

CRYSTALLINE AND NONCRYSTALLINE MATERIALS

3.16 SINGLE CRYSTALS

For a crystalline solid, when the periodic and repeated arrangement of atoms is perfect or extends throughout the entirety of the specimen without interruption, the result is a **single crystal**. All unit cells interlock in the same way and have the same orientation. Single crystals exist in nature, but they may also be produced artificially. They are ordinarily difficult to grow, because the environment must be carefully controlled.

If the extremities of a single crystal are permitted to grow without any external constraint, the crystal will assume a regular geometric shape having flat faces, as with some of the gem stones; the shape is indicative of the crystal structure. A photograph of several single crystals is shown in Figure 3.32. Within the past few years, single crystals have become extremely important in many of our modern technologies, in particular electronic microcircuits, which employ single crystals of silicon and other semiconductors.

3.17 POLYCRYSTALLINE MATERIALS

Most crystalline solids are composed of a collection of many small crystals or **grains**; such materials are termed **polycrystalline**. Various stages in the solidification of a polycrystalline specimen are represented schematically in Figure 3.33. Initially, small crystals or nuclei form at various positions. These have random crystallographic orientations, as indicated by the square grids. The small grains grow by the successive addition from the surrounding liquid of atoms to the structure of each. The extremities of adjacent grains impinge on one another as the solidification process approaches completion. As indicated in Figure 3.33, the crystallographic orientation varies from grain to grain. Also, there exists some atomic mismatch within the region where two grains meet; this area, called a **grain boundary**, is discussed in more detail in Section 5.8.



FIGURE 3.32 Photograph showing several single crystals of fluorite, CaF_2 . (Smithsonian Institution photograph number 38181P.)

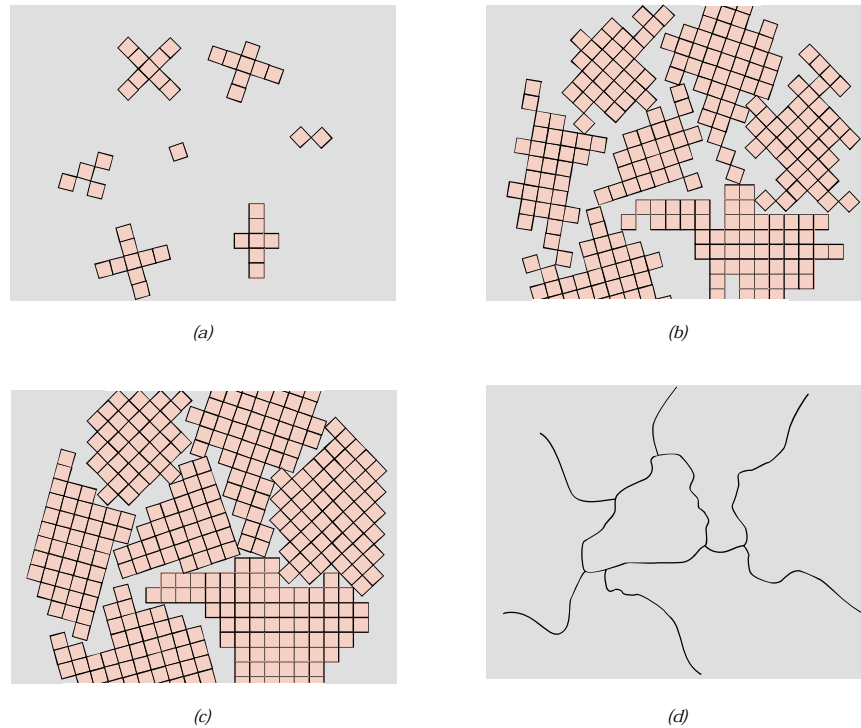


FIGURE 3.33 Schematic diagrams of the various stages in the solidification of a polycrystalline material; the square grids depict unit cells. (a) Small crystallite nuclei. (b) Growth of the crystallites; the obstruction of some grains that are adjacent to one another is also shown. (c) Upon completion of solidification, grains having irregular shapes have formed. (d) The grain structure as it would appear under the microscope; dark lines are the grain boundaries. (Adapted from W. Rosenhain, *An Introduction to the Study of Physical Metallurgy*, 2nd edition, Constable & Company Ltd., London, 1915.)

3.18 ANISOTROPY

The physical properties of single crystals of some substances depend on the crystallographic direction in which measurements are taken. For example, the elastic modulus, the electrical conductivity, and the index of refraction may have different values in the $[100]$ and $[111]$ directions. This directionality of properties is termed **anisotropy**, and it is associated with the variance of atomic or ionic spacing with crystallographic direction. Substances in which measured properties are independent of the direction of measurement are **isotropic**. The extent and magnitude of anisotropic effects in crystalline materials are functions of the symmetry of the crystal structure; the degree of anisotropy increases with decreasing structural symmetry—triclinic structures normally are highly anisotropic. The modulus of elasticity values at $[100]$, $[110]$, and $[111]$ orientations for several materials are presented in Table 3.7.

For many polycrystalline materials, the crystallographic orientations of the individual grains are totally random. Under these circumstances, even though each

Table 3.7 Modulus of Elasticity Values for Several Metals at Various Crystallographic Orientations

<i>Metal</i>	<i>Modulus of Elasticity (GPa)</i>		
	<i>[100]</i>	<i>[110]</i>	<i>[111]</i>
Aluminum	63.7	72.6	76.1
Copper	66.7	130.3	191.1
Iron	125.0	210.5	272.7
Tungsten	384.6	384.6	384.6

Source: R. W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd edition. Copyright © 1989 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

grain may be anisotropic, a specimen composed of the grain aggregate behaves isotropically. Also, the magnitude of a measured property represents some average of the directional values. Sometimes the grains in polycrystalline materials have a preferential crystallographic orientation, in which case the material is said to have a “texture.”

3.19 X-RAY DIFFRACTION: DETERMINATION OF CRYSTAL STRUCTURES (CD-ROM)

3.20 NONCRYSTALLINE SOLIDS

It has been mentioned that **noncrystalline** solids lack a systematic and regular arrangement of atoms over relatively large atomic distances. Sometimes such materials are also called **amorphous** (meaning literally without form), or supercooled liquids, inasmuch as their atomic structure resembles that of a liquid.

An amorphous condition may be illustrated by comparison of the crystalline and noncrystalline structures of the ceramic compound silicon dioxide (SiO_2), which may exist in both states. Figures 3.38*a* and 3.38*b* present two-dimensional schematic diagrams for both structures of SiO_2 , in which the SiO_4^{4-} tetrahedron is the basic unit (Figure 3.10). Even though each silicon ion bonds to four oxygen ions for both states, beyond this, the structure is much more disordered and irregular for the noncrystalline structure.

Whether a crystalline or amorphous solid forms depends on the ease with which a random atomic structure in the liquid can transform to an ordered state during solidification. Amorphous materials, therefore, are characterized by atomic or molecular structures that are relatively complex and become ordered only with some difficulty. Furthermore, rapidly cooling through the freezing temperature favors the formation of a noncrystalline solid, since little time is allowed for the ordering process.

Metals normally form crystalline solids; but some ceramic materials are crystalline, whereas others (i.e., the silica glasses) are amorphous. Polymers may be completely noncrystalline and semicrystalline consisting of varying degrees of crystallin-

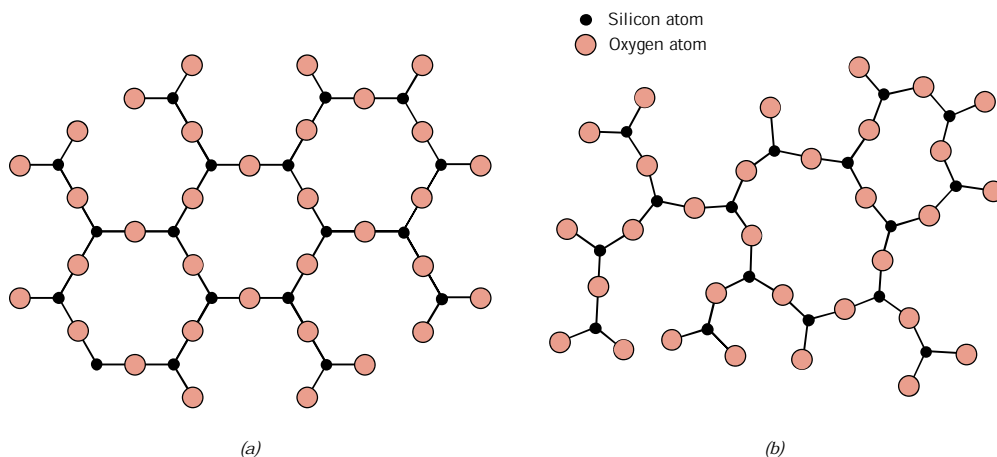


FIGURE 3.38 Two-dimensional schemes of the structure of (a) crystalline silicon dioxide and (b) noncrystalline silicon dioxide.

ity. More about the structure and properties of these amorphous materials is discussed below and in subsequent chapters.

SILICA GLASSES

Silicon dioxide (or silica, SiO_2) in the noncrystalline state is called *fused silica*, or *vitreous silica*; again, a schematic representation of its structure is shown in Figure 3.38b. Other oxides (e.g., B_2O_3 and GeO_2) may also form glassy structures (and polyhedral oxide structures {similar to those shown in Figure 3.12}); these materials, as well as SiO_2 , are *network formers*.

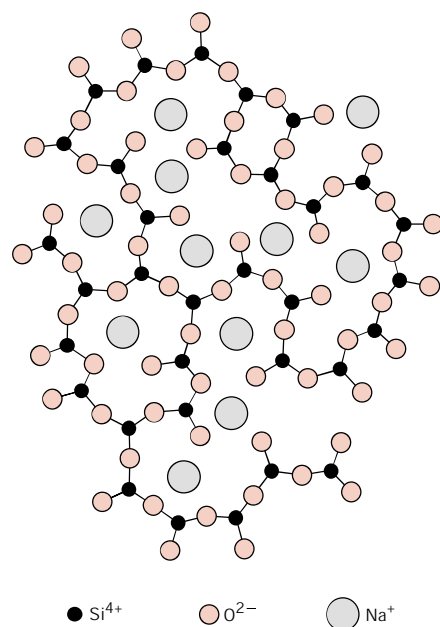
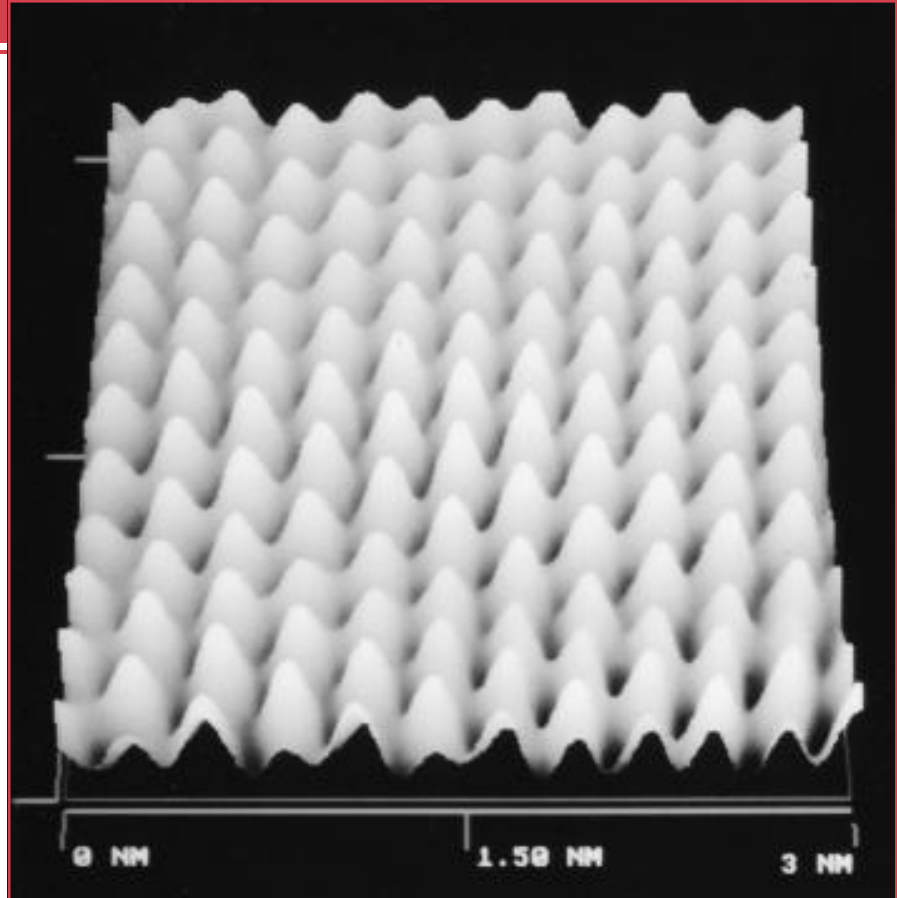


FIGURE 3.39 Schematic representation of ion positions in a sodium-silicate glass.

Chapter 2 / Atomic Structure and Interatomic Bonding

This micrograph, which represents the surface of a gold specimen, was taken with a sophisticated atomic force microscope (AFM). Individual atoms for this (111) crystallographic surface plane are resolved. Also note the dimensional scale (in the nanometer range) below the micrograph. (Image courtesy of Dr. Michael Green, TopoMetrix Corporation.)



Why Study Atomic Structure and Interatomic Bonding?

An important reason to have an understanding of interatomic bonding in solids is that, in some instances, the type of bond allows us to explain a material's properties. For example, consider carbon, which may exist as both graphite and diamond. Whereas graphite is relatively soft and

has a "greasy" feel to it, diamond is the hardest known material. This dramatic disparity in properties is directly attributable to a type of interatomic bonding found in graphite that does not exist in diamond (see Section 3.9).

Learning Objectives

After careful study of this chapter you should be able to do the following:

1. Name the two atomic models cited, and note the differences between them.
2. Describe the important quantum-mechanical principle that relates to electron energies.
3. (a) Schematically plot attractive, repulsive, and net energies versus interatomic separation for two atoms or ions.
- (b) Note on this plot the equilibrium separation and the bonding energy.
4. (a) Briefly describe ionic, covalent, metallic, hydrogen, and van der Waals bonds.
- (b) Note what materials exhibit each of these bonding types.

2.1 INTRODUCTION

Some of the important properties of solid materials depend on geometrical atomic arrangements, and also the interactions that exist among constituent atoms or molecules. This chapter, by way of preparation for subsequent discussions, considers several fundamental and important concepts, namely: atomic structure, electron configurations in atoms and the periodic table, and the various types of primary and secondary interatomic bonds that hold together the atoms comprising a solid. These topics are reviewed briefly, under the assumption that some of the material is familiar to the reader.

ATOMIC STRUCTURE

2.2 FUNDAMENTAL CONCEPTS

Each atom consists of a very small nucleus composed of protons and neutrons, which is encircled by moving electrons. Both electrons and protons are electrically charged, the charge magnitude being 1.60×10^{-19} C, which is negative in sign for electrons and positive for protons; neutrons are electrically neutral. Masses for these subatomic particles are infinitesimally small; protons and neutrons have approximately the same mass, 1.67×10^{-27} kg, which is significantly larger than that of an electron, 9.11×10^{-31} kg.

Each chemical element is characterized by the number of protons in the nucleus, or the **atomic number** (Z).¹ For an electrically neutral or complete atom, the atomic number also equals the number of electrons. This atomic number ranges in integral units from 1 for hydrogen to 92 for uranium, the highest of the naturally occurring elements.

The *atomic mass* (A) of a specific atom may be expressed as the sum of the masses of protons and neutrons within the nucleus. Although the number of protons is the same for all atoms of a given element, the number of neutrons (N) may be variable. Thus atoms of some elements have two or more different atomic masses, which are called **isotopes**. The **atomic weight** of an element corresponds to the weighted average of the atomic masses of the atom's naturally occurring isotopes.² The **atomic mass unit (amu)** may be used for computations of atomic weight. A scale has been established whereby 1 amu is defined as $\frac{1}{12}$ of the atomic mass of

¹ Terms appearing in boldface type are defined in the Glossary, which follows Appendix E.

² The term "atomic mass" is really more accurate than "atomic weight" inasmuch as, in this context, we are dealing with masses and not weights. However, atomic weight is, by convention, the preferred terminology, and will be used throughout this book. The reader should note that it is *not* necessary to divide molecular weight by the gravitational constant.

the most common isotope of carbon, carbon 12 (^{12}C) ($A = 12.00000$). Within this scheme, the masses of protons and neutrons are slightly greater than unity, and

$$A \cong Z + N \quad (2.1)$$

The atomic weight of an element or the molecular weight of a compound may be specified on the basis of amu per atom (molecule) or mass per mole of material. In one **mole** of a substance there are 6.023×10^{23} (Avogadro's number) atoms or molecules. These two atomic weight schemes are related through the following equation:

$$1 \text{ amu/atom (or molecule)} = 1 \text{ g/mol}$$

For example, the atomic weight of iron is 55.85 amu/atom, or 55.85 g/mol. Sometimes use of amu per atom or molecule is convenient; on other occasions g (or kg)/mol is preferred; the latter is used in this book.

2.3 ELECTRONS IN ATOMS

ATOMIC MODELS

During the latter part of the nineteenth century it was realized that many phenomena involving electrons in solids could not be explained in terms of classical mechanics. What followed was the establishment of a set of principles and laws that govern systems of atomic and subatomic entities that came to be known as **quantum mechanics**. An understanding of the behavior of electrons in atoms and crystalline solids necessarily involves the discussion of quantum-mechanical concepts. However, a detailed exploration of these principles is beyond the scope of this book, and only a very superficial and simplified treatment is given.

One early outgrowth of quantum mechanics was the simplified **Bohr atomic model**, in which electrons are assumed to revolve around the atomic nucleus in discrete orbitals, and the position of any particular electron is more or less well defined in terms of its orbital. This model of the atom is represented in Figure 2.1.

Another important quantum-mechanical principle stipulates that the energies of electrons are quantized; that is, electrons are permitted to have only specific values of energy. An electron may change energy, but in doing so it must make a quantum jump either to an allowed higher energy (with absorption of energy) or to a lower energy (with emission of energy). Often, it is convenient to think of these allowed electron energies as being associated with *energy levels* or *states*.

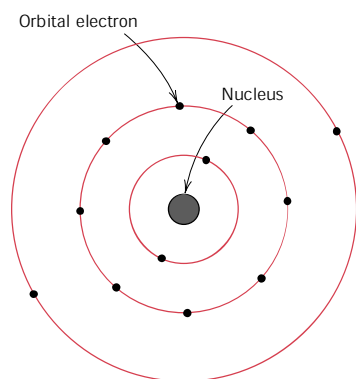
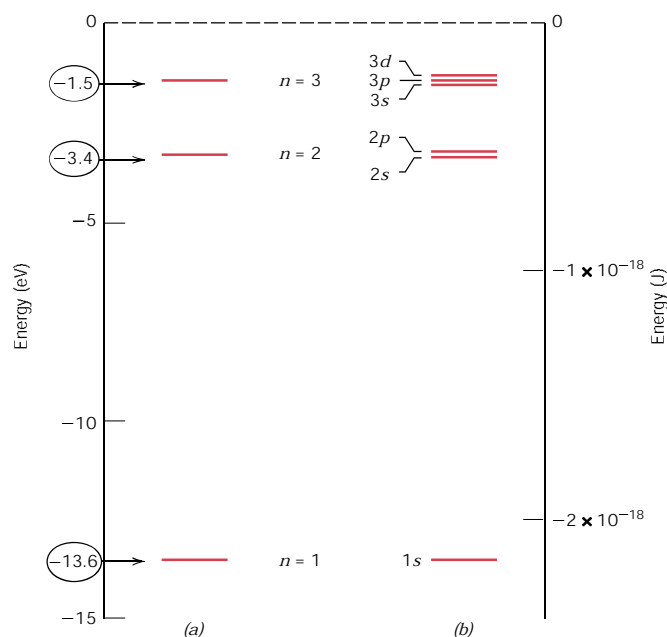


FIGURE 2.1 Schematic representation of the Bohr atom.

FIGURE 2.2 (a) The first three electron energy states for the Bohr hydrogen atom. (b) Electron energy states for the first three shells of the wave-mechanical hydrogen atom. (Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 10. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)



These states do not vary continuously with energy; that is, adjacent states are separated by finite energies. For example, allowed states for the Bohr hydrogen atom are represented in Figure 2.2a. These energies are taken to be negative, whereas the zero reference is the unbound or free electron. Of course, the single electron associated with the hydrogen atom will fill only one of these states.

Thus, the Bohr model represents an early attempt to describe electrons in atoms, in terms of both position (electron orbitals) and energy (quantized energy levels).

This Bohr model was eventually found to have some significant limitations because of its inability to explain several phenomena involving electrons. A resolution was reached with a **wave-mechanical model**, in which the electron is considered to exhibit both wavelike and particle-like characteristics. With this model, an electron is no longer treated as a particle moving in a discrete orbital; but rather, position is considered to be the probability of an electron's being at various locations around the nucleus. In other words, position is described by a probability distribution or electron cloud. Figure 2.3 compares Bohr and wave-mechanical models for the hydrogen atom. Both these models are used throughout the course of this book; the choice depends on which model allows the more simple explanation.

QUANTUM NUMBERS

Using wave mechanics, every electron in an atom is characterized by four parameters called **quantum numbers**. The size, shape, and spatial orientation of an electron's probability density are specified by three of these quantum numbers. Furthermore, Bohr energy levels separate into electron subshells, and quantum numbers dictate the number of states within each subshell. Shells are specified by a *principal quantum number* n , which may take on integral values beginning with unity; sometimes these shells are designated by the letters *K*, *L*, *M*, *N*, *O*, and so on, which correspond, respectively, to $n = 1, 2, 3, 4, 5, \dots$, as indicated in Table 2.1. It should also be

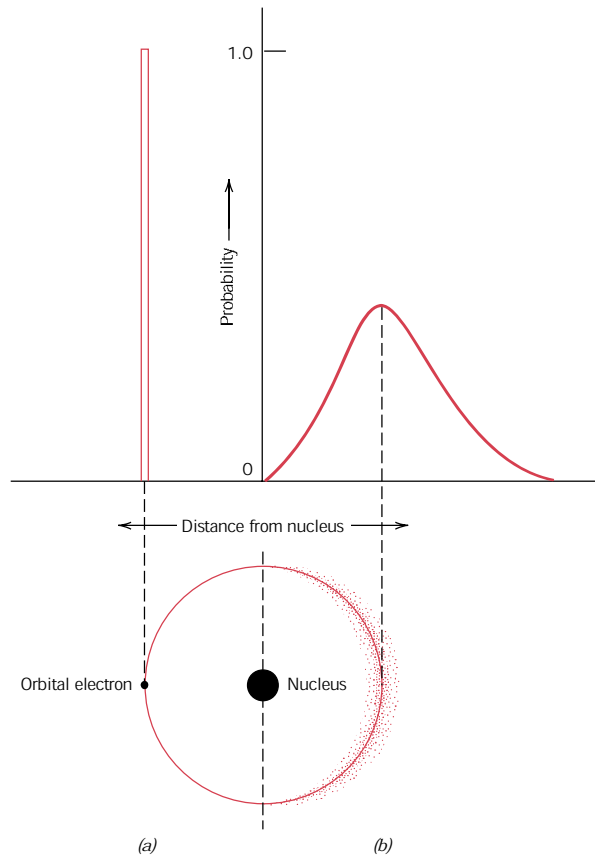


FIGURE 2.3 Comparison of the (a) Bohr and (b) wave-mechanical atom models in terms of electron distribution. (Adapted from Z. D. Jastrzebski, *The Nature and Properties of Engineering Materials*, 3rd edition, p. 4. Copyright © 1987 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

Table 2.1 The Number of Available Electron States in Some of the Electron Shells and Subshells

Principal Quantum Number n	Shell Designation	Subshells	Number of States	Number of Electrons	
				Per Subshell	Per Shell
1	K	s	1	2	2
2	L	s	1	2	8
		p	3	6	
3	M	s	1	2	18
		p	3	6	
		d	5	10	
		f	7	14	
4	N	s	1	2	32
		p	3	6	
		d	5	10	
		f	7	14	

noted that this quantum number, and it only, is also associated with the Bohr model. This quantum number is related to the distance of an electron from the nucleus, or its position.

The second quantum number, l , signifies the subshell, which is denoted by a lowercase letter—an s , p , d , or f ; it is related to the shape of the electron subshell. In addition, the number of these subshells is restricted by the magnitude of n . Allowable subshells for the several n values are also presented in Table 2.1. The number of energy states for each subshell is determined by the third quantum number, m_l . For an s subshell, there is a single energy state, whereas for p , d , and f subshells, three, five, and seven states exist, respectively (Table 2.1). In the absence of an external magnetic field, the states within each subshell are identical. However, when a magnetic field is applied these subshell states split, each state assuming a slightly different energy.

Associated with each electron is a *spin moment*, which must be oriented either up or down. Related to this spin moment is the fourth quantum number, m_s , for which two values are possible ($+\frac{1}{2}$ and $-\frac{1}{2}$), one for each of the spin orientations.

Thus, the Bohr model was further refined by wave mechanics, in which the introduction of three new quantum numbers gives rise to electron subshells within each shell. A comparison of these two models on this basis is illustrated, for the hydrogen atom, in Figures 2.2a and 2.2b.

A complete energy level diagram for the various shells and subshells using the wave-mechanical model is shown in Figure 2.4. Several features of the diagram are worth noting. First, the smaller the principal quantum number, the lower the energy level; for example, the energy of a $1s$ state is less than that of a $2s$ state, which in turn is lower than the $3s$. Second, within each shell, the energy of a subshell level increases with the value of the l quantum number. For example, the energy of a $3d$ state is greater than a $3p$, which is larger than $3s$. Finally, there may be overlap in energy of a state in one shell with states in an adjacent shell, which is especially true of d and f states; for example, the energy of a $3d$ state is greater than that for a $4s$.

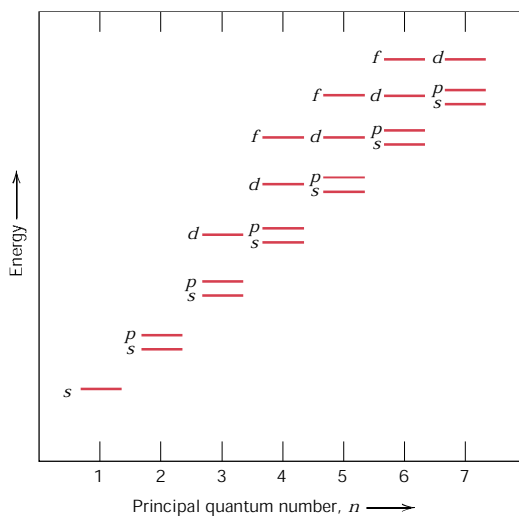


FIGURE 2.4 Schematic representation of the relative energies of the electrons for the various shells and subshells. (From K. M. Ralls, T. H. Courtney, and J. Wulff, *Introduction to Materials Science and Engineering*, p. 22. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

ELECTRON CONFIGURATIONS

The preceding discussion has dealt primarily with **electron states**—values of energy that are permitted for electrons. To determine the manner in which these states are filled with electrons, we use the **Pauli exclusion principle**, another quantum-mechanical concept. This principle stipulates that each electron state can hold no more than two electrons, which must have opposite spins. Thus, *s*, *p*, *d*, and *f* subshells may each accommodate, respectively, a total of 2, 6, 10, and 14 electrons; Table 2.1 summarizes the maximum number of electrons that may occupy each of the first four shells.

Of course, not all possible states in an atom are filled with electrons. For most atoms, the electrons fill up the lowest possible energy states in the electron shells and subshells, two electrons (having opposite spins) per state. The energy structure for a sodium atom is represented schematically in Figure 2.5. When all the electrons occupy the lowest possible energies in accord with the foregoing restrictions, an atom is said to be in its **ground state**. However, electron transitions to higher energy states are possible, as discussed in Chapters 12 {and 19.} The **electron configuration** or structure of an atom represents the manner in which these states are occupied. In the conventional notation the number of electrons in each subshell is indicated by a superscript after the shell–subshell designation. For example, the electron configurations for hydrogen, helium, and sodium are, respectively, $1s^1$, $1s^2$, and $1s^2 2s^2 2p^6 3s^1$. Electron configurations for some of the more common elements are listed in Table 2.2.

At this point, comments regarding these electron configurations are necessary. First, the **valence electrons** are those that occupy the outermost filled shell. These electrons are extremely important; as will be seen, they participate in the bonding between atoms to form atomic and molecular aggregates. Furthermore, many of the physical and chemical properties of solids are based on these valence electrons.

In addition, some atoms have what are termed “stable electron configurations”; that is, the states within the outermost or valence electron shell are completely filled. Normally this corresponds to the occupation of just the *s* and *p* states for the outermost shell by a total of eight electrons, as in neon, argon, and krypton; one exception is helium, which contains only two *1s* electrons. These elements (Ne, Ar, Kr, and He) are the inert, or noble, gases, which are virtually unreactive chemically. Some atoms of the elements that have unfilled valence shells assume

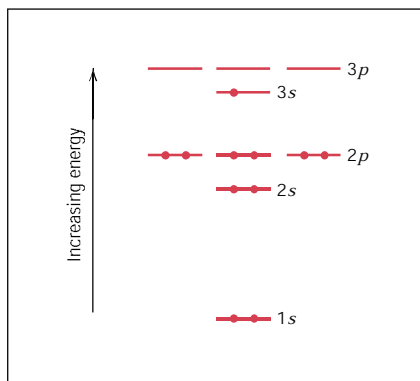


FIGURE 2.5 Schematic representation of the filled energy states for a sodium atom.

Table 2.2 A Listing of the Expected Electron Configurations for Some of the Common Elements^a

<i>Element</i>	<i>Symbol</i>	<i>Atomic Number</i>	<i>Electron Configuration</i>
Hydrogen	H	1	$1s^1$
Helium	He	2	$1s^2$
Lithium	Li	3	$1s^2 2s^1$
Beryllium	Be	4	$1s^2 2s^2$
Boron	B	5	$1s^2 2s^2 2p^1$
Carbon	C	6	$1s^2 2s^2 2p^2$
Nitrogen	N	7	$1s^2 2s^2 2p^3$
Oxygen	O	8	$1s^2 2s^2 2p^4$
Fluorine	F	9	$1s^2 2s^2 2p^5$
Neon	Ne	10	$1s^2 2s^2 2p^6$
Sodium	Na	11	$1s^2 2s^2 2p^6 3s^1$
Magnesium	Mg	12	$1s^2 2s^2 2p^6 3s^2$
Aluminum	Al	13	$1s^2 2s^2 2p^6 3s^2 3p^1$
Silicon	Si	14	$1s^2 2s^2 2p^6 3s^2 3p^2$
Phosphorus	P	15	$1s^2 2s^2 2p^6 3s^2 3p^3$
Sulfur	S	16	$1s^2 2s^2 2p^6 3s^2 3p^4$
Chlorine	Cl	17	$1s^2 2s^2 2p^6 3s^2 3p^5$
Argon	Ar	18	$1s^2 2s^2 2p^6 3s^2 3p^6$
Potassium	K	19	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
Calcium	Ca	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Scandium	Sc	21	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$
Titanium	Ti	22	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
Vanadium	V	23	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$
Chromium	Cr	24	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
Manganese	Mn	25	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$
Iron	Fe	26	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
Cobalt	Co	27	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$
Nickel	Ni	28	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$
Copper	Cu	29	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
Zinc	Zn	30	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$
Gallium	Ga	31	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$
Germanium	Ge	32	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$
Arsenic	As	33	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$
Selenium	Se	34	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$
Bromine	Br	35	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$
Krypton	Kr	36	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

^a When some elements covalently bond, they form *sp* hybrid bonds. This is especially true for C, Si, and Ge.

stable electron configurations by gaining or losing electrons to form charged ions, or by sharing electrons with other atoms. This is the basis for some chemical reactions, and also for atomic bonding in solids, as explained in Section 2.6.

Under special circumstances, the *s* and *p* orbitals combine to form hybrid *spⁿ* orbitals, where *n* indicates the number of *p* orbitals involved, which may have a value of 1, 2, or 3. The 3A, 4A, and 5A group elements of the periodic table (Figure 2.6) are those which most often form these hybrids. The driving force for the formation of hybrid orbitals is a lower energy state for the valence electrons. For carbon the *sp³* hybrid is of primary importance in organic and polymer chemistries.

The shape of the sp^3 hybrid is what determines the 109° (or tetrahedral) angle found in polymer chains (Chapter 4).

2.4 THE PERIODIC TABLE

All the elements have been classified according to electron configuration in the **periodic table** (Figure 2.6). Here, the elements are situated, with increasing atomic number, in seven horizontal rows called periods. The arrangement is such that all elements that are arrayed in a given column or group have similar valence electron structures, as well as chemical and physical properties. These properties change gradually and systematically, moving horizontally across each period.

The elements positioned in Group 0, the rightmost group, are the inert gases, which have filled electron shells and stable electron configurations. Group VIIA and VIA elements are one and two electrons deficient, respectively, from having stable structures. The Group VIIA elements (F, Cl, Br, I, and At) are sometimes termed the halogens. The alkali and the alkaline earth metals (Li, Na, K, Be, Mg, Ca, etc.) are labeled as Groups IA and IIA, having, respectively, one and two electrons in excess of stable structures. The elements in the three long periods, Groups IIIB through IIB, are termed the transition metals, which have partially filled *d* electron states and in some cases one or two electrons in the next higher energy shell. Groups IIIA, IVA, and VA (B, Si, Ge, As, etc.) display characteristics that are intermediate between the metals and nonmetals by virtue of their valence electron structures.

[illegible]

FIGURE 2.6 The periodic table of the elements. The numbers in parentheses are the atomic weights of the most stable or common isotopes.

IA																										0
1 H 2.1	IIA																				2 He -					
3 Li 1.0	4 Be 1.5															IIIA		IVA	VA	VIA	VIIA	10 Ne -				
11 Na 0.9	12 Mg 1.2			IIIB	IVB	VB	VIB	VIIIB	VIII			IB	IIB	13 Al 1.5	14 Si 1.8	15 P 2.1	16 S 2.5	17 Cl 3.0	18 Ar -							
19 K 0.8	20 Ca 1.0	21 Sc 1.3	22 Ti 1.5	23 V 1.6	24 Cr 1.6	25 Mn 1.5	26 Fe 1.8	27 Co 1.8	28 Ni 1.8	29 Cu 1.9	30 Zn 1.6	31 Ga 1.6	32 Ge 1.8	33 As 2.0	34 Se 2.4	35 Br 2.8	36 Kr -									
37 Rb 0.8	38 Sr 1.0	39 Y 1.2	40 Zr 1.4	41 Nb 1.6	42 Mo 1.8	43 Tc 1.9	44 Ru 2.2	45 Rh 2.2	46 Pd 2.2	47 Ag 1.9	48 Cd 1.7	49 In 1.7	50 Sn 1.8	51 Sb 1.9	52 Te 2.1	53 I 2.5	54 Xe -									
55 Cs 0.7	56 Ba 0.9	57-71 La-Lu 1.1-1.2	72 Hf 1.3	73 Ta 1.5	74 W 1.7	75 Re 1.9	76 Os 2.2	77 Ir 2.2	78 Pt 2.2	79 Au 2.4	80 Hg 1.9	81 Tl 1.8	82 Pb 1.8	83 Bi 1.9	84 Po 2.0	85 At 2.2	86 Rn -									
87 Fr 0.7	88 Ra 0.9	89-102 Ac-No 1.1-1.7																								

FIGURE 2.7 The electronegativity values for the elements. (Adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition. Copyright 1939 and 1940, 3rd edition copyright © 1960, by Cornell University. Used by permission of the publisher, Cornell University Press.)

As may be noted from the periodic table, most of the elements really come under the metal classification. These are sometimes termed **electropositive** elements, indicating that they are capable of giving up their few valence electrons to become positively charged ions. Furthermore, the elements situated on the right-hand side of the table are **electronegative**; that is, they readily accept electrons to form negatively charged ions, or sometimes they share electrons with other atoms. Figure 2.7 displays electronegativity values that have been assigned to the various elements arranged in the periodic table. As a general rule, electronegativity increases in moving from left to right and from bottom to top. Atoms are more likely to accept electrons if their outer shells are almost full, and if they are less “shielded” from (i.e., closer to) the nucleus.

ATOMIC BONDING IN SOLIDS

2.5 BONDING FORCES AND ENERGIES

An understanding of many of the physical properties of materials is predicated on a knowledge of the interatomic forces that bind the atoms together. Perhaps the principles of atomic bonding are best illustrated by considering the interaction between two isolated atoms as they are brought into close proximity from an infinite separation. At large distances, the interactions are negligible; but as the atoms approach, each exerts forces on the other. These forces are of two types, attractive and repulsive, and the magnitude of each is a function of the separation or interatomic distance. The origin of an attractive force F_A depends on the particular type of bonding that exists between the two atoms. Its magnitude varies with the distance, as represented schematically in Figure 2.8*a*. Ultimately, the outer electron shells of the two atoms begin to overlap, and a strong repulsive force F_R comes into play. The net force F_N between the two atoms is just the sum of both attractive and repulsive components; that is,

$$F_N = F_A + F_R \quad (2.2)$$

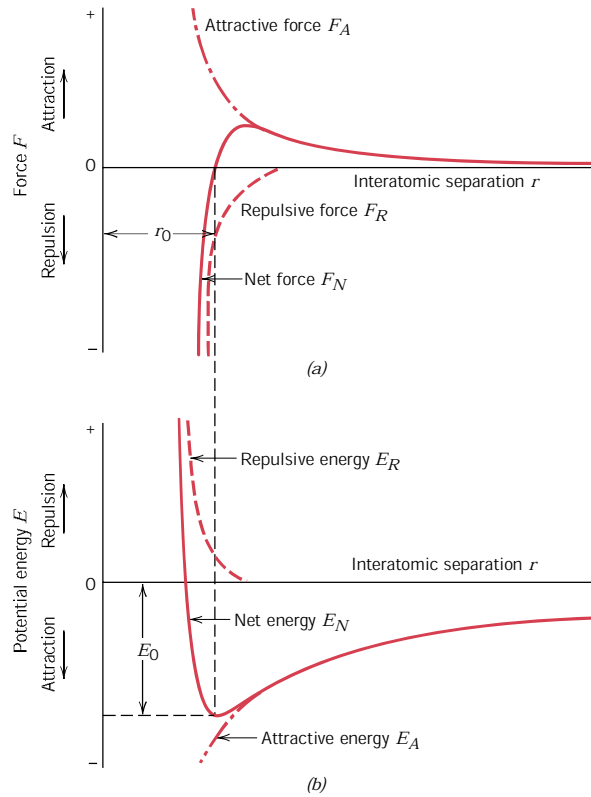


FIGURE 2.8 (a) The dependence of repulsive, attractive, and net forces on interatomic separation for two isolated atoms. (b) The dependence of repulsive, attractive, and net potential energies on interatomic separation for two isolated atoms.

which is also a function of the interatomic separation, as also plotted in Figure 2.8a. When F_A and F_R balance, or become equal, there is no net force; that is,

$$F_A + F_R = 0 \quad (2.3)$$

Then a state of equilibrium exists. The centers of the two atoms will remain separated by the equilibrium spacing r_0 , as indicated in Figure 2.8a. For many atoms, r_0 is approximately 0.3 nm (3 Å). Once in this position, the two atoms will counteract any attempt to separate them by an attractive force, or to push them together by a repulsive action.

Sometimes it is more convenient to work with the potential energies between two atoms instead of forces. Mathematically, energy (E) and force (F) are related as

$$E = \int F dr \quad (2.4)$$

Or, for atomic systems,

$$E_N = \int_{\infty}^r F_N dr \quad (2.5)$$

$$= \int_{\infty}^r F_A dr + \int_{\infty}^r F_R dr \quad (2.6)$$

$$= E_A + E_R \quad (2.7)$$

in which E_N , E_A , and E_R are respectively the net, attractive, and repulsive energies for two isolated and adjacent atoms.

Figure 2.8*b* plots attractive, repulsive, and net potential energies as a function of interatomic separation for two atoms. The net curve, which is again the sum of the other two, has a potential energy trough or well around its minimum. Here, the same equilibrium spacing, r_0 , corresponds to the separation distance at the minimum of the potential energy curve. The **bonding energy** for these two atoms, E_0 , corresponds to the energy at this minimum point (also shown in Figure 2.8*b*); it represents the energy that would be required to separate these two atoms to an infinite separation.

Although the preceding treatment has dealt with an ideal situation involving only two atoms, a similar yet more complex condition exists for solid materials because force and energy interactions among many atoms must be considered. Nevertheless, a bonding energy, analogous to E_0 above, may be associated with each atom. The magnitude of this bonding energy and the shape of the energy-versus-interatomic separation curve vary from material to material, and they both depend on the type of atomic bonding. Furthermore, a number of material properties depend on E_0 , the curve shape, and bonding type. For example, materials having large bonding energies typically also have high melting temperatures; at room temperature, solid substances are formed for large bonding energies, whereas for small energies the gaseous state is favored; liquids prevail when the energies are of intermediate magnitude. In addition, as discussed in Section 7.3, the mechanical stiffness (or modulus of elasticity) of a material is dependent on the shape of its force-versus-interatomic separation curve (Figure 7.7). The slope for a relatively stiff material at the $r = r_0$ position on the curve will be quite steep; slopes are shallower for more flexible materials. Furthermore, how much a material expands upon heating or contracts upon cooling (that is, its linear coefficient of thermal expansion) is related to the shape of its E_0 -versus- r_0 curve {(see Section 17.3).} A deep and narrow “trough,” which typically occurs for materials having large bonding energies, normally correlates with a low coefficient of thermal expansion and relatively small dimensional alterations for changes in temperature.

Three different types of primary or chemical bond are found in solids—ionic, covalent, and metallic. For each type, the bonding necessarily involves the valence electrons; furthermore, the nature of the bond depends on the electron structures of the constituent atoms. In general, each of these three types of bonding arises from the tendency of the atoms to assume stable electron structures, like those of the inert gases, by completely filling the outermost electron shell.

Secondary or physical forces and energies are also found in many solid materials; they are weaker than the primary ones, but nonetheless influence the physical properties of some materials. The sections that follow explain the several kinds of primary and secondary interatomic bonds.

2.6 PRIMARY INTERATOMIC BONDS

IONIC BONDING

Perhaps **ionic bonding** is the easiest to describe and visualize. It is always found in compounds that are composed of both metallic and nonmetallic elements, elements that are situated at the horizontal extremities of the periodic table. Atoms of a metallic element easily give up their valence electrons to the nonmetallic atoms. In the process all the atoms acquire stable or inert gas configurations and, in addition, an electrical charge; that is, they become ions. Sodium chloride (NaCl) is the classical ionic material. A sodium atom can assume the electron structure of neon (and a net single positive charge) by a transfer of its one valence 3s electron

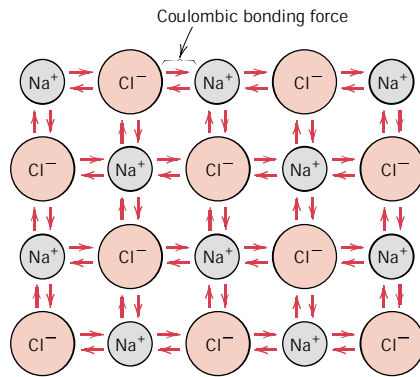


FIGURE 2.9 Schematic representation of ionic bonding in sodium chloride (NaCl).

to a chlorine atom. After such a transfer, the chlorine ion has a net negative charge and an electron configuration identical to that of argon. In sodium chloride, all the sodium and chlorine exist as ions. This type of bonding is illustrated schematically in Figure 2.9.

The attractive bonding forces are **coulombic**; that is, positive and negative ions, by virtue of their net electrical charge, attract one another. For two isolated ions, the attractive energy E_A is a function of the interatomic distance according to³

$$E_A = -\frac{A}{r} \quad (2.8)$$

An analogous equation for the repulsive energy is

$$E_R = \frac{B}{r^n} \quad (2.9)$$

In these expressions, A , B , and n are constants whose values depend on the particular ionic system. The value of n is approximately 8.

Ionic bonding is termed nondirectional, that is, the magnitude of the bond is equal in all directions around an ion. It follows that for ionic materials to be stable, all positive ions must have as nearest neighbors negatively charged ions in a three-dimensional scheme, and vice versa. The predominant bonding in ceramic materials is ionic. Some of the ion arrangements for these materials are discussed in Chapter 3.

Bonding energies, which generally range between 600 and 1500 kJ/mol (3 and 8 eV/atom), are relatively large, as reflected in high melting temperatures.⁴ Table

³ The constant A in Equation 2.8 is equal to

$$\frac{1}{4\pi\epsilon_0} (Z_1 e) (Z_2 e)$$

where ϵ_0 is the permittivity of a vacuum (8.85×10^{-12} F/m), Z_1 and Z_2 are the valences of the two ion types, and e is the electronic charge (1.602×10^{-19} C).

⁴ Sometimes bonding energies are expressed per atom or per ion. Under these circumstances the electron volt (eV) is a conveniently small unit of energy. It is, by definition, the energy imparted to an electron as it falls through an electric potential of one volt. The joule equivalent of the electron volt is as follows: 1.602×10^{-19} J = 1 eV.

Table 2.3 Bonding Energies and Melting Temperatures for Various Substances

<i>Bonding Type</i>	<i>Substance</i>	<i>Bonding Energy</i>		<i>Melting Temperature (°C)</i>
		<i>kJ/mol (kcal/mol)</i>	<i>eV/Atom, Ion, Molecule</i>	
Ionic	NaCl	640 (153)	3.3	801
	MgO	1000 (239)	5.2	2800
Covalent	Si	450 (108)	4.7	1410
	C (diamond)	713 (170)	7.4	>3550
Metallic	Hg	68 (16)	0.7	−39
	Al	324 (77)	3.4	660
	Fe	406 (97)	4.2	1538
	W	849 (203)	8.8	3410
van der Waals	Ar	7.7 (1.8)	0.08	−189
	Cl ₂	31 (7.4)	0.32	−101
Hydrogen	NH ₃	35 (8.4)	0.36	−78
	H ₂ O	51 (12.2)	0.52	0

2.3 contains bonding energies and melting temperatures for several ionic materials. Ionic materials are characteristically hard and brittle and, furthermore, electrically and thermally insulative. As discussed in subsequent chapters, these properties are a direct consequence of electron configurations and/or the nature of the ionic bond.

COVALENT BONDING

In **covalent bonding** stable electron configurations are assumed by the sharing of electrons between adjacent atoms. Two atoms that are covalently bonded will each contribute at least one electron to the bond, and the shared electrons may be considered to belong to both atoms. Covalent bonding is schematically illustrated in Figure 2.10 for a molecule of methane (CH₄). The carbon atom has four valence electrons, whereas each of the four hydrogen atoms has a single valence electron. Each hydrogen atom can acquire a helium electron configuration (two 1s valence electrons) when the carbon atom shares with it one electron. The carbon now has four additional shared electrons, one from each hydrogen, for a total of eight valence

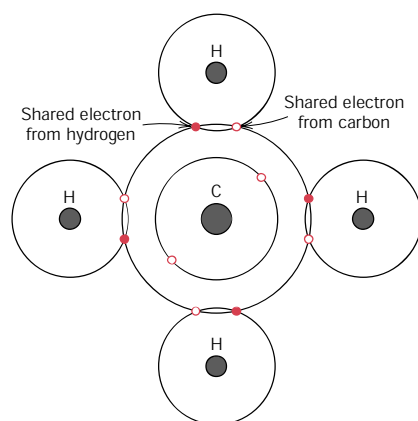


FIGURE 2.10 Schematic representation of covalent bonding in a molecule of methane (CH₄).

electrons, and the electron structure of neon. The covalent bond is directional; that is, it is between specific atoms and may exist only in the direction between one atom and another that participates in the electron sharing.

Many nonmetallic elemental molecules (H_2 , Cl_2 , F_2 , etc.) as well as molecules containing dissimilar atoms, such as CH_4 , H_2O , HNO_3 , and HF , are covalently bonded. Furthermore, this type of bonding is found in elemental solids such as diamond (carbon), silicon, and germanium and other solid compounds composed of elements that are located on the right-hand side of the periodic table, such as gallium arsenide (GaAs), indium antimonide (InSb), and silicon carbide (SiC).

The number of covalent bonds that is possible for a particular atom is determined by the number of valence electrons. For N' valence electrons, an atom can covalently bond with at most $8 - N'$ other atoms. For example, $N' = 7$ for chlorine, and $8 - N' = 1$, which means that one Cl atom can bond to only one other atom, as in Cl_2 . Similarly, for carbon, $N' = 4$, and each carbon atom has $8 - 4$, or four, electrons to share. Diamond is simply the three-dimensional interconnecting structure wherein each carbon atom covalently bonds with four other carbon atoms. This arrangement is represented in Figure 3.16.

Covalent bonds may be very strong, as in diamond, which is very hard and has a very high melting temperature, $>3550^\circ C$ ($6400^\circ F$), or they may be very weak, as with bismuth, which melts at about $270^\circ C$ ($518^\circ F$). Bonding energies and melting temperatures for a few covalently bonded materials are presented in Table 2.3. Polymeric materials typify this bond, the basic molecular structure being a long chain of carbon atoms that are covalently bonded together with two of their available four bonds per atom. The remaining two bonds normally are shared with other atoms, which also covalently bond. Polymeric molecular structures are discussed in detail in Chapter 4.

It is possible to have interatomic bonds that are partially ionic and partially covalent, and, in fact, very few compounds exhibit pure ionic or covalent bonding. For a compound, the degree of either bond type depends on the relative positions of the constituent atoms in the periodic table (Figure 2.6) or the difference in their electronegativities (Figure 2.7). The wider the separation (both horizontally—relative to Group IVA—and vertically) from the lower left to the upper-right-hand corner (i.e., the greater the difference in electronegativity), the more ionic the bond. Conversely, the closer the atoms are together (i.e., the smaller the difference in electronegativity), the greater the degree of covalency. The percent ionic character of a bond between elements A and B (A being the most electronegative) may be approximated by the expression

$$\% \text{ ionic character} = \{1 - \exp[-(0.25)(X_A - X_B)^2]\} \times 100 \quad (2.10)$$

where X_A and X_B are the electronegativities for the respective elements.

METALLIC BONDING

Metallic bonding, the final primary bonding type, is found in metals and their alloys. A relatively simple model has been proposed that very nearly approximates the bonding scheme. Metallic materials have one, two, or at most, three valence electrons. With this model, these valence electrons are not bound to any particular atom in the solid and are more or less free to drift throughout the entire metal. They may be thought of as belonging to the metal as a whole, or forming a “sea of electrons” or an “electron cloud.” The remaining nonvalence electrons and atomic nuclei form what are called *ion cores*, which possess a net positive charge equal in magnitude to the total valence electron charge per atom. Figure 2.11 is a

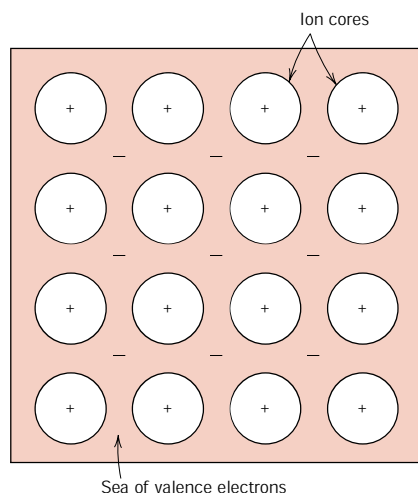


FIGURE 2.11 Schematic illustration of metallic bonding.

schematic illustration of metallic bonding. The free electrons shield the positively charged ion cores from mutually repulsive electrostatic forces, which they would otherwise exert upon one another; consequently the metallic bond is nondirectional in character. In addition, these free electrons act as a “glue” to hold the ion cores together. Bonding energies and melting temperatures for several metals are listed in Table 2.3. Bonding may be weak or strong; energies range from 68 kJ/mol (0.7 eV/atom) for mercury to 850 kJ/mol (8.8 eV/atom) for tungsten. Their respective melting temperatures are -39 and 3410°C (-38 and 6170°F).

Metallic bonding is found for Group IA and IIA elements in the periodic table, and, in fact, for all elemental metals.

Some general behaviors of the various material types (i.e., metals, ceramics, polymers) may be explained by bonding type. For example, metals are good conductors of both electricity and heat, as a consequence of their free electrons (see Sections 12.5, 12.6, {and 17.4}). By way of contrast, ionically and covalently bonded materials are typically electrical and thermal insulators, due to the absence of large numbers of free electrons.

Furthermore, in Section 8.5 we note that at room temperature, most metals and their alloys fail in a ductile manner; that is, fracture occurs after the materials have experienced significant degrees of permanent deformation. This behavior is explained in terms of deformation mechanism (Section 8.3), which is implicitly related to the characteristics of the metallic bond. Conversely, at room temperature ionically bonded materials are intrinsically brittle as a consequence of the electrically charged nature of their component ions (see Section 8.15).

2.7 SECONDARY BONDING OR VAN DER WAALS BONDING

Secondary, van der Waals, or physical bonds are weak in comparison to the primary or chemical ones; bonding energies are typically on the order of only 10 kJ/mol (0.1 eV/atom). Secondary bonding exists between virtually all atoms or molecules, but its presence may be obscured if any of the three primary bonding types is present. Secondary bonding is evidenced for the inert gases, which have stable

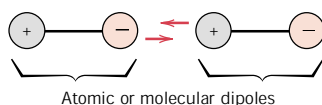


FIGURE 2.12 Schematic illustration of van der Waals bonding between two dipoles.

electron structures, and, in addition, between molecules in molecular structures that are covalently bonded.

Secondary bonding forces arise from atomic or molecular **dipoles**. In essence, an electric dipole exists whenever there is some separation of positive and negative portions of an atom or molecule. The bonding results from the coulombic attraction between the positive end of one dipole and the negative region of an adjacent one, as indicated in Figure 2.12. Dipole interactions occur between induced dipoles, between induced dipoles and polar molecules (which have permanent dipoles), and between polar molecules. **Hydrogen bonding**, a special type of secondary bonding, is found to exist between some molecules that have hydrogen as one of the constituents. These bonding mechanisms are now discussed briefly.

FLUCTUATING INDUCED DIPOLE BONDS

A dipole may be created or induced in an atom or molecule that is normally electrically symmetric; that is, the overall spatial distribution of the electrons is symmetric with respect to the positively charged nucleus, as shown in Figure 2.13a. All atoms are experiencing constant vibrational motion that can cause instantaneous and short-lived distortions of this electrical symmetry for some of the atoms or molecules, and the creation of small electric dipoles, as represented in Figure 2.13b. One of these dipoles can in turn produce a displacement of the electron distribution of an adjacent molecule or atom, which induces the second one also to become a dipole that is then weakly attracted or bonded to the first; this is one type of van der Waals bonding. These attractive forces may exist between large numbers of atoms or molecules, which forces are temporary and fluctuate with time.

The liquefaction and, in some cases, the solidification of the inert gases and other electrically neutral and symmetric molecules such as H_2 and Cl_2 are realized because of this type of bonding. Melting and boiling temperatures are extremely low in materials for which induced dipole bonding predominates; of all possible intermolecular bonds, these are the weakest. Bonding energies and melting temperatures for argon and chlorine are also tabulated in Table 2.3.

POLAR MOLECULE-INDUCED DIPOLE BONDS

Permanent dipole moments exist in some molecules by virtue of an asymmetrical arrangement of positively and negatively charged regions; such molecules are termed **polar molecules**. Figure 2.14 is a schematic representation of a hydrogen

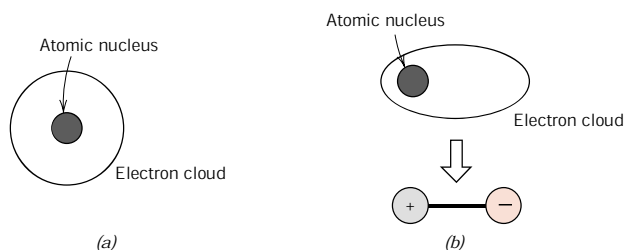


FIGURE 2.13 Schematic representations of (a) an electrically symmetric atom and (b) an induced atomic dipole.

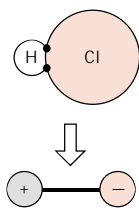


FIGURE 2.14 Schematic representation of a polar hydrogen chloride (HCl) molecule.

chloride molecule; a permanent dipole moment arises from net positive and negative charges that are respectively associated with the hydrogen and chlorine ends of the HCl molecule.

Polar molecules can also induce dipoles in adjacent nonpolar molecules, and a bond will form as a result of attractive forces between the two molecules. Furthermore, the magnitude of this bond will be greater than for fluctuating induced dipoles.

PERMANENT DIPOLE BONDS

Van der Waals forces will also exist between adjacent polar molecules. The associated bonding energies are significantly greater than for bonds involving induced dipoles.

The strongest secondary bonding type, the hydrogen bond, is a special case of polar molecule bonding. It occurs between molecules in which hydrogen is covalently bonded to fluorine (as in HF), oxygen (as in H_2O), and nitrogen (as in NH_3). For each $\text{H}-\text{F}$, $\text{H}-\text{O}$, or $\text{H}-\text{N}$ bond, the single hydrogen electron is shared with the other atom. Thus, the hydrogen end of the bond is essentially a positively charged bare proton that is unscreened by any electrons. This highly positively charged end of the molecule is capable of a strong attractive force with the negative end of an adjacent molecule, as demonstrated in Figure 2.15 for HF. In essence, this single proton forms a bridge between two negatively charged atoms. The magnitude of the hydrogen bond is generally greater than that of the other types of secondary bonds, and may be as high as 51 kJ/mol (0.52 eV/molecule), as shown in Table 2.3. Melting and boiling temperatures for hydrogen fluoride and water are abnormally high in light of their low molecular weights, as a consequence of hydrogen bonding.

2.8 MOLECULES

At the conclusion of this chapter, let us take a moment to discuss the concept of a **molecule** in terms of solid materials. A molecule may be defined as a group of atoms that are bonded together by strong primary bonds. Within this context, the entirety of ionic and metallically bonded solid specimens may be considered as a single molecule. However, this is not the case for many substances in which covalent bonding predominates; these include elemental diatomic molecules (F_2 , O_2 , H_2 , etc.) as well as a host of compounds (H_2O , CO_2 , HNO_3 , C_6H_6 , CH_4 , etc.). In the

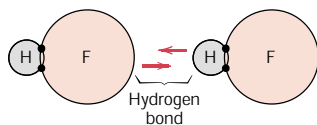


FIGURE 2.15 Schematic representation of hydrogen bonding in hydrogen fluoride (HF).

condensed liquid and solid states, bonds between molecules are weak secondary ones. Consequently, molecular materials have relatively low melting and boiling temperatures. Most of those that have small molecules composed of a few atoms are gases at ordinary, or ambient, temperatures and pressures. On the other hand, many of the modern polymers, being molecular materials composed of extremely large molecules, exist as solids; some of their properties are strongly dependent on the presence of van der Waals and hydrogen secondary bonds.

SUMMARY

This chapter began with a survey of the fundamentals of atomic structure, presenting the Bohr and wave-mechanical models of electrons in atoms. Whereas the Bohr model assumes electrons to be particles orbiting the nucleus in discrete paths, in wave mechanics we consider them to be wavelike and treat electron position in terms of a probability distribution.

Electron energy states are specified in terms of quantum numbers that give rise to electron shells and subshells. The electron configuration of an atom corresponds to the manner in which these shells and subshells are filled with electrons in compliance with the Pauli exclusion principle. The periodic table of the elements is generated by arrangement of the various elements according to valence electron configuration.

Atomic bonding in solids may be considered in terms of attractive and repulsive forces and energies. The three types of primary bond in solids are ionic, covalent, and metallic. For ionic bonds, electrically charged ions are formed by the transference of valence electrons from one atom type to another; forces are coulombic. There is a sharing of valence electrons between adjacent atoms when bonding is covalent. With metallic bonding, the valence electrons form a “sea of electrons” that is uniformly dispersed around the metal ion cores and acts as a form of glue for them.

Both van der Waals and hydrogen bonds are termed secondary, being weak in comparison to the primary ones. They result from attractive forces between electric dipoles, of which there are two types—induced and permanent. For the hydrogen bond, highly polar molecules form when hydrogen covalently bonds to a nonmetallic element such as fluorine.

IMPORTANT TERMS AND CONCEPTS

Atomic mass unit (amu)	Electronegative	Periodic table
Atomic number	Electropositive	Polar molecule
Atomic weight	Ground state	Primary bonding
Bohr atomic model	Hydrogen bond	Quantum mechanics
Bonding energy	Ionic bond	Quantum number
Coulombic force	Isotope	Secondary bonding
Covalent bond	Metallic bond	Valence electron
Dipole (electric)	Mole	van der Waals bond
Electron configuration	Molecule	Wave-mechanical model
Electron state	Pauli exclusion principle	

Note: In each chapter, most of the terms listed in the “Important Terms and Concepts” section are defined in the Glossary, which follows Appendix E. The others are important enough to warrant treatment in a full section of the text and can be referenced from the table of contents or the index.