2–2.2). The major requirement in an ionically bonded material is that the number of positive charges equals the number of negative charges. Thus, sodium chloride has a composition of NaCl. Magnesium chloride has a composition of $MgCl_2$, because the magnesium atom can supply two electrons from its valence shell but each chlorine atom can accept only one.

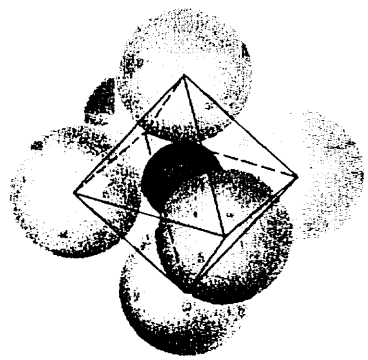

Fig. 2–2.2 Three-dimensional structure of sodium chloride. The positive sodium ion is coordinated with and has equal attraction for all six neighboring negative chlorine ions. (Compare with Fig. 3–1.1 where the structure reveals that Na^+ ions also surround Cl^- ions.)

Since these coulombic attractions involve all neighbors, ionically bonded materials may be very stable, particularly if multivalent ions are involved. As an example, when magnesium and oxygen combine to form MgO, 570 kJ/mole are released, i.e., 570,000 joules (or 136,000 calories) per 0.6×10^{24} Mg^{2+} ions and 0.6×10^{24} O^{2-} ions in the product. Thus, MgO must be raised to approximately 2800°C (~5000°F) before it overcomes this energy and melts.

Covalent bonds Another primary force of strong attraction is the *covalent* bond in which electrons are shared. Figure 2–2.3 shows two representations of this sharing for two fluorine atoms in F_2. Commonly the first representation (electron dots, or a "bond line") will suffice for our purposes, e.g., Fig. 2–2.4(a) for carbon. However, the reader should be aware that electrons cannot be precisely located without a

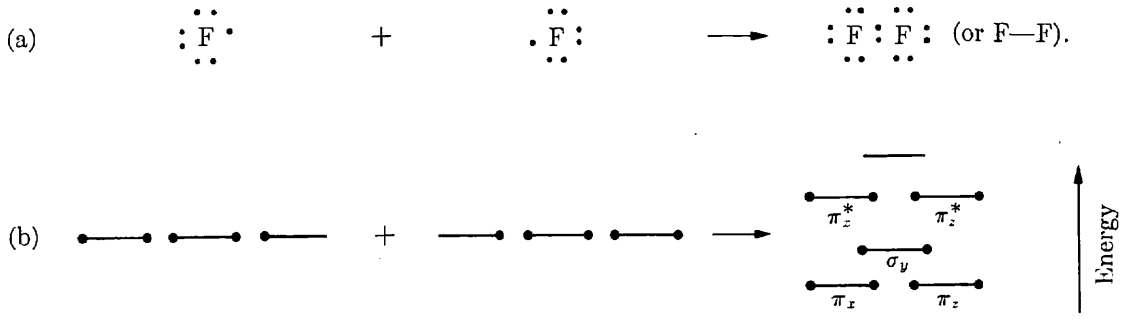

Fig. 2–2.3 Covalent bonding (fluorine). (a) Either the "electron dot" or the "bond line" is commonly used for simplicity. (b) Orbital energy levels (schematic). It takes 160,000 joules (38,000 calories) to break a mole (0.6×10^{24}) of these bonds. (Only the 2*p* electrons are shown in part (b).)

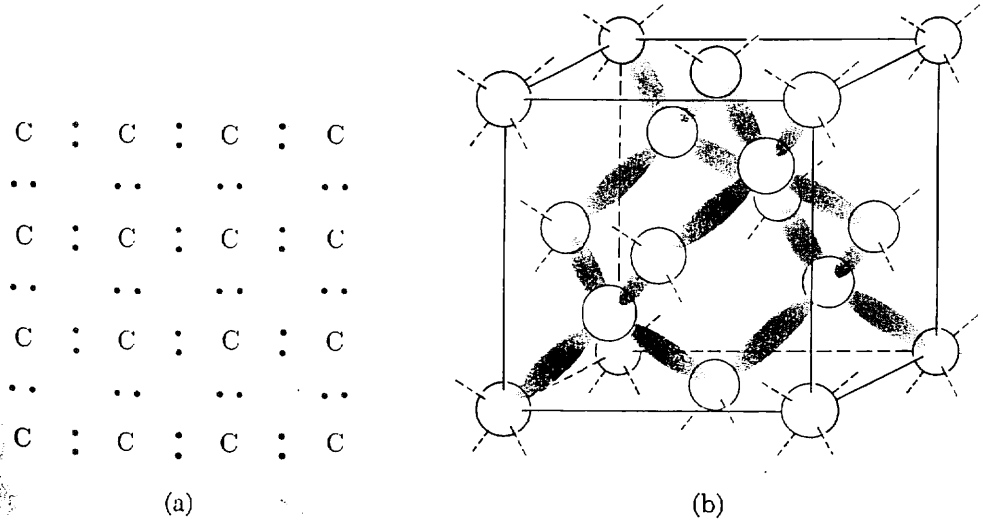

Fig. 2–2.4 Diamond structure. The strength of the covalent bonds is what accounts for the great hardness of diamond. (a) Two-dimensional representation. (b) Three-dimensional representation with the bond shown as the region of high electron probability (shaded).

degree of uncertainty. Therefore, this presentation will not always be satisfactory. An alternative is the schematic representation in Fig. 2–2.4(b) where a shaded region is used to indicate the location of high probability for the pair of shared electrons.

Figure 2–2.3(b) focuses on the energies of the valence electrons (*2p orbitals*) of fluorine as they combine into molecular orbitals. Note that the *average* energy of the outer or valence electrons drops when the molecule is formed from the two individual atoms. Therefore, we may consider covalent bonds in terms of energy, because energy would be required to reverse the reaction sketched in Fig. 2–2.3(b).

That covalent bonds provide strong attractive forces between atoms is evidenced in diamond, which is the hardest material found in nature, and which is wholly carbon. Each carbon has four valence electrons. These are shared with adjacent atoms to form a three-dimensional lattice entirely bonded by covalent pairs (Fig. 2–2.4). The strength of the covalent bond in carbon is demonstrated not only by the great hardness of diamond but also by the extremely high temperature ($>3000°C$) to which it can be heated before the structure is disrupted (melted) by thermal energy.*

Unlike coulombic attractions that bring as many unlike ions into neighboring positions as space will allow, covalent bonds are formed between specific atoms. In the diamond of Fig. 2–2.4(b), the number of neighbors is limited by the number of bonds and not by the available space. In Fig. 2–2.3, the two fluorines are held together with a covalent connection of $160\ kJ/0.6 \times 10^{24}$ bonds. However, neither of these two atoms develops strong attractions to other fluorine atoms (or molecules) that may approach them. As evidence, F_2 vaporizes to a gas at 85 K ($-188°C$ or $-306°F$) with only ~ 3 kJ/mole. When the bond involves a given pair of atoms, we apply the term *stereospecific*, and they are therefore directional.

An exception to the above stereospecificity of covalent bonds occurs in compounds with a benzene ring, which is discussed in chemistry texts (Fig. 2–2.5). One electron per carbon atom (for a total of six) is *delocalized.* These six electrons have equal probability of being found anywhere around the ring.† They can respond to alternating electric fields by moving from one side of the molecule to another but cannot leave the molecule (except under unusually catastrophic conditions). There are as many wave patterns for these delocalized electrons *as there are atoms in the ring.*

Metallic bonds In addition to ionic and covalent bonds, a third type of primary interatomic attractive mechanism is the metallic bond. The model of metallic bonding is not as simple to construct as the other two. However, we can adapt the concept of delocalized electrons from the previous paragraph to serve our purpose. First consider graphite (Fig. 2–2.6); the layers of carbon atoms in graphite possess delocalized electrons (as well as electron pairs between specific atoms). The delocalized electrons can respond to electric fields, moving within the graphite sheet in a wavelike pattern.‡ In fact, conductivity becomes possible if a positive electrode is present to

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* It would take about 750 kJ, or 180 kcal, to break all the bonds in a mole (0.6×10^{24}) of carbon atoms.

† They reside in π bonds which are perpendicular to the plane of the molecule.

‡ As with the benzene ring, there are as many wave patterns possible *as there are carbon atoms in the layer.* Also note that while the delocalized electrons can readily move within the layer, there is not a comparable mechanism to move from one layer to another. (See discussion question Z_2 at the end of the chapter.)

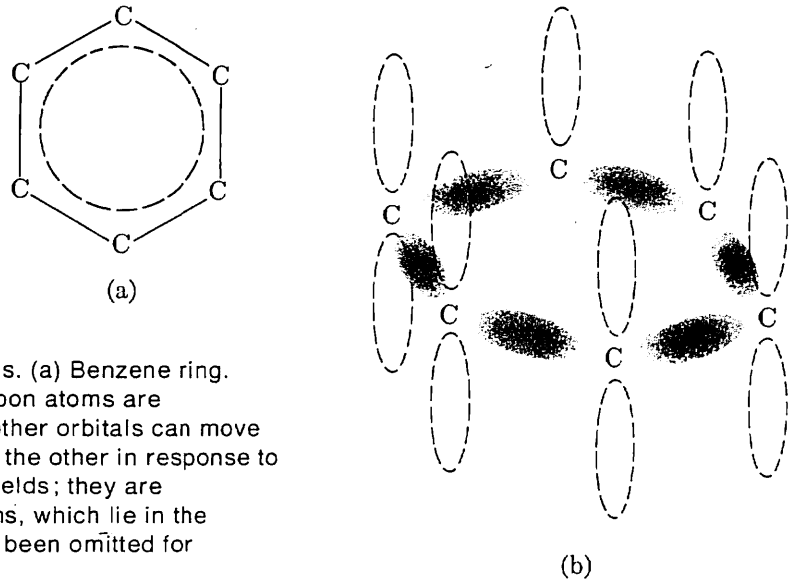


Fig. 2–2.5 Delocalized electrons. (a) Benzene ring. (b) The orbitals between the carbon atoms are stereospecific. Electrons in the other orbitals can move from one side of the molecule to the other in response to internal and external electrical fields; they are delocalized. (The hydrogen atoms, which lie in the plane of the carbon atoms, have been omitted for clarity.)

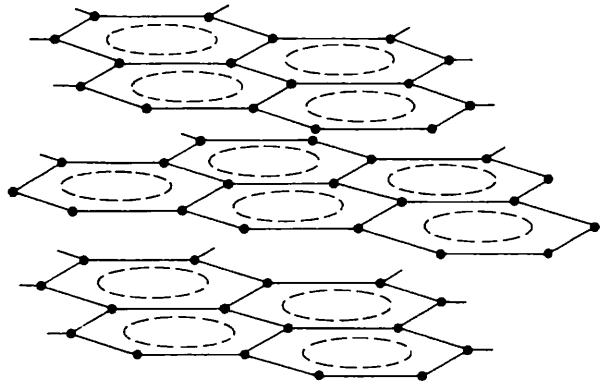


Fig. 2–2.6 Delocalized electrons in graphite layers. Each layer contains "multiple benzene rings" (Fig. 2–2.5). The conductivity is more than 100 times greater in the parallel direction than in the perpendicular direction.

remove electrons from one end of the layer, and a negative electrode is available to supply electrons to the other end.

Typical metals have delocalized electrons that can move in three dimensions. It is thus common to speak of an electron "cloud" or "gas" because the outer, least strongly bonded electrons are able to move throughout the metal structure. The orbitals for metals are sketched schematically in Fig. 2–2.7 for sodium. Just as the molecular orbitals of F_2 on the right side of Fig. 2–2.3(b) are modified from the atomic orbitals, the energy levels in multiatomic sodium differ from that of the single-atom orbitals that were first shown in Fig. 2–1.3. The prime change between Fig. 2–2.7(a) and 2–2.7(b) is that the upper valence orbital has split into as many levels as there are atoms in the system. Note that the average energy of the electrons in the valence band of Fig. 2–2.7(b) is below the energy of the 3*s* orbital for the individual atom. This accounts for the bonding in metals; in brief, energy would have to be supplied to overcome the metallic bond and separate the atoms from one another and to reestablish the individual atomic orbitals. Qualitatively speaking, we find very strong bonds holding tungsten atoms together. Its melting and boiling temperatures

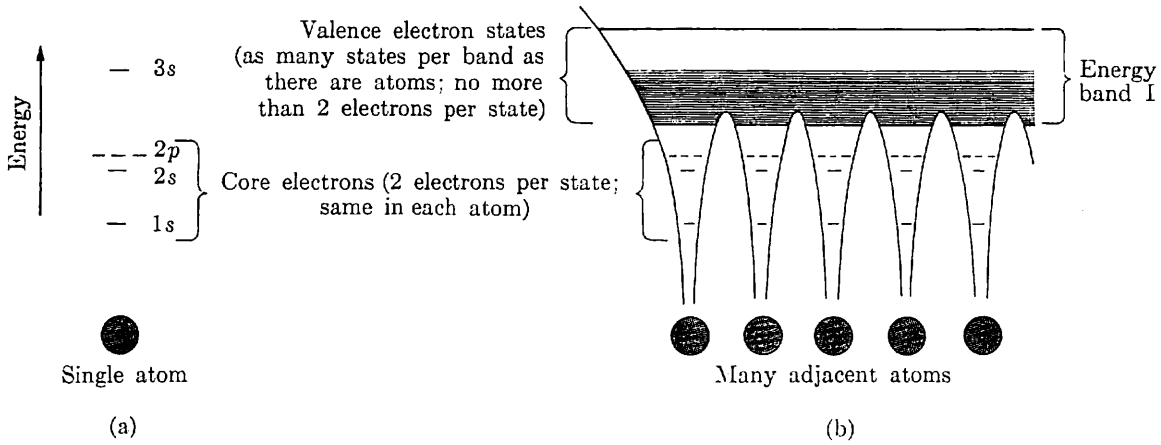


Fig. 2–2.7 Valence electrons in metal (sodium). The valence electrons are delocalized into an energy band. These electrons are able to move throughout the metal. The valence electrons fill only the bottom half of the band. Their average energy is lower than that of the 3*s* electrons with individual atoms. This energy difference provides the metallic bond.

are very high ($\sim$3400 and 5900°C, respectively); also, it has an extremely high modulus of elasticity (50,000,000 psi, or 345,000 MPa; see Appendix C for comparisons). In contrast, the bonds in sodium are low as evidenced by its melting point (97.8°C) and soft behavior. Both have delocalized electrons for electrical and thermal conduction.

Before concluding this section on primary bonds, or strong attractive forces, we should observe that while one bond type may be prevalent in a material, other bond types can be present, too; so *mixed-bond types* are widespread.

Example 2–2.1 The covalent bond between two carbon atoms, C—C, is 370 kJ/mole (88 kcal/0.6×10^{24} bonds). The energy of light is

$$E = h\nu \tag{2–2.1}$$

where h is Planck's constant (0.66×10^{-33} joule·sec) and ν is the frequency of light. What wavelength λ is required to break a C—C bond?

Solution

$$370{,}000 \text{ J}/0.6 \times 10^{24} = (0.66 \times 10^{-33} \text{ J·s})\nu,$$

$$\nu = 9.34 \times 10^{14}/\text{s} = c/\lambda,$$

where c is the velocity of light.

$$\lambda = (0.299 \times 10^{9} \text{ m/s})/(9.34 \times 10^{14}/\text{s})$$
$$= 0.320 \times 10^{-6} \text{ m } (= 320 \text{ nm}).$$

Comments. This is in the ultraviolet range. It is for this reason that ultraviolet light can cause deterioration in plastics that contain C—C covalent bonds. ◀

2–3 MOLECULES

A *molecule* may be defined as a group of atoms that are strongly bonded together, but whose bonds to other, similar groups of atoms are relatively weak. Our prototype for a molecule may be fluorine, F_2, which was discussed in the previous section. Recall that 160 kJ/mole ($\sim$1.65 eV/bond) would have to be present to break the covalent bond joining the two atoms (Fig. 2–2.3). In contrast, only 3 kJ/mole (0.03 eV/bond) provided the thermal agitation that is required to separate the molecules into a gas by boiling.

The more common examples of molecules include compounds such as H_2O, CO_2, CCl_4, O_2, N_2, and HNO_3. Other small molecules are shown in Fig. 2–3.1. Within each of these molecules, the atoms are held together by strong attractive forces that usually have covalent bonds, although ionic bonds are not uncommon. Unlike the forces that hold atoms together, the bonds between molecules are weak and consequently each molecule is free to act more or less independently. These observations are borne out by the following facts: (1) Each of these molecular compounds has a low melting and a low boiling temperature compared with other materials. (2) The molecular solids are soft because the molecules can slide past each other with small stress applications. (3) The molecules may remain intact in the liquid and gaseous forms.

The molecules listed above are comparatively small; other molecules have large numbers of atoms. For example, pentatriacontane (shown in Fig. 2–3.2c) has over 100 atoms, and some molecules contain many thousand. Whether the molecule is small like CH_4 or much larger than that shown in Fig. 2–3.2(c), the distinction between the strong *intra*molecular and the weaker *inter*molecular bonds still holds.

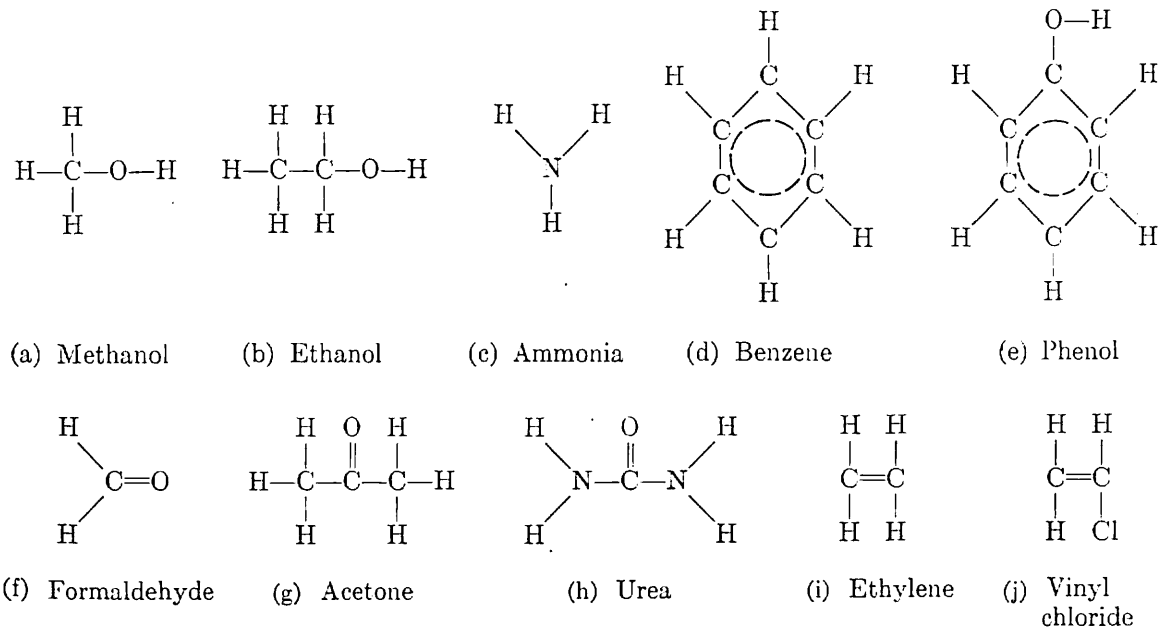
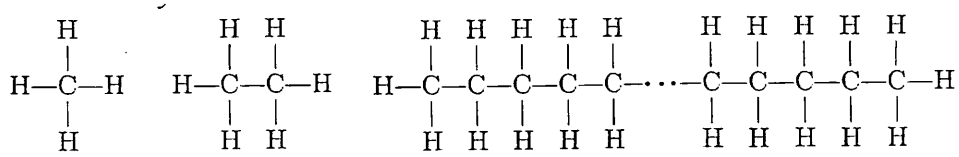


Fig. 2–3.1 Small organic molecules. Each carbon is surrounded by four bonds, each nitrogen by three, each oxygen by two, and each hydrogen and chlorine by one.



(a) Methane (b) Ethane (c) $C_{35}H_{72}$, pentatriacontane (i.e., 35-ane)

Fig. 2–3.2 Examples of molecules. Molecules are discrete groups of atoms. Primary bonds hold the atoms together within the molecule. Weaker, secondary forces attract molecules to each other.

Other materials such as metals, MgO, SiO_2, and phenol-formaldehyde plastics have continuing three-dimensional structures of primary bonds. The difference between the structures of molecular materials and those with primary bonds continuing in all three dimensions produces major differences in properties. These differences will be considered in subsequent chapters.

Bond lengths and energies The strength of bonds between atoms in a molecule, of course, depends on the kind of atoms and the other neighboring bonds. Table 2–3.1 is a compilation of bond lengths and energies for those atom couples most frequently encountered in molecular structures. The energy reported is the amount required to break one mole (Avogadro's number) of bonds. For example, 370,000 joules of energy are required to break 0.602×10^{24} C—C bonds, or $370{,}000/(0.602 \times 10^{24})$ joules per bond. Likewise, this same amount of energy is released (-0.61×10^{-18} J) if one of these C—C bonds is formed. Only the sign is changed.

Bond angles The chemist recognizes hybrid orbitals in certain covalent compounds, where the *s* and *p* orbitals are amalgamated. The most important hybrid for us to review is the sp^3 orbital. We have already sketched it in Fig. 2–2.4 for the four bonds of carbon in diamond. Four equal orbitals are formed instead of having distinct 2*s* and 2*p* orbitals that occur in individual atoms (e.g., the individual sodium and fluorine atoms of Fig. 2–2.1a). Methane (CH_4) and carbon tetrachloride (CCl_4), like diamond, have sp^3 orbitals that connect four identical atoms to the central carbon. Therefore, we find them equally spaced around the central carbon at 109.5° from each other.* Geometrically, this is equivalent to placing the carbon at a cube center and pointing the orbitals toward four of the eight corners (Fig. 2–3.3a). However, if the orbitals do not bond identical atoms to the central carbon, these time-averaged angles are distorted slightly, as shown for CH_3Cl (Fig. 2–3.3b).

Greater distortions occur in hybrid orbitals when some of the electrons occur as *lone pairs* rather than in the covalent bond. This is particularly evident in NH_3 and H_2O (Fig. 2–3.4) where 107.3° and 104.5° are the time-averaged values for H—N—H and H—O—H, respectively.

* The angle 109.5° is a time-averaged value. Any particular H—C—H angle in CH_4 will vary rapidly as a result of thermal vibrations.

Table 2–3.1
Bond energies and lengths

Bond	Bond energy*		Bond length, nm
	kcal/mole	kJ/mole	
C—C	88†	370†	0.154
C=C	162	680	0.13
C≡C	213	890	0.12
C—H	104	435	0.11
C—N	73	305	0.15
C—O	86	360	0.14
C=O	128	535	0.12
C—F	108	450	0.14
C—Cl	81	340	0.18
O—H	119	500	0.10
O—O	52	220	0.15
O—Si	90	375	0.16
N—H	103	430	0.10
N—O	60	250	0.12
F—F	38	160	0.14
H—H	104	435	0.074

* Approximate. The values vary with the type of neighboring bonds. For example, methane (CH_4) has the above value for its C—H bond; however the C—H bond energy is about 5% less in CH_3Cl, and 15% less in $CHCl_3$.

† All values are negative for forming bonds (energy is released), and positive for breaking bonds (energy is required).

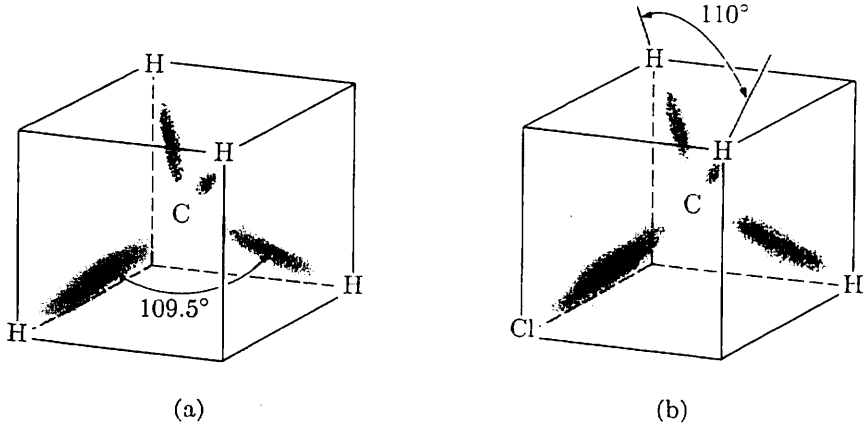
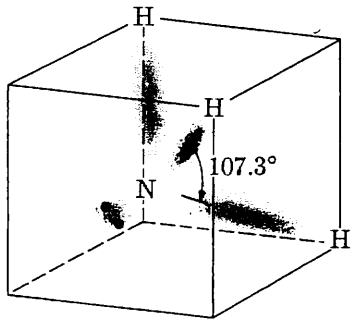
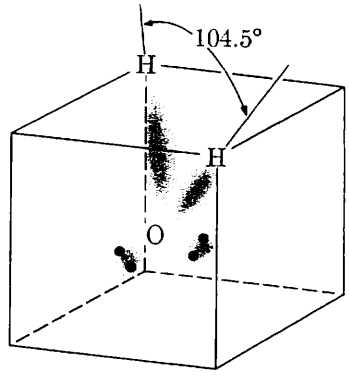


Fig. 2–3.3 Bond angles. (a) Methane, CH_4, is symmetrical with each of the six angles equal to 109.5°. (b) Chloromethane, CH_3Cl, is distorted.



(a)



(b)

Fig. 2–3.4 Bond angles. (a) Ammonia, NH_3, and (b) water have angles between the 109.5° of Fig. 2–3.3(a) and 90°. Ammonia has one lone-pair of electrons; water, two.

One of the bond angles most frequently encountered in the study of materials is the C—C—C angle of the hydrocarbon chains (Fig. 2–3.5). While this will differ slightly, depending upon whether hydrogen or some other side radical is present, we may assume for our purposes that the C—C—C angle is close to 109.5°.

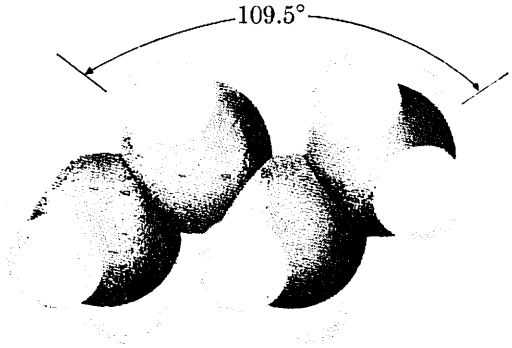


Fig. 2–3.5 Bond angles (butane). Although we commonly draw straight chains (Figs. 2–3.2c and 2–3.7b), there is a C—C—C bond angle of about 109°.

Isomers In molecules of the same composition, more than one atomic arrangement is usually possible. This is illustrated in Fig. 2–3.6 for propyl and isopropyl alcohol. Variations in the structure of molecules with the same composition are called *isomers*. Differences in structure affect the properties of molecules because of the resulting change in molecular polarity (Section 2–4). For example, the melting and boiling temperatures for propyl alcohol are −127°C and 97.2°C, respectively, whereas for isopropyl alcohol the corresponding temperatures are −89°C and 82.3°C.

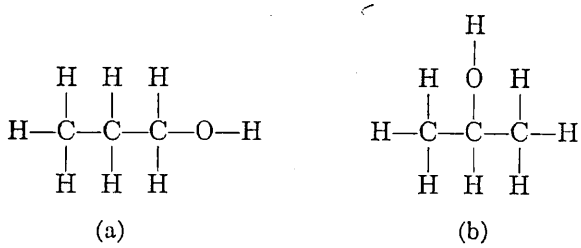


Fig. 2–3.6 Isomers of propanol. (a) Normal propyl alcohol. (b) Isopropyl alcohol. The molecules have the same composition but different structures. Consequently, the properties are different. Compare with polymorphism of crystalline materials (Section 3–4).

Example 2–3.1 How much energy is given off when 70 g of ethylene (Fig. 2–3.7a) react to give polyethylene (Fig. 2–3.7b)?

Solution: Each added C_2H_4 molecule breaks one C=C bond and forms two C—C bonds. From Table 2–3.1:

$$\frac{+680{,}000\ \text{J}}{0.602 \times 10^{24}\ \text{molecules}} - \frac{2(370{,}000\ \text{J})}{0.602 \times 10^{24}\ \text{molecules}} = -9.96 \times 10^{-20}\ \text{J/C}_2\text{H}_4,$$

$$70\ \text{g}\ (0.602 \times 10^{24}\ \text{amu/g})/(28\ \text{amu/C}_2\text{H}_4) = 1.5 \times 10^{24}\ \text{C}_2\text{H}_4,$$

$$(-9.96 \times 10^{-20}\ \text{J/C}_2\text{H}_2)(1.5 \times 10^{24}\ \text{C}_2\text{H}_4 = -150{,}000\ \text{J},$$

or

$$-150{,}000\ \text{J}\ (0.239\ \text{cal/J}) = -36\ \text{kcal}.$$

Comment. Convention treats required energy as (+) and released energy as (−). The reaction of Fig. 2–3.7 is the basic reaction for making large vinyl-type molecules that are used in plastics (Chapter 7). ◀

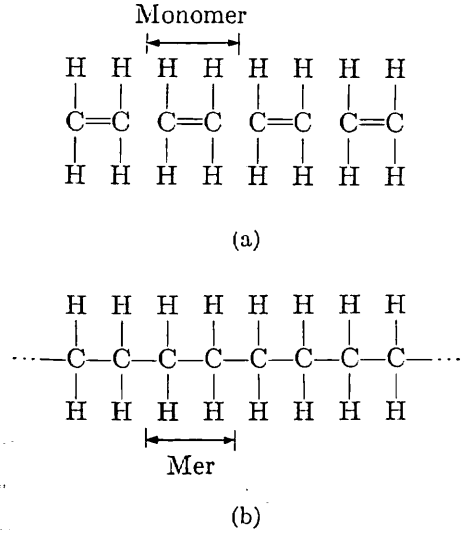


Fig. 2–3.7 Addition polymerization of ethylene. (a) Monomers of ethylene. (b) Polymer containing many C_2H_4 mers, or units. The original double bond of the ethylene monomer is broken to form two single bonds and thus connect adjacent mers.

Example 2–3.2 Show sketches (carbon atoms only) of the various isomers of heptane, C_7H_{16}.

Sketches

a) C—C—C—C—C—C—C

b)
```
      C
      |
C—C—C—C—C—C
```

c)
```
      C
      |
C—C—C—C—C—C
```

d)
```
    C C
    | |
C—C—C—C—C
```

e)
```
    C   C
    |   |
C—C—C—C—C
```

f)
```
      C
      |
C—C—C—C—C
|
C
```

g)
```
      C
      |
C—C—C—C—C
    |
    C
```

h)
```
    C C
    | |
C—C—C—C
|
C
```

Comment. Other arrangements, for example,
```
      C
      |
      C
      |
C—C—C—C
|
C
```
duplicate one of the above alternatives (in this case, sketch *g*). ◀

•2–4 SECONDARY BONDING FORCES*

The three types of bonds considered in Section 2–2 are all relatively strong primary bonds that hold atoms together. Weaker, secondary bonds, which supply interatomic attraction, are grouped here as *van der Waals forces*, although there are actually several different mechanisms involved. Were it not for the fact that sometimes they are the only forces that operate, van der Waals bonding might be overlooked.

In a noble gas like helium, the initial orbital, with its two electrons, is complete; and other noble gases, such as neon and argon, have a full complement of eight electrons in their valence orbitals. In these stable situations none of the primary bonds can be effective, since covalent, ionic, and metallic bonds all require adjustments in the valence electrons. As a result, atoms of these noble gases have little attraction for one another, and with rare exceptions they remain monatomic at ordinary temperatures. Only at extremely low temperatures, when thermal vibrations have been greatly reduced, do these elemental gases condense (Table 2–4.1A). It is this condensation that makes it evident that there are weak interatomic attractions that pull the atoms together.

Similar evidence for these weak attractions is found in the molecules listed in Table 2–4.1(B). As pointed out earlier, these gases have satisfied their valence requirements by covalent bonding within the molecule. The condensation of these simple molecules occurs only when thermal vibrations are sufficiently reduced in energy to permit the weak van der Waals forces to become noticeable.

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* See Preface for the bullet, •, notation.

Table 2–4.1
Melting and boiling temperatures of gases (absolute temperature)

A. Noble gases			B. Simple molecules		
Gas	Melting temperature, K	Boiling temperature, K	Molecule	Melting temperature, K	Boiling temperature, K
			Symmetric		
He	0.96*	4.25	H_2	14.02	21
Ne	24.5	27	N_2	63	78
Ar	84	87.5	O_2	55	90
Kr	116	120	CH_4	88	145
Xe	161	166	CCl_4	250	349
Rn	202	211	C_4H_{10}	135	274
			Polar		
			NH_3	195	240
			CH_3Cl	113	259
			H_2O	273	373

* Melting point with 26 atmospheres of pressure. At one atmosphere pressure, helium remains as a liquid as 0 K (−273.16°C) is approached.

Induced dipoles All but the last three of the gases and molecules of Table 2–4.1 are symmetric; i.e., over any extended period of time, the center of positive charges from the protons in the nuclei, and the center of negative charges from the electrons, are at the center of each molecule (or noble gas atom). Continually, however, the electron motions and the atom vibrations disrupt this electrical symmetry. When this happens, a small electrical *dipole* is established. In each small fraction of a second,* the centers of positive and negative charges are not coincident, so an electrical dipole is established giving the molecule a positive end and a negative end. In turn, this induces a dipole into the adjacent molecules by displacing their electrons in response to this minute electric field. Therefore, attractive forces are established, though admittedly weak. This is demonstrated by the data of Table 2–4.1, which shows that these gases do condense; however, not until low temperatures are reached.

Polar molecules Asymmetric molecules, such as NH_3, CH_3Cl, and H_2O, always have a noncoincidence of their positive and negative charges. This *polarity* is best illustrated in Fig. 2–3.4 for ammonia (NH_3). Three hydrogen nuclei, which are no more than bare protons (+), are exposed to the upper right. The lone pair of electrons on the other side of the molecule makes that position the negative end of the molecule. The *inter*molecular bonding forces of symmetrical CH_4 and asymmetric NH_3 may be compared through their melting and boiling temperatures, since each has about the same mass (16 amu and 17 amu, respectively). Table 2–4.1 shows that NH_3 must be raised to 240 K (−33°C) before thermal agitation breaks the *inter*molecular bonds

* Between 10^{-16} and 10^{-12} sec.

to form a gas. The more weakly bonded, symmetrical CH_4 is vaporized at 145 K ($-128°C$). In further contrast, CH_3Cl (Fig. 2–3.3b) does not vaporize until 259 K ($-14°C$) because the chlorine possesses a large number of electrons that are located relatively far from the center of the molecule and therefore give strong attractions to neighboring molecular dipoles.

Hydrogen bridge This third type of van der Waals bonding force is actually a special case of a polar molecule. However, it is by far the strongest of these secondary bonding forces and is widely encountered. It therefore warrants special attention and a special name.

The exposed proton at the end of a C—H, O—H, or N—H bond is not screened by electrons. Therefore, this positive charge can be attracted to valence electrons of adjacent molecules. A coulombic-type bond is developed, called a *hydrogen bridge.* Our most common example of this is found in water, where the proton of the hydrogen in one molecule is attracted to the lone pairs of electrons on the oxygen in an adjacent molecule (Fig. 2–4.1). The maximum energy of this bond is about 30 kJ/mole (7 kcal/mole). This is in contrast to (1) a maximum of 5 kJ/mole (and usually $\ll$ 1 kJ/mole) for the other types of van der Waals bonds, and (2) several hundred kilojoules per 0.6×10^{24} bonds for primary bonds (Section 2–2).

Chemists point out that it would be difficult to overemphasize the importance of the hydrogen bridge. For example, H_2O, with a molecular weight of only 18 amu, has the highest boiling temperature of any molecule with a molecular weight of less than 100 amu. If it had a boiling point comparable to other 3- or 4-atom molecules, our oceans would be nonexistent and all biological and geological conditions would be completely altered. In our study of materials, the hydrogen bridge affects the properties and behavior of plastics (Chapter 7) and certain ceramics (Chapter 8).

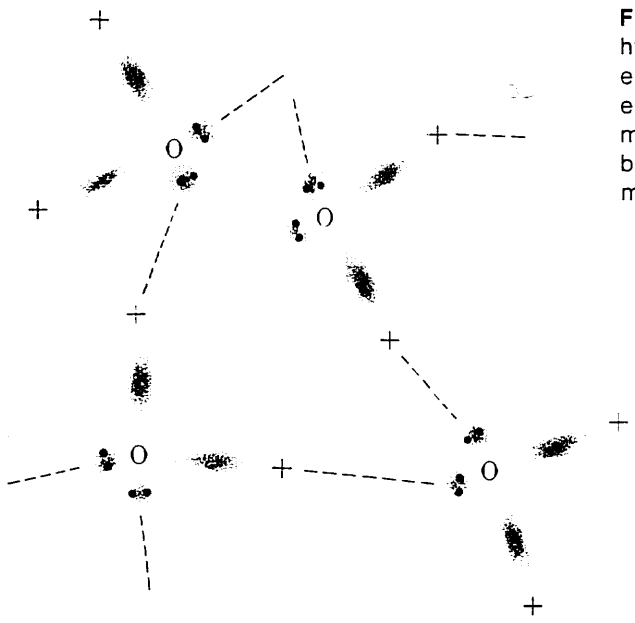

Fig. 2–4.1 Hydrogen bridge (in water). The hydrogen at the end of the orbital is an exposed proton (+). It is attracted to the electron lone-pairs of the adjacent water molecules. (Cf. Fig. 2–3.4b.) The hydrogen bridge makes water the highest boiling of any material with a low molecular weight (18 amu).

Example 2–4.1 Each OH arm of a water molecule has an electric dipole of moment 5×10^{-30} coul·m. What is the dipole moment of the whole molecule?

Solution: Solve for the resultant of the two dipoles at 104.5° (Fig. 2–3.4).

$$p = 2(5 \times 10^{-30} \text{ coul·m}) \cos (104.5°/2)$$
$$= 6 \times 10^{-30} \text{ C·m}.$$

Comment. The *dipole moment* is the product of the charge and the distance between the centers of positive and negative charges. ◀

Example 2–4.2 The H_2O molecule has one proton in each hydrogen atom and eight in the oxygen atom. (a) How far apart are the centers of positive and negative charges?

The H_2O molecule may also be considered to have a positive end from the two exposed protons (H^+), and a negative end from the oxygen atom with its eight protons and complement of ten electrons (O^{2-}). (b) How far apart are the ends of the dipole defined in this manner?

Solution: From Example 2–4.1, the dipole moment ($p = Qd$) of the H_2O molecule is 6×10^{-30} coul·m.

a) $$Qd = 10(0.16 \times 10^{-18} \text{ C})d = 6 \times 10^{-30} \text{ C·m};$$
$$d = (6 \times 10^{-30} \text{ C·m})/(1.6 \times 10^{-18} \text{ C})$$
$$= 3.8 \times 10^{-12} \text{ m} \quad (=0.004 \text{ nm}).$$

b) $$Qd = 2(0.16 \times 10^{-18} \text{ C})d = 6 \times 10^{-30} \text{ C·m};$$
$$d = 19 \times 10^{-12} \text{ m} \quad (=0.02 \text{ nm}).$$

Comments. Either concept is satisfactory for pointing out that the centers of positive and negative charges are not coincident. The first considers the elementary charged particles (electrons and protons); the latter assigns the charges to the ionized atoms. ◀

2–5 INTERATOMIC DISTANCES

Although in the case of diatomic molecules there is bonding and coordination of only two atoms, most materials involve a coordination of many atoms into an integrated structure. Two main factors, interatomic distances and spatial arrangements, are of importance. Let us therefore consider them in some detail.

The forces of attraction between atoms, which we considered in the preceding sections, pull the atoms together; but what keeps the atoms from being drawn still closer together? It should be apparent from the preceding figures and the discussion that there is much vacant "space" in the volume surrounding the nucleus of an atom. The existence of this space is evidenced by the fact that neutrons can move through the fuel and the other materials of a nuclear reactor, traveling among many atoms before they are finally stopped (see Fig. 6–9.1).

The space between atoms is caused by interatomic repulsive forces, which exist in addition to the interatomic attractive forces described in Sections 2–2 and 2–4. Mutual repulsion results primarily because the close proximity of two atoms places

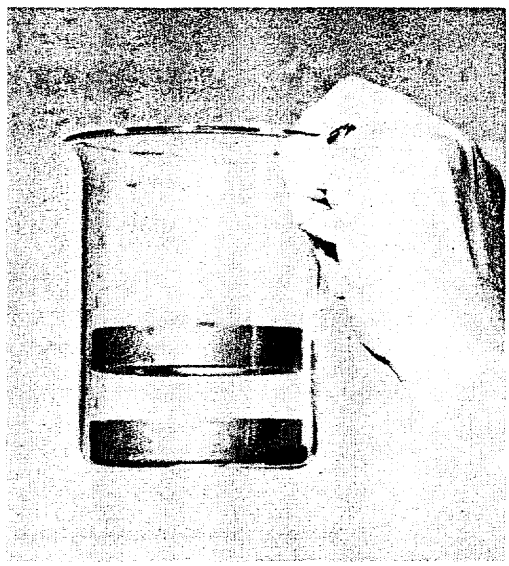

Fig. 2–5.1 Balance of forces (ceramic ring magnets). Downward force on upper ring is caused by gravity. Upward force is caused by magnetic repulsion. Space remains between the two magnets at the equilibrium position. (Of course the forces in this analogy are not identical to those between atoms; however, the principle of opposing forces is comparable.) (Courtesy of the North American Philips Co.)

too many electrons into interacting locations. The equilibrium distance is that distance at which the repulsive and the attractive forces are equal. An analogy may be made between the interatomic distances among atoms and the spacing between the two ring magnets of Fig. 2–5.1. (In this example, the magnets are aligned to give repulsion rather than attraction.) Of course the forces in this analogy are not identical to those between atoms; however, the principle of force balances is comparable. The top ring magnet is moved by a force (gravity) toward the lower ring magnet (which in this case is fixed by the container). Since the force of gravity is essentially constant over the distance considered here, the top magnet falls to the point where it is repulsed by an equal magnetic force, of opposite direction. Because the repulsive force increases as an inverse function of the distance, equilibrium distance is achieved. Note that the magnets remain separated by space. (A nonmagnetic material may move through this space, just as a neutron (neutrons have no charge) may move among atoms in a solid.)

Coulombic forces The ionic bond will be used to illustrate the balance between attractive and repulsive forces in materials. The coulombic force F_C developed between two point charges is related to the quantity of the two charges Z_1q and Z_2q, and their separation distance a_{1-2} as follows:

$$F_C = -k_0(Z_1q)(Z_2q)/a_{1-2}^2, \qquad (2\text{–}5.1)$$

where Z is the valence (+ or −) and q is 0.16×10^{-18} coulomb. The proportionality constant k_0 depends on the units used when we are considering adjacent ions.*

Electronic repulsive forces The repelling force F_R between the electronic fields of two atoms or ions is also an inverse function with distance, but to a higher power:

$$F_R = -bn/a_{1-2}^{n+1}. \qquad (2\text{–}5.2)$$

* With SI units, k_0 is 9×10^9 V·m/C, since $k_0 = 1/4\pi\epsilon_0$.

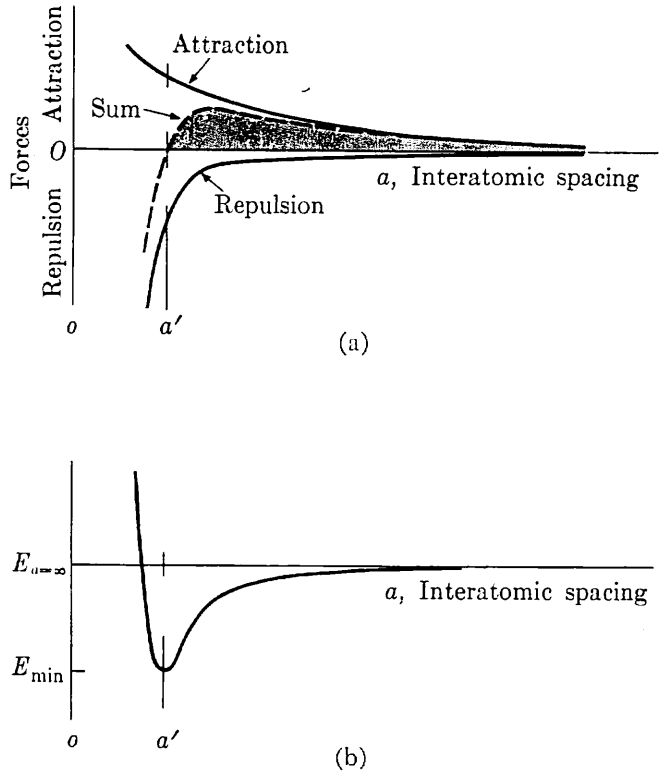

Fig. 2–5.2 Interatomic distances. (a) The equilibrium spacing o–a' is the distance at which the attractive forces equal the repulsive forces. (b) The lowest potential energy occurs when o–a' is the interatomic distance. Since $E = \int F\,da$, the shaded area of (a) equals the depth of the energy trough in (b).

Both b and n are empirical constants, with n equal to approximately 9 in ionic solids. Comparing, $F_C \propto a^{-2}$, and $F_R \propto a^{-10}$. Thus, the attractive forces predominate at greater distances of atomic separation, and the repulsive forces predominate at closer interatomic spacings (Fig. 2–5.2a). The equilibrium spacing, o–a', is a natural result when

$$F_C + F_R = 0. \tag{2–5.3}$$

A tension force is required to overcome the predominant forces of attraction if the spacing is to be increased. Conversely, a compressive force has to be applied to push the atoms closer together against the rapidly increasing electronic repulsion.

The equilibrium spacing is a very specific distance for a given pair of atoms, or ions. It can be measured to five significant figures by x-ray diffraction (Chapter 3), if temperature and other factors are controlled. It takes a large force to stretch or compress that distance as much as one percent. (Based on Young's modulus, a stress of 2000 MPa (300,000 psi) is required for iron.) It is for this reason that the *hard ball* provides a usable model for atoms for many purposes where strength or atom arrangements are considered.*

* The hard-ball model is not suitable for all explanations of atomic behavior. For example, a neutron (which doesn't have a charge) can travel through the space among the atoms without being affected by the electronic repulsive forces just described. Likewise, atomic nuclei can be vibrated vigorously by increased thermal energy, with only a small expansion of the *average* interatomic spacing. Finally, by a momentary distortion of their electrical fields, atoms can move past one another in a crowded solid. (See diffusion in Chapter 4.)

Bonding energy The sum of the above two forces provides us with a basis for bonding energies (Fig. 2–5.2b). Since the product of force and distance is energy,

$$E = \int_{\infty}^{a} (F_C + F_R)\, da. \tag{2–5.4}$$

We will use infinite atomic separation as our energy reference, $E_{a=\infty} = 0$. As the atoms come together, energy is *released* in an amount equal to the shaded area of Fig. 2–5.2(a). The amount of energy released is shown in Fig. 2–5.2(b). Note, however, that at o–a', where $F = 0 = dE/da$, there is a minimum of energy because energy would have to be supplied to force the atoms still closer together. The depth of this *energy well*, $E_{a=\infty} - E_{\min}$, represents the bonding energy, because that much energy would be released (−) as two atoms are brought together (at 0 K). The data of Table 2–3.1 list such values for covalent bonds.*

The schematic representations of Fig. 2–5.2 will be useful to us on various occasions in subsequent sections, when we pay attention to elastic moduli, thermal expansion, theoretical strengths, melting and vaporization temperatures, etc.

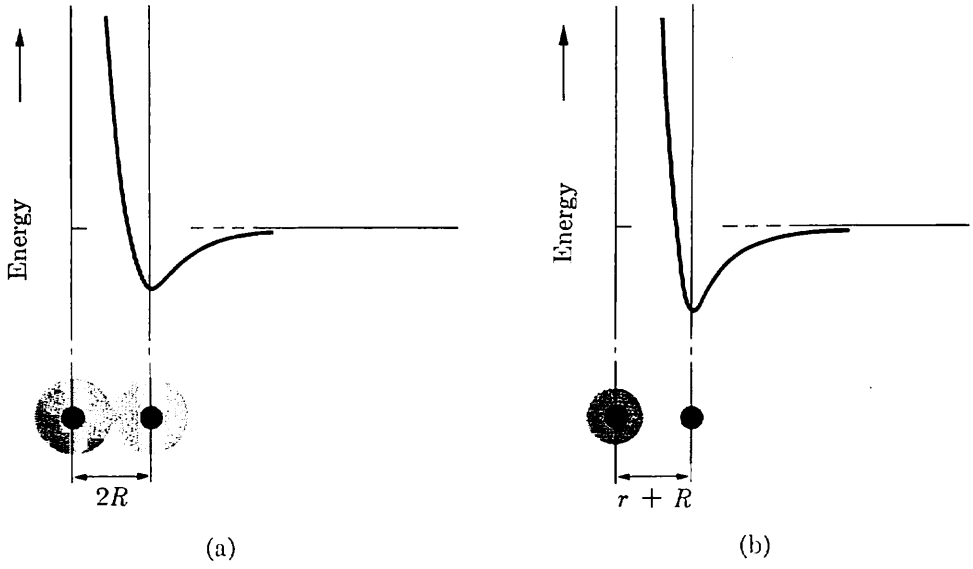

Fig. 2–5.3 Bond lengths. The distance of minimum energy between two adjacent atoms is the bond length. It is equal to the sum of the two radii. (a) In a pure metal, all atoms have the same radius. (b) In an ionic solid, the radii are different because the two adjacent ions are never identical.

Atomic and ionic radii The equilibrium distance between the centers of two neighboring atoms may be considered to be the sum of their radii (Fig. 2–5.3). In metallic iron, for example, the mean distance between the centers of the atoms is 0.2482 nm (or 2.482 Å) at room temperature. Since both atoms are the same, the radius of the iron atom is 0.1241 nm.

* The attraction forces of covalent bonds are more complicated than those of the coulombic forces which were presented in Eq. (2–5.1). However, a comparable energy well exists.

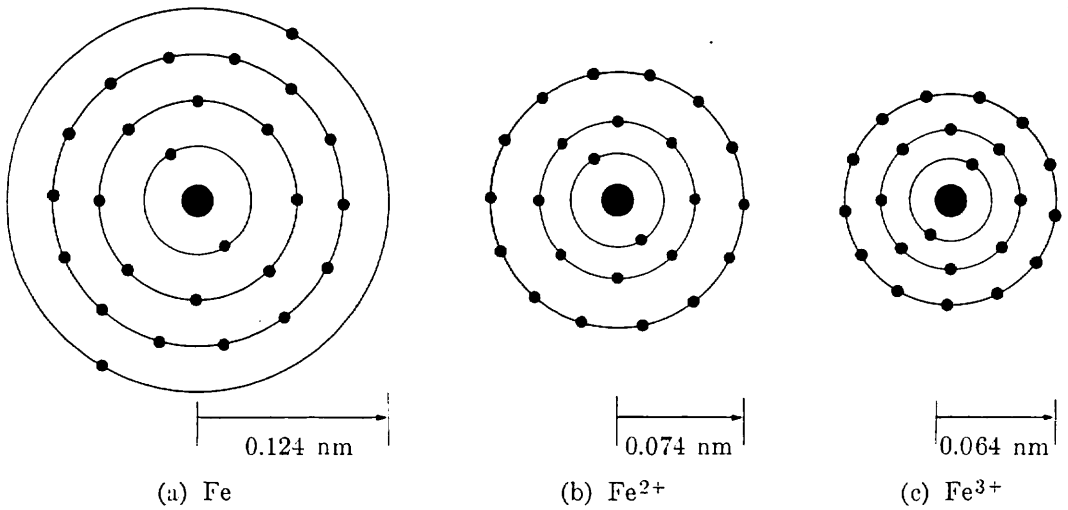

Fig. 2–5.4 Atom and ion sizes (schematic). (a) Both iron atoms and iron ions have the same number of protons (26). (b) If two electrons are removed, the remaining 24 electrons and adjacent negative ions are pulled closer to the 26-proton nucleus. (c) A ferric ion holds its 23 electrons still closer to the nucleus.

Several factors can change this distance between atom centers. The first is temperature. Any increase in energy above the minimum point shown in Fig. 2–5.2(b) will increase the mean distance because the energy trough is asymmetric. This increase in the mean spacing between atoms accounts for the thermal expansion of materials.

Ionic valence also influences interatomic spacing. The ferrous iron ion (Fe^{2+}) has a radius of 0.074 nm, which is smaller than that of the metallic iron atom (Table 2–5.1 and Appendix B*). Since the two outer valence electrons of the iron ion have been removed (Fig. 2–5.4), the remaining 24 electrons are pulled in closer to the nucleus, which still maintains a positive charge of 26. A further reduction in interatomic spacing is observed when another electron is removed to produce the ferric ion (Fe^{3+}). The radius of this ion is 0.064 nm or only about one half that of metallic iron.

A negative ion is larger than its corresponding atom. Since there are more electrons surrounding the nucleus than there are protons in the nucleus, the added electrons are not as closely attracted to the nucleus as were the original electrons.

A third factor affecting the size of the atom or ion is the number of adjacent atoms. An iron atom has a radius of 0.1241 nm when it is in contact with eight adjacent iron atoms, which is the normal arrangement at room temperature. If the atoms are rearranged to place this one iron atom in contact with twelve other iron atoms, the radius of each atom is increased slightly, to ~0.127 nm. With a large number of adjacent atoms, there is more electronic repulsion from neighboring atoms, and consequently the interatomic distances are increased. (Table 2–5.1).

* The metallic radii used in this book are from the ASM *Metals Handbook*. The ionic radii are patterned after Ahrens.

Table 2–5.1
Selected atomic radii

Element	Metallic atoms		Ions			Covalent bonds	
	CN*	Radius, nm	Valence	CN*	Radius, nm†	(Bond distance)/2, nm	
Carbon						Single	0.077
						Double	0.065
						Triple	0.06
Silicon			4+	6	0.042	Single	0.117
			4+	4	0.038		
Oxygen			2−	8	0.144	Single	0.075
			2−	6	0.140	Double	0.065
			2−	4	0.127		
			2−	2	~0.114		
Chlorine			1−	8	0.187	Single	0.099
			1−	6	0.181		
Sodium	8	0.1857	1+	6	0.097		
Magnesium	12	0.161	2+	6	0.066		
Aluminum	12	0.1431	3+	6	0.051		
			3+	4	0.046		
Iron	8	0.1241	2+	6	0.074		
	12	~0.127	3+	6	0.064		
Copper	12	0.1278	1+	6	0.096		

* CN = coordination number, i.e., the number of immediate neighbors. For ions, 1.1 $R_{CN=4} \approx R_{CN=6} \approx 0.97\ R_{CN=8}$.
† These values vary slightly with the system used. Patterned after Ahrens.

We generally do not speak of atomic radii in covalently bonded materials because the electron distributions may be far from spherical (Fig. 2–3.3a). Furthermore, with stereospecific bonds (Section 2–2), the limiting factor in atomic coordination is not the atom size, but rather the number of electron pairs available. Even so, we may make some comparisons of interatomic distances when we look at Table 2–5.1. In ethane with a single C—C bond, this nucleus-to-nucleus distance is 0.154 nm as compared with 0.13 nm for a C=C bond and 0.12 nm for the C≡C bond. This change is to be expected, since the bonding energies are greater with the multiple bonds (Table 2–3.1).

• **Example 2–5.1** MgO and NaCl are comparable, except that Mg^{2+} and O^{2-} ions are divalent and Na^+ and Cl^- ions are monovalent. Therefore, the Mg—O interatomic distance is 0.21 nm while the latter is 0.28 nm. Compare the coulombic attractive forces ($\rightarrow\leftarrow$) that are developed at these two distances for the two pairs of ions.

Solution: From Eq. (2–5.1) and the adjacent footnote,

$$F_{Mg\rightarrow\leftarrow O} = -(9 \times 10^9\ V\cdot m/C)\left(\frac{(+2)(-2)(0.16 \times 10^{-18}\ C)^2}{(0.21 \times 10^{-9}\ m)^2}\right)$$

$$= 20.9 \times 10^{-9}\ J/m.$$

Similarly,

$$F_{Na\rightarrow\leftarrow Cl} = 2.9 \times 10^{-9}\ \text{J/m}.$$

Comments. The opposing electronic repulsive forces (Eq. 2–5.2) will be -20.9 nJ/m and -2.9 nJ/m at these equilibrium distances. Thus, from Eq. (2–5.2), the empirical constant b is $\sim 0.4 \times 10^{-105}$ Jm^9 for MgO, and $\sim 10^{-105}$ Jm^9 for NaCl (assuming $n = 9$). ◀

• **Example 2–5.2** Compare the energy of the $Mg^{2+} \rightarrow\leftarrow O^{2-}$ bond with the energy of the $Na^{+} \rightarrow\leftarrow Cl^{-}$ bond. By combining Eqs. (2–5.1) and (2–5.2) into Eq. (2–5.4), and integrating from ∞ to a, we obtain

$$E = k_0 Z_1 Z_2 q^2/a + b/a^n. \tag{2–5.5}$$

Solution: Using data from Example 2–5.1,

$$E_{Mg-O} = \frac{(9 \times 10^9\ \text{V·m/C})(-4)(0.16 \times 10^{-18}\ \text{C})^2}{0.21 \times 10^{-9}\ \text{m}} + \frac{0.4 \times 10^{-105}\ \text{Jm}^9}{(0.21 \times 10^{-9}\ \text{m})^9}$$

$$= -4.4 \times 10^{-18}\ \text{J} + 0.5 \times 10^{-18}\ \text{J}$$

$$= -3.9 \times 10^{-18}\ \text{J};$$

$$E_{Na-Cl} = -0.8 \times 10^{-18}\ \text{J} + 0.1 \times 10^{-18}\ \text{J}$$

$$= -0.7 \times 10^{-18}\ \text{J}.$$

Comments. We integrated from ∞ to a, rather than from a to ∞, since our reference energy is at infinite separation. The negative values indicate that energy is given off as the ions approach each other from a distance. In this energy range, it is common to use electron volts (1 joule = 6.24×10^{18} eV); therefore, the two calculated energies are -24 eV and -4.4 eV, respectively. ◀

2–6 COORDINATION NUMBER

Much of our discussion has been about diatomic combinations that involve only two atoms. However, since most engineering materials have coordinated groups of many atoms, attention must be given to polyatomic groups. Therefore, when we are analyzing the bonding of atoms within materials, we speak of a *coordination number.* The coordination number, CN, simply refers to the number of first neighbors that an atom has. Thus, in Fig. 2–3.3, the coordination number for carbon is four. In contrast, the hydrogens have only one immediate neighbor, so that their coordination numbers are only one. In Fig. 2–6.1, the Mg^{2+} ion has CN = 6.

Two factors control the coordination number of an atom. The first is covalency. Specifically, the number of covalent bonds around an atom is dependent on the number of its valence electrons. Thus the halides, which are in Group VII of the periodic table (Fig. 2–1.1), form only one bond and thus have a coordination number of one when bonded covalently. The members of the oxygen family in Group VI are held in a molecule with two bonds and normally have a maximum coordination number of two. (Of course, oxygen may be coordinated with only one other atom through a double bond.) The nitrogen elements have a maximum coordination number of three since they are in Group V. Finally, carbon and silicon, in Group IV, have four bonds with other atoms, and a maximum coordination number of four (Fig. 2–2.4b).

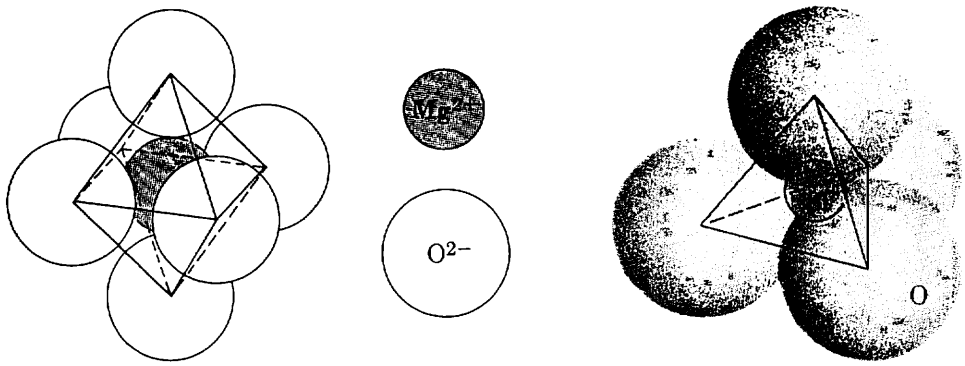

Fig. 2–6.1 Coordination numbers for ionic bonding. (a) A maximum of six oxygen ions (O^{2-}) can surround each magnesium ion (Mg^{2+}). (b) The coordination number of Si^{4+} among O^{2-} is only four because the ion-size ratio is less than 0.41 (Table 2–6.1).

The second factor affecting the coordination number is efficient atomic packing. Since energy is released as ions of unlike charges approach each other, ionic compounds generally have high *coordination numbers*, i.e., as many neighbors as possible without introducing the strong mutual repulsion forces between ions of like charges. This was illustrated in Fig. 2–2.2 with NaCl and is shown again in Fig. 2–6.1(a) with Mg^{2+} ions surrounded by O^{2-} ions. The Mg^{2+} ion has a radius r of 0.066 nm (Table 2–5.1 and Appendix B). This is large enough to permit six O^{2-} ions ($R = 0.140$ nm) to surround it without direct "contact" of negative ions with one another. The minimum radius ratio (r/R), possible for six neighbors without interference, is 0.41 (Table 2–6.1). A coordination number of six (CN = 6) is encountered widely in ionic compounds.

Table 2–6.1
COORDINATION NUMBERS VERSUS MINIMUM RADII RATIOS

Coordination number	Radii ratios, r/R*	Coordination geometry
3-fold	≥0.155	
4	≥0.225	
6	≥0.414	
8	≥0.732	
12	1.0	—

* r—smaller radius; R—larger radius.

Later, in Chapter 8, we will observe that silicon of SiO_2 has CN = 4 because an Si^{4+} ion is too small to have six coordinating oxygen ions. Since r/R for Si/O is approximately 0.3, this is consistent with the prediction of Table 2–6.1 and is shown schematically in Fig. 2–6.1(b). Another factor also favors CN = 4 for silicon among oxygens. There is considerable electron sharing between the two atoms. (Recall that the last short paragraph of Section 2–2 indicated that mixed bonding is widespread.) As with carbon, four is the maximum number of covalent bonds for silicon under normal conditions. Thus, with sharing, the probability of a CN = 4 is increased over what it would be on the basis of radius alone.

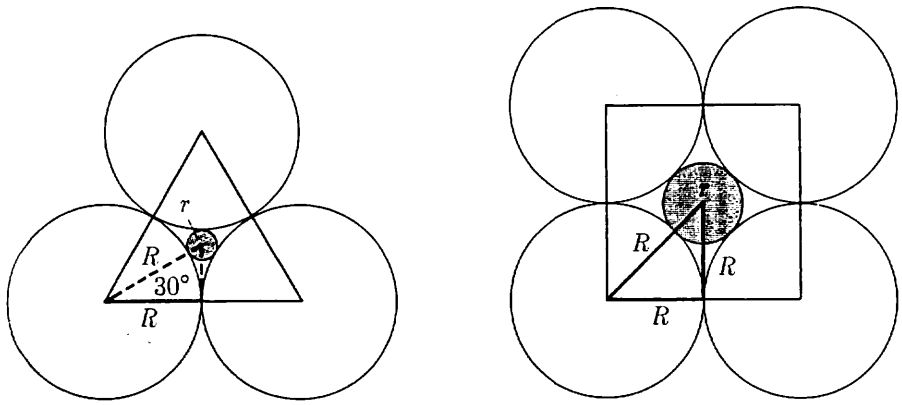

Fig. 2–6.2 Coordination calculations. (a) Three-fold coordination. (b) Six-fold coordination. (Compare with Example problems and Fig. 2–6.1a.)

Example 2–6.1 Show the significance of 0.15 as the minimum ratio for a coordination number of three (Table 2–6.1).

Solution: The minimum ratio of sizes possible to permit a coordination number of three is shown in Fig. 2–6.2(a). In this relationship,

$$\cos 30^\circ = \frac{R}{R + r} = 0.866. \qquad \frac{r}{R} = \frac{1 - 0.866}{0.866} = 0.15. \blacktriangleleft$$

Example 2–6.2 Show the significance of 0.41 as the minimum ratio for a coordination number of six.

Solution: The minimum ratio of sizes possible to permit a coordination number of six is shown in Fig. 2–6.2(b). In this relationship,

$$(r + R)^2 = R^2 + R^2, \qquad r = \sqrt{2}\,R - R, \qquad \text{and} \qquad \frac{r}{R} = 0.41.$$

Comment. From Fig. 2–6.1(a), note that the fifth and sixth ions sit above and below the center ion of Fig. 2–6.2(b). ◀