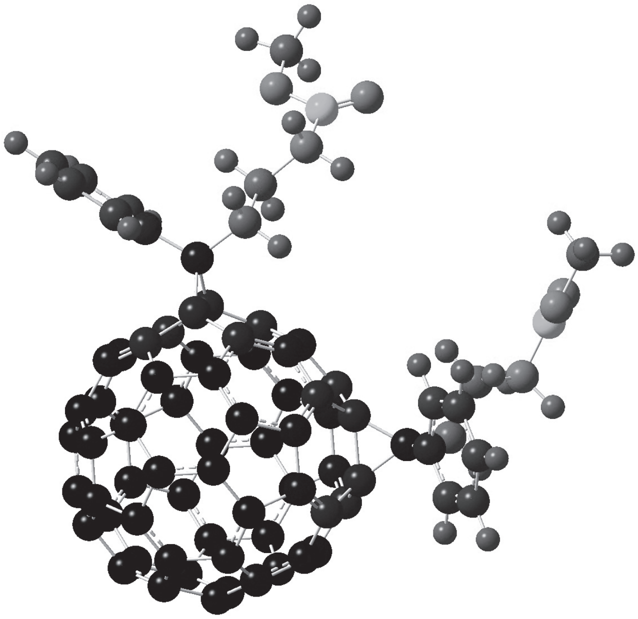
CHAPTER 2
Atomic Bonding



Computer models of the structures of materials on the atomic scale require accurate knowledge of the bonding between adjacent atoms. In this model of a molecule that plays an important role in organic photovoltaic materials, atoms are shown as spheres joined by covalent bonds. (Courtesy of Roland Faller, Adam Moule, and Varuni Dantanarayana, University of California, Davis.)

Chapter 1 introduced the basic types of materials available to engineers. One basis of that classification system is found in the nature of atomic bonding in materials. Atomic bonding falls into two general categories. *Primary bonding* involves the transfer or sharing of electrons and produces a relatively strong joining of adjacent atoms. Ionic, covalent, and metallic bonds are in this category. *Secondary bonding* involves a relatively weak attraction between atoms in which no electron transfer or sharing occurs. Van der Waals bonds are in this category. Each of the five fundamental types of engineering materials (metals, ceramics, glasses, polymers, and semiconductors) is associated with a certain type (or types) of atomic bonding. Composites, of course, are combinations of fundamental types.

2.1 Atomic Structure

In order to understand bonding between atoms, we must appreciate the structure within the individual atoms. For this purpose, it is sufficient to use a relatively simple planetary model of atomic structure—that is, **electrons** (the planets) orbit about a **nucleus** (the sun).

It is not necessary to consider the detailed structure of the nucleus for which physicists have catalogued a vast number of elementary particles. We need consider only the number of **protons** and **neutrons** in the nucleus as the basis of the chemical identification of a given atom. Figure 2.1 is a planetary model of a carbon atom. This illustration is schematic and definitely not to scale. In reality, the nucleus is much smaller, even though it contains nearly all the mass of the atom. Each proton and neutron has a mass of approximately 1.66×10^{-24} g. This value is referred to as an **atomic mass unit (amu)**. It is convenient to express the mass of elemental materials in these units. For instance, the most common

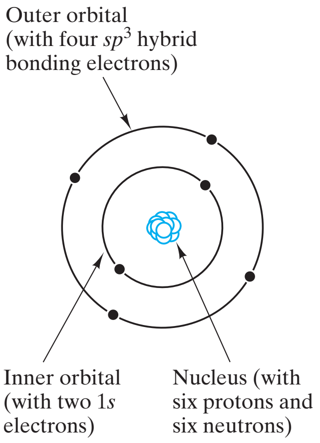


FIGURE 2.1 *Schematic of the planetary model of a* ^{12}C *atom.*

isotope of carbon, ^{12}C (shown in Figure 2.1), contains in its nucleus six protons and six neutrons, for an **atomic mass** of 12 amu. It is also convenient to note that there are 0.6023×10^{24} amu per gram. This large value, known as **Avogadro's**[*] **number**, represents the number of protons or neutrons necessary to produce a mass of 1 g. Avogadro's number of atoms of a given element is termed a **gram-atom**. For a compound, the corresponding term is **mole**; that is, one mole of NaCl contains Avogadro's number of Na atoms *and* Avogadro's number of Cl atoms.

Avogadro's number of ^{12}C atoms would have a mass of 12.00 g. Naturally occurring carbon actually has an atomic mass of 12.011 amu because not all carbon atoms contain six neutrons in their nuclei. Instead, some contain seven. Different numbers of neutrons (six or seven) identify different **isotopes**—various forms of an element that differ in the number of neutrons in the nucleus. In nature, 1.1% of the carbon atoms are the isotope ^{13}C. However, the nuclei of all carbon atoms contain six protons. In general, the number of protons in the nucleus is known as the **atomic number** of the element. The well-known periodicity of chemical elements is based on this system of elemental atomic numbers and atomic masses arranged in chemically similar **groups** (vertical columns) in a **periodic table** (Figure 2.2).

While chemical identification is done relative to the nucleus, atomic bonding involves electrons and **electron orbitals**. The electron, with a mass of

I A	II A	III B	IV B	V B	VI B	VII B	VIII			I B	II B	III A	IV A	V A	VI A	VII A	0
1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.71	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.07	45 Rh 102.91	46 Pd 106.4	47 Ag 107.87	48 Cd 112.4	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.30
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.22	78 Pt 195.09	79 Au 196.97	80 Hg 200.59	81 Tl 204.37	82 Pb 207.2	83 Bi 208.98	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.03	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)												

58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.4	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (254)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lw (260)

FIGURE 2.2 *Periodic table of the elements indicating atomic number and atomic mass (in amu).*

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[*] Amadeo Avogadro (1776–1856), Italian physicist, who, among other contributions, coined the word *molecule*. Unfortunately, his hypothesis that all gases (at a given temperature and pressure) contain the same number of molecules per unit volume was not generally acknowledged as correct until after his death.

0.911×10^{-27} g, makes a negligible contribution to the atomic mass of an element. However, this particle has a negative charge of 0.16×10^{-18} coulomb (C), equal in magnitude to the $+0.16 \times 10^{-18}$ C charge of each proton. (The neutron is, of course, electrically neutral.)

Electrons are excellent examples of the wave-particle duality; that is, they are atomic-scale entities exhibiting both wavelike and particlelike behavior. It is beyond the scope of this book to deal with the principles of quantum mechanics that define the nature of electron orbitals (based on the wavelike character of electrons). However, a brief summary of the nature of electron orbitals is helpful. As shown schematically in Figure 2.1, electrons are grouped at fixed orbital positions about a nucleus. In addition, each orbital radius is characterized by an **energy level**, a fixed binding energy between the electron and its nucleus. Figure 2.3 shows an *energy level diagram* for the electrons in a ^{12}C atom. It is important to note that the electrons around a ^{12}C nucleus occupy these specific energy levels, with intermediate energies forbidden. The forbidden energies correspond to unacceptable quantum mechanical conditions; that is, standing waves cannot be formed.

A detailed list of electronic configurations for the elements of the periodic table is given in Appendix 1, together with various useful data. The arrangement of the periodic table (Figure 2.2) is largely a manifestation of the systematic "filling" of the electron orbitals with electrons, as summarized in Appendix 1. The notation for labeling electron orbitals is derived from the quantum numbers of wave mechanics. These integers relate to solutions to the appropriate wave equations. We do not deal with this numbering system in detail in this book; instead, it is sufficient to appreciate the basic labeling system. For instance, Appendix 1 tells us that there are two electrons in the 1*s* orbital. The 1 is a principal quantum number, identifying this energy level as the first one which is closest to the atomic nucleus. There are also two electrons each associated with the 2*s* and 2*p* orbitals. The *s, p*, and so on, notation refers to an additional set of quantum numbers. The rather cumbersome letter notation is derived from the terminology of early spectrographers. The six electrons in the ^{12}C atom are then described as a

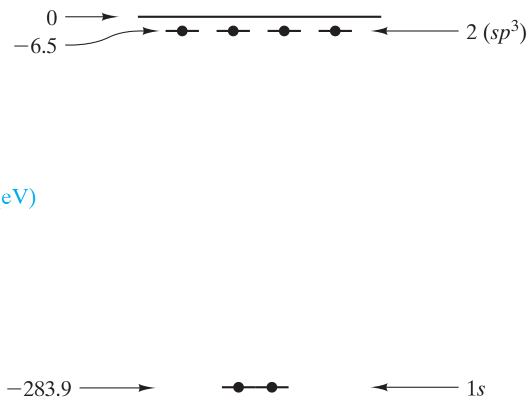


FIGURE 2.3 *Energy-level diagram for the orbital electrons in a* ^{12}C *atom. Notice the sign convention. An attractive energy is negative. The 1s electrons are closer to the nucleus (see Figure 2.1) and more strongly bound (*binding energy = −283.9 eV*). The outer orbital electrons have a binding energy of only* −6.5 eV. *The zero level of binding energy corresponds to an electron completely removed from the attractive potential of the nucleus.*

POWERS OF 10

In Section 13.2, we shall see that energy level diagrams like this are central to the understanding of energy band gap structures that are, in turn, at the heart of semiconductor technology.

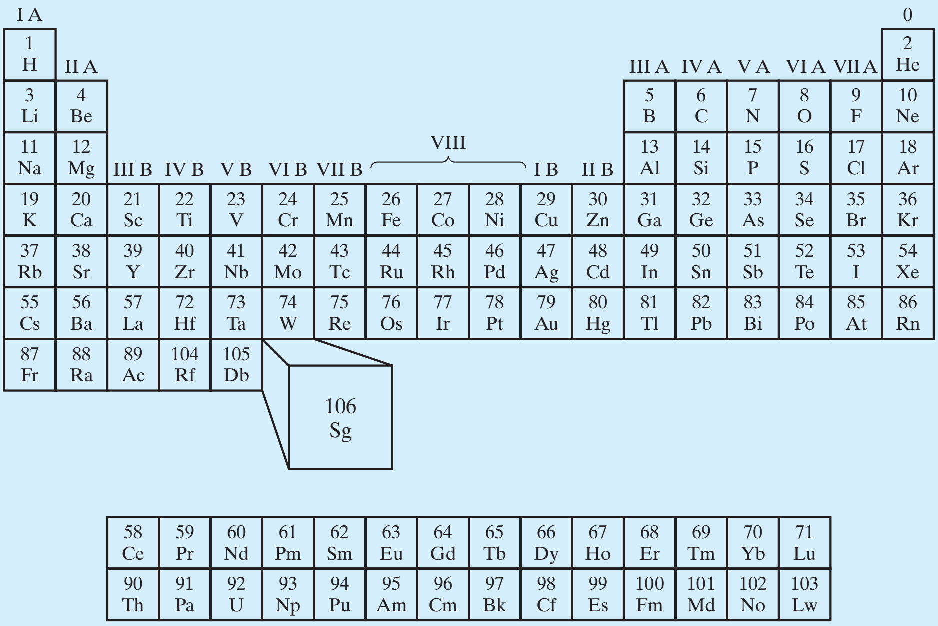
$1s^2 2s^2 2p^2$ distribution; that is, two electrons in the $1s$ orbital, two in $2s$, and two in $2p$. In fact, the four electrons in the outer orbital of ^{12}C redistribute themselves in a more symmetrical fashion to produce the characteristic geometry of bonding between carbon atoms and adjacent atoms (generally described as $1s^2 2s^1 2p^3$). This sp^3 configuration in the second energy level of carbon, called **hybridization**, is indicated in Figures 2.1 and 2.3 and is discussed in further detail in Section 2.3. (Note especially Figure 2.19.)

The bonding of adjacent atoms is essentially an electronic process. Strong **primary bonds** are formed when outer orbital electrons are transferred or shared between atoms. Weaker **secondary bonds** result from a more subtle attraction between positive and negative charges with no actual transfer or sharing of electrons. In the next section, we will look at the various possibilities of bonding in a systematic way, beginning with the ionic bond.

THE MATERIAL WORLD

Naming a New Chemical Element

The periodic table is generally one of the first items to which we are introduced as we begin to seriously explore modern science. This systematic arrangement of the chemical elements is, of course, useful for providing a visual understanding of the similarities and differences of the various chemical elements. The periodic table's role as a permanent record of this important information sometimes overshadows the fact that, at some point in time, each element had to be given a name. Some names, such as *iron*, simply have evolved from earlier languages (the Old High German *isarn* that led to the Old English *iren*, with the chemical symbol Fe coming from the Latin *ferrum*).

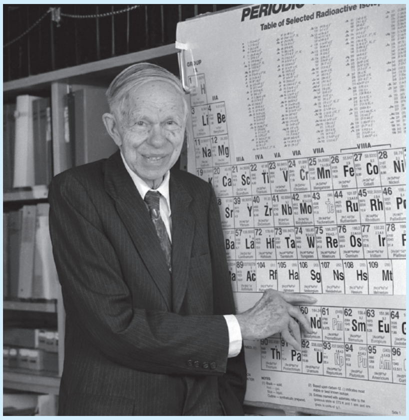


I A	II A	III B	IV B	V B	VI B	VII B	VIII			I B	II B	III A	IV A	V A	VI A	VII A	0
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg												

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lw

As some elements were discovered, they were given names in honor of the country in which they were discovered or synthesized (e.g., *germanium* for Germany). The advances in physics and chemistry in the 20th century made possible the synthesis of new elements that are not found in nature and that have atomic numbers greater than that of uranium (92). These transuranic elements were often named in honor of great scientists of the past (e.g., *mendelevium* for Dmitri Mendeleev, the 19th-century Russian chemist who devised the periodic table). The leading authority in synthesizing the transuranic elements was Dr. Glenn Seaborg (1913–1999), Professor of Chemistry at the University of California, Berkeley. (It was Seaborg's idea to reconfigure Mendeleev's original periodic table by breaking out the actinide series below the main table.) Seaborg and his team discovered plutonium and nine other transuranic elements, including element 106, which was named *seaborgium* after him.

Professor Seaborg received the singular honor of being the first person ever to have an element named after him while he was still alive. He rightfully viewed this honor as much greater than his Nobel Prize in Chemistry awarded in 1951. While seaborgium has been synthesized only in minute amounts and may not play a significant role in materials science and engineering, its namesake, Professor Seaborg, was a great advocate of the field. His enthusiasm for materials came in no small measure from his long term of service as Chair of the Atomic Energy Commission (the predecessor of today's Department of Energy). He was quoted in the January 1980 issue of *ASM News* as saying that "materials science and engineering will be essential for the solution of the problems attendant with the energy sources of the future." Professor Seaborg's vision is as true today as it was more than three decades ago.



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EXAMPLE 2.1

Chemical analysis in materials science laboratories is frequently done by means of the scanning electron microscope. In this instrument, an electron beam generates characteristic x-rays that can be used to identify chemical elements. This instrument samples a roughly cylindrical volume at the surface of a solid material. Calculate the number of atoms sampled in a 1-μm-diameter by 1-μm-deep cylinder in the surface of solid copper.

SOLUTION

From Appendix 1,

$$\text{density of copper} = 8.93\ \text{g/cm}^3$$

and

$$\text{atomic mass of copper} = 63.55\ \text{amu}.$$

The atomic mass indicates that there are

$$\frac{63.55 \text{ g Cu}}{\text{Avogadros number of Cu atoms}}.$$

The volume sampled is

$$\begin{aligned} V_{\text{sample}} &= \left(\frac{1\ \mu\text{m}}{2}\right)^2 \times 1\ \mu\text{m} \\ &= 0.785\ \mu\text{m}^3 \times \left(\frac{1 \text{ cm}}{10^4 \mu\text{m}}\right)^3 \\ &= 0.785 \times 10^{-12} \text{ cm}^3. \end{aligned}$$

Thus, the number of atoms sampled is

$$\begin{aligned} N_{\text{sample}} &= \frac{8.93 \text{ g}}{\text{cm}^3} \times 0.785 \times 10^{-12} \text{cm}^3 \times \frac{0.602 \times 10^{24} \text{atoms}}{63.55 \text{ g}} \\ &= 6.64 \times 10^{10} \text{atoms}. \end{aligned}$$

EXAMPLE 2.2

One mole of solid MgO occupies a cube 22.37 mm on a side. Calculate the density of MgO (in g/cm^3).

SOLUTION

From Appendix 1,

$$\begin{aligned} \text{mass of 1 mol of MgO} &= \text{atomic mass of Mg (in g)} \\ &\quad + \text{atomic mass of O (in g)} \\ &= 24.31 \text{ g} + 16.00 \text{ g} = 40.31 \text{ g}. \end{aligned}$$

$$\begin{aligned} \text{density} &= \frac{\text{mass}}{\text{volume}} \\ &= \frac{40.31 \text{ g}}{(22.37 \text{ mm})^3 \times 10^{-3} \text{ cm}^3/\text{mm}^3} \\ &= 3.60 \text{ g/cm}^3. \end{aligned}$$

EXAMPLE 2.3

Calculate the dimensions of a cube containing 1 mol of solid magnesium.

SOLUTION

From Appendix 1,

$$\begin{aligned} \text{density of Mg} &= 1.74 \text{ g/cm}^3. \\ \text{atomic mass of Mg} &= 24.31 \text{ amu}. \end{aligned}$$

$$\text{volume of 1 mol} = \frac{24.31\ \text{g/mol}}{1.74\ \text{g/cm}^3}$$

$$= 13.97\ \text{cm}^3/\text{mol}.$$

$$\text{edge of cube} = (13.97)^{1/3}\ \text{cm}$$

$$= 2.408\ \text{cm} \times 10\ \text{mm/cm}$$

$$= 24.08\ \text{mm}.$$

Beginning at this point, a few elementary problems, called Practice Problems, will be provided immediately following the solved example. These exercises follow directly from the preceding solutions and are intended to provide a carefully guided journey into the first calculations in each new area. More independent and challenging problems are provided at the conclusion of the chapter. Answers for nearly all of the practice problems are given following the appendices.

PRACTICE PROBLEM 2.1

Calculate the number of atoms contained in a cylinder 1 μm in diameter by 1 μm deep of **(a)** magnesium and **(b)** lead. (See Example 2.1.)

PRACTICE PROBLEM 2.2

Using the density of MgO calculated in Example 2.2, calculate the mass of an MgO refractory (temperature-resistant) brick with dimensions 50 mm × 100 mm × 200 mm.

PRACTICE PROBLEM 2.3

Calculate the dimensions of **(a)** a cube containing 1 mol of copper and **(b)** a cube containing 1 mol of lead. (See Example 2.3.)

2.2 The Ionic Bond

An **ionic bond** is the result of *electron transfer* from one atom to another. Figure 2.4 illustrates an ionic bond between sodium and chlorine. The transfer of an electron *from* sodium is favored because it produces a more stable electronic configuration; that is, the resulting Na^+ species has a full outer **orbital shell**, defined as a set of electrons in a given orbital. Similarly, the chlorine readily accepts the electron, producing a stable Cl^- species, also with a full outer orbital shell. The charged species (Na^+ and Cl^-) are termed **ions**, giving rise to the name *ionic bond*. The positive species (Na^+) is a **cation**, and the negative species (Cl^-) is an **anion**.

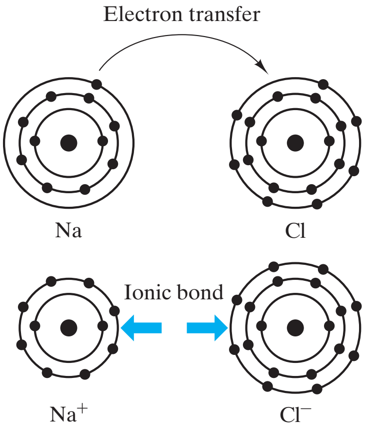

FIGURE 2.4 *Ionic bonding between sodium and chlorine atoms. Electron transfer from* Na *to* Cl *creates a cation* (Na^+) *and an anion* (Cl^-). *The ionic bond is due to the coulombic attraction between the ions of opposite charge.*

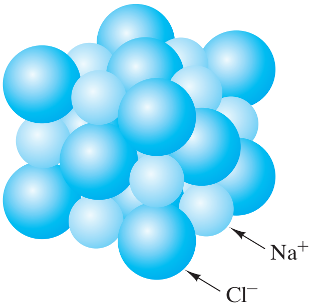

FIGURE 2.5 *Regular stacking of* Na^+ *and* Cl^- *ions in solid* NaCl, *which is indicative of the nondirectional nature of ionic bonding.*

It is important to note that the ionic bond is *nondirectional*. A positively charged Na^+ will attract any adjacent Cl^- equally in all directions. Figure 2.5 shows how Na^+ and Cl^- ions are stacked together in solid sodium chloride (rock salt). Details about this structure will be discussed in Chapter 3. For now, it is sufficient to note that this structure is an excellent example of ionically bonded material, and the Na^+ and Cl^- ions are stacked together systematically to maximize the number of oppositely charged ions adjacent to any given ion. In NaCl, six Na^+ surround each Cl^-, and six Cl^- surround each Na^+.

The ionic bond is the result of the **coulombic[*] attraction** between the oppositely charged species. It is convenient to illustrate the nature of the bonding force for the ionic bond because the coulombic attraction force follows a simple, well-known relationship,

$$F_c = \frac{-K}{a^2}, \tag{2.1}$$

where F_c is the coulombic force of attraction between two oppositely charged ions, a is the separation distance between the *centers* of the ions, and K is

$$K = k_0(Z_1 q)(Z_2 q). \tag{2.2}$$

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[*] Charles Augustin de Coulomb (1736–1806), French physicist, was first to experimentally demonstrate the nature of Equations 2.1 and 2.2 (for large spheres, not ions). Beyond major contributions to the understanding of electricity and magnetism, Coulomb was an important pioneer in the field of applied mechanics (especially in the areas of friction and torsion).

In the preceding equation, Z is the **valence** of the charged ion (e.g., +1 for Na^+ and −1 for Cl^-), q is the charge of a single electron (0.16×10^{-18}C), and k_0 is a proportionality constant ($9 \times 10^9 \; V \cdot m/C$).

A plot of Equation 2.1, shown in Figure 2.6, demonstrates that the coulombic force of attraction increases dramatically as the separation distance between adjacent ion centers (a) decreases. This relationship, in turn, implies that the **bond length** (a) would ideally be zero. In fact, bond lengths are most definitely not zero because the attempt to move two oppositely charged ions closer together to increase coulombic attraction is counteracted by an opposing **repulsive force**, F_R, which is due to the overlapping of the similarly charged (negative) electric fields from each ion, as well as the attempt to bring the two positively charged nuclei closer together. The repulsive force as a function of a follows an exponential relationship

$$F_R = \lambda e^{-a/r}, \tag{2.3}$$

where λ and ρ are experimentally determined constants for a given ion pair. **Bonding force** is the net force of attraction (or repulsion) as a function of the separation distance between two atoms or ions. Figure 2.7 shows the *bonding force curve* for an ion pair in which the *net* bonding force, F $(= F_c + F_R)$, is plotted against a. The *equilibrium bond length*, a_0, occurs at the point where the forces of attraction and repulsion are precisely balanced ($F_c + F_R = 0$). It should be noted that the coulombic force (Equation 2.1) dominates for larger values of a, whereas the repulsive force (Equation 2.3) dominates for small values of a. Up to this point, we have concentrated on the attractive coulombic force between two ions of opposite charge. Of course, bringing two similarly charged ions together would produce a coulombic *repulsive force* (separate from the F_R term). In an ionic solid such as that shown in Figure 2.5, the

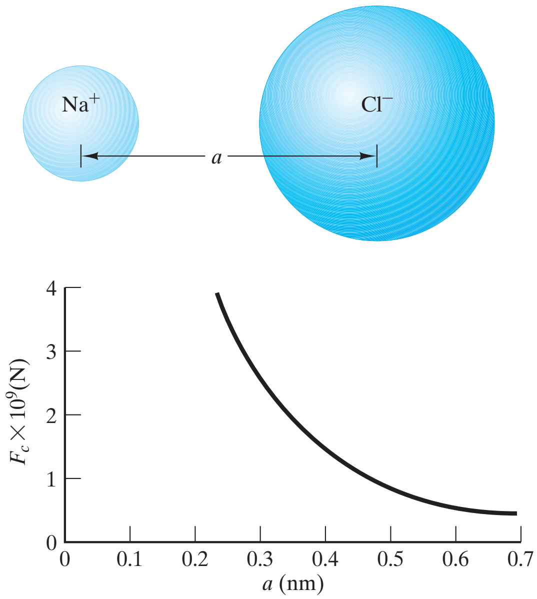


FIGURE 2.6 *Plot of the coulombic force (Equation 2.1) for a* $Na^+ - Cl^-$ *pair.*

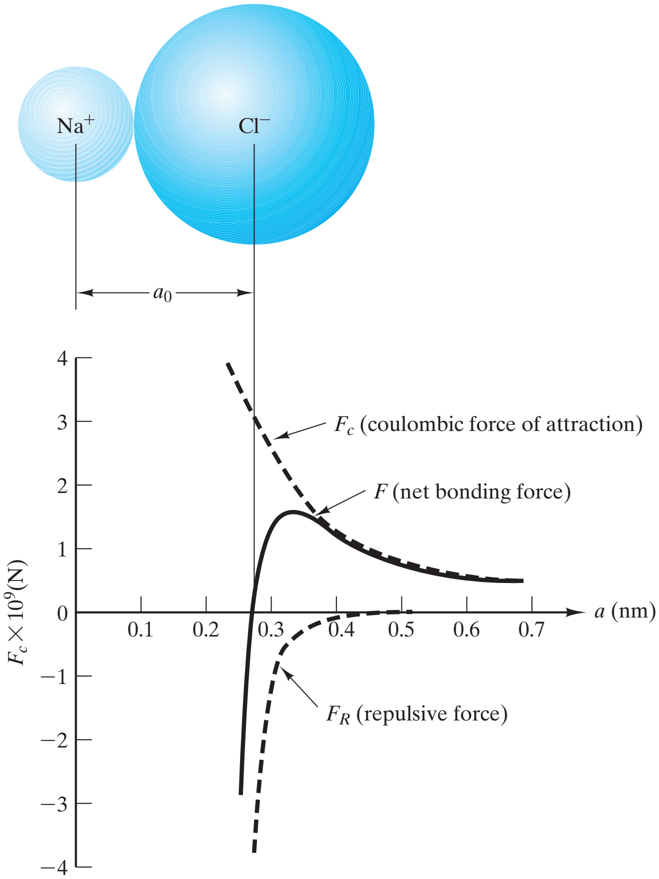


FIGURE 2.7 *Net bonding force curve for a* $Na^+ - Cl^-$ *pair showing an equilibrium bond length of* $a_0 = 0.28$ nm.

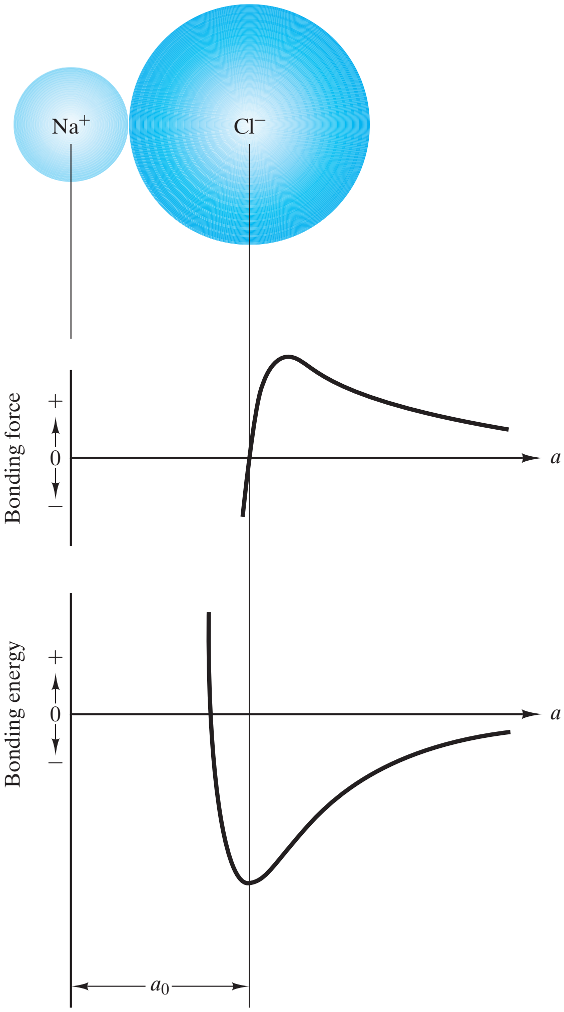


FIGURE 2.8 *Comparison of the bonding force curve and the bonding energy curve for a* $Na^+ - Cl^-$ *pair. Since* $F = dE/da$, *the equilibrium bond length* (a_0) *occurs where* $F = 0$ *and* E *is a minimum (see Equation 2.5).*

similarly charged ions experience this “coulombic repulsion” force. The net cohesiveness of the solid is due to the fact that any given ion is immediately surrounded by ions of opposite sign for which the coulombic term (Equations 2.1 and 2.2) is positive. This overcomes the smaller, repulsive term due to more distant ions of like sign.

It should also be noted that an externally applied compressive force is required to push the ions closer together (i.e., closer than a_0). Similarly, an externally applied tensile force is required to pull the ions farther apart. This requirement has implications for the mechanical behavior of solids, which is discussed in detail later (especially in Chapter 6).

The atomic scale bonding force and energy curves shown on previous page will help us understand the nature of elastic deformation in Section 6.2.

Bonding energy, E, is related to bonding force through the differential expression

$$F = \frac{dE}{da}.$$

In this way, the net bonding force curve shown in Figure 2.7 is the derivative of the bonding energy curve. This relationship is shown in Figure 2.8. The relationship demonstrates that the equilibrium bond length, a_0, which corresponds to $F = 0$, also corresponds to a minimum in the energy curve. This correspondence is a consequence of Equation 2.5; that is, the slope of the energy curve at a minimum equals zero:

$$F = 0 = \left(\frac{dE}{da}\right)_{a=a_0}.$$

This important concept in materials science will be seen again many times throughout the book. The stable ion positions correspond to an energy minimum. To move the ions from their equilibrium spacing, energy must be supplied to this system (e.g., by compressive or tensile loading).

Having established that there is an equilibrium bond length, a_0, it follows that this bond length is the sum of two ionic radii; that is, for NaCl,

$$a_0 = r_{\mathrm{Na}^+} + r_{\mathrm{Cl}^-}.$$

This equation implies that the two ions are hard spheres touching at a single point. In Section 2.1 it was noted that, while electron orbitals are represented as particles orbiting at a fixed radius, electron charge is found in a range of radii. This is true for ions as well as for neutral atoms. An **ionic**, or **atomic, radius** is, then, the radius corresponding to the average electron density in the outermost electron orbital. Figure 2.9 compares three models of an $\mathrm{Na}^+ - \mathrm{Cl}^-$ ion pair: (a) shows a simple planetary model of the two ions, (b) shows a **hard-sphere** model of the pair, and (c) shows the **soft-sphere** model in which the actual electron density in the outer orbitals of Na^+ and Cl^- extends farther out than is shown for the hard sphere. The precise nature of actual bond lengths, a_0, allows us to use the hard-sphere model almost exclusively throughout the remainder of the book. Appendix 2 provides a detailed list of calculated ionic radii for a large number of ionic species.

Ionization has a significant effect on the effective (hard-sphere) radii for the atomic species involved. Although Figure 2.4 did not indicate this factor, the loss or gain of an electron by a neutral atom changes its radius. Figure 2.10 illustrates again the formation of an ionic bond between Na^+ and Cl^-. (Compare this figure with Figure 2.4.) In this case, atomic and ionic sizes are shown to correct scale. The loss of an electron by the sodium atom leaves 10 electrons to be drawn closer around the nucleus that still contains 11 protons. Conversely, a gain of 1 electron by the chlorine atom gives 18 electrons around a nucleus with 17 protons and, therefore, a larger effective radius.

COORDINATION NUMBER

Earlier in this section, the nondirectional nature of the ionic bond was introduced. Figure 2.5 shows a structure for NaCl in which six Na^+ surround each Cl^-, and vice versa. The **coordination number** (CN) is the number of adjacent ions

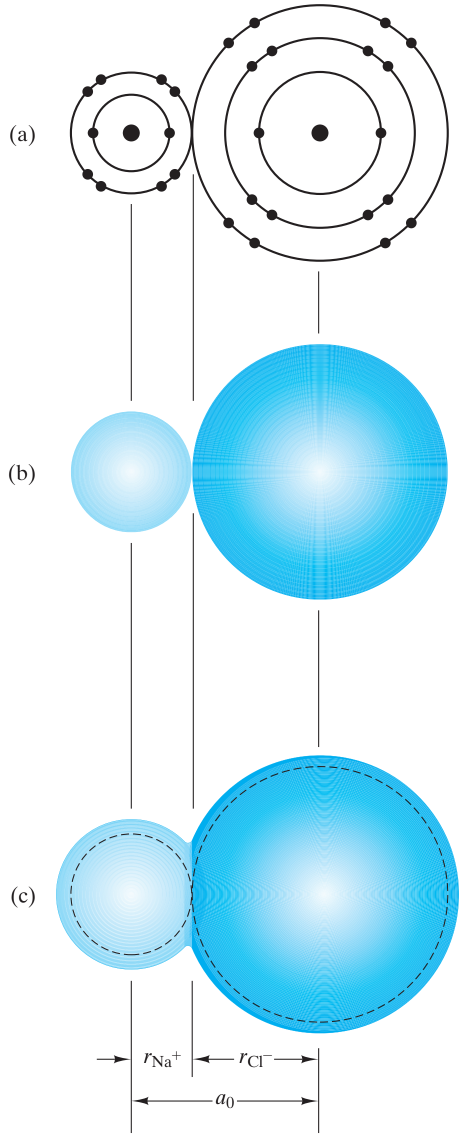


FIGURE 2.9 *Comparison of (a) a planetary model of a* $Na^+ - Cl^-$ *pair with (b) a hard-sphere model and (c) a soft-sphere model.*

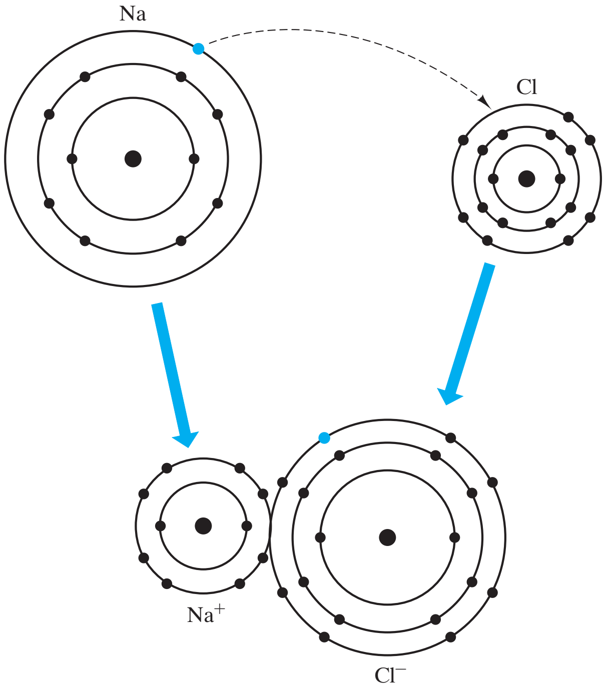


FIGURE 2.10 *Formation of an ionic bond between sodium and chlorine in which the effect of ionization on atomic radius is illustrated. The cation* (Na^+) *becomes smaller than the neutral atom* (Na)*, while the anion* (Cl^-) *becomes larger than the neutral atom* (Cl)*.*

(or atoms) surrounding a reference ion (or atom). For each ion shown in Figure 2.5, the CN is 6; that is, each ion has six nearest neighbors.

For ionic compounds, the coordination number of the smaller ion can be calculated in a systematic way by considering the greatest number of larger ions (of opposite charge) that can be in contact with, or coordinate with, the smaller one. This number (CN) depends directly on the relative sizes of the oppositely charged ions. This relative size is characterized by the **radius ratio** (r/R), where r is the radius of the smaller ion and R is the radius of the larger one.

To illustrate the dependence of CN on radius ratio, consider the case of $r/R = 0.20$. Figure 2.11 shows how the greatest number of larger ions that can

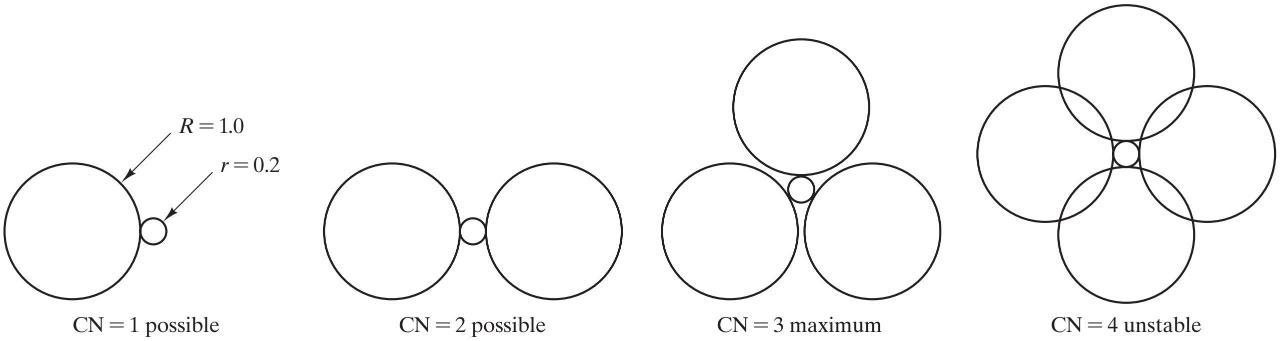


FIGURE 2.11 *The largest number of ions of radius R that can coordinate an atom of radius r is* 3 *when the radius ratio* $r/R = 0.2$. *(Note: The instability for* CN = 4 *can be reduced, but not eliminated, by allowing a three-dimensional, rather than a coplanar, stacking of the larger ions.)*

coordinate the smaller one is three. Any attempt to place four larger ions in contact with the smaller one requires the larger ions to overlap, which is a condition of great instability because of high repulsive forces. The minimum value of r/R that can produce threefold coordination ($r/R = 0.155$) is shown in Figure 2.12; that is, the larger ions are just touching the smaller ion as well as just touching each other. In the same way that fourfold coordination was unstable in Figure 2.11, an r/R value of *less* than 0.155 cannot allow threefold coordination. As r/R increases above 0.155, threefold coordination is stable (e.g., Figure 2.11 for $r/R = 0.20$) until fourfold coordination becomes possible at $r/R = 0.225$. Table 2.1 summarizes the relationship between coordination number and radius ratio. As r/R increases to 1.0, a coordination number as high as 12 is possible. As will be noted in Example 2.8, calculations based on Table 2.1 serve as guides, not as absolute predictors.

An obvious question is "Why doesn't Table 2.1 include radius ratios greater than 1?" Certainly, more than 12 small ions could simultaneously touch a single larger one. However, there are practical constraints in connecting the coordination groups of Table 2.1 into a periodic, three-dimensional structure, and the coordination number for the larger ions tends to be less than 12. A good example is again shown in Figure 2.5, in which the coordination number of Na^+ is 6, as predicted by the r/R value ($= 0.098$ nm$/0.181$ nm $= 0.54$), and the regular stacking of the six coordinated sodiums, in turn, gives Cl^- a coordination number of 6. These structural details will be discussed further in Chapter 3. One might also inquire why coordination numbers of 5, 7, 9, 10, and 11 are absent. These numbers cannot be integrated into the repetitive crystalline structures described in Chapter 3.

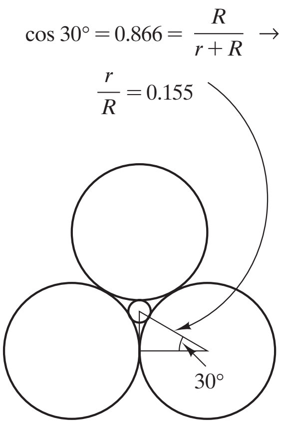


FIGURE 2.12 *The minimum radius ratio, r/R, that can produce threefold coordination is* 0.155.

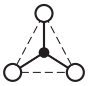
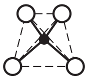
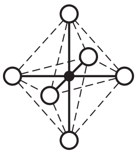
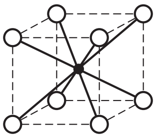
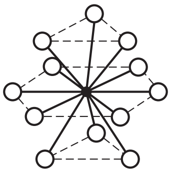
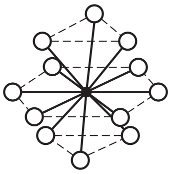
EXAMPLE 2.4

(a) Compare the electronic configurations for the atoms and ions shown in Figure 2.4.

(b) Which noble gas atoms have electronic configurations equivalent to those for the ions shown in Figure 2.4?

TABLE 2.1

Coordination Numbers for Ionic Bonding

Coordination number	Radius ratio, r/R	Coordination geometry
2	$0 < \frac{r}{R} < 0.155$	
3	$0.155 \le \frac{r}{R} < 0.225$	
4	$0.225 \le \frac{r}{R} < 0.414$	
6	$0.414 \le \frac{r}{R} < 0.732$	
8	$0.732 \le \frac{r}{R} < 1$	
12	1	 or[a] 

[a] The geometry on the left is for the hexagonal close-packed (hcp) structure, and the geometry on the right is for the face-centered cubic (fcc) structure. These crystal structures are discussed in Chapter 3.

SOLUTION

(a) From Appendix 1,

$$\text{Na: } 1s^2 2s^2 2p^6 3s^1$$

and

$$\text{Cl: } 1s^2 2s^2 2p^6 3s^2 3p^5.$$

Because Na loses its outer orbital ($3s$) electron in becoming Na^+,

$$\text{Na}^+\text{: } 1s^2 2s^2 2p^6.$$

Because Cl gains an outer orbital electron in becoming Cl^-, its $3p$ shell becomes filled:

$$\text{Cl}^-\text{: } 1s^2 2s^2 2p^6 3s^2 3p^6.$$

(b) From Appendix 1,

$$\text{Ne: } 1s^2 2s^2 2p^6,$$

which is equivalent to Na^+ (of course, the nuclei of Ne and Na^+ differ), and

$$\text{Ar: } 1s^2 2s^2 2p^6 3s^2 3p^6,$$

which is equivalent to Cl^- (again, the nuclei differ).

EXAMPLE 2.5

(a) Using the ionic radii data in Appendix 2, calculate the coulombic force of attraction between Na^+ and Cl^- in NaCl.

(b) What is the repulsive force in this case?

SOLUTION

(a) From Appendix 2,

$$r_{\mathrm{Na}^+} = 0.098 \text{ nm}$$

and

$$r_{\mathrm{Cl}^-} = 0.181 \text{ nm}.$$

Then,

$$\begin{aligned} a_0 &= r_{\mathrm{Na}^+} + r_{\mathrm{Cl}^-} = 0.098 \text{ nm} + 0.181 \text{ nm} \\ &= 0.278 \text{ nm}. \end{aligned}$$

From Equations 2.1 and 2.2,

$$F_c = -\frac{k_0(Z_1q)(Z_2q)}{a_0^2},$$

where the equilibrium bond length is used. Substituting the numerical data into the coulombic force equation, we get

$$F_c = -\frac{(9 \times 10^9 \text{ V}\cdot\text{m/C})(+1)(0.16 \times 10^{-18}\text{ C})(-1)(0.16 \times 10^{-18}\text{ C})}{(0.278 \times 10^{-9}\text{ m})^2}.$$

Noting that 1 V · C = 1 J, we obtain

$$F_c = 2.98 \times 10^{-9}\text{ N}.$$

Note. This result can be compared to the data shown in Figures 2.6 and 2.7.

(b) Because $F_c + F_R = 0$,

$$F_R = -F_c = -2.98 \times 10^{-9}\,\text{N}.$$

EXAMPLE 2.6

Repeat Example 2.5 for Na_2O, an oxide component in many ceramics and glasses.

SOLUTION

(a) From Appendix 2,

$$r_{\text{Na}^+} = 0.098\text{ nm}$$

and

$$r_{\text{O}^{2-}} = 0.132\text{ nm}.$$

Then,

$$\begin{aligned} a_0 &= r_{\text{Na}^+} + r_{\text{O}^{2-}} = 0.098\text{ nm} + 0.132\text{ nm} \\ &= 0.231\text{ nm}. \end{aligned}$$

Again,

$$\begin{aligned} F_c &= -\frac{k_0(Z_1 q)(Z_2 q)}{a_0^2} \\ &= -\frac{(9 \times 10^9\,\text{V}\cdot\text{m/C})(+1)(0.16 \times 10^{-18}\,\text{C})(-2)(0.16 \times 10^{-18}\,\text{C})}{(0.231 \times 10^{-9}\,\text{m})^2} \\ &= 8.64 \times 10^{-9}\,\text{N}. \end{aligned}$$

(b) $F_R = -F_c = -8.64 \times 10^{-9}\,\text{N}.$

EXAMPLE 2.7

Calculate the minimum radius ratio for a coordination number of 8.

SOLUTION

From Table 2.1, it is apparent that the ions are touching along a body diagonal. If the cube edge length is termed *l*, then

$$2R + 2r = \sqrt{3}l.$$

For the minimum radius ratio coordination, the large ions are also touching each other (along a cube edge), giving

$$2R = l.$$

Combining the two equations gives us

$$2R + 2r = \sqrt{3}(2R).$$

Then

$$2r = 2R(\sqrt{3} - 1)$$

and

$$\frac{r}{R} = \sqrt{3} - 1 = 1.732 - 1$$
$$= 0.732.$$

Note. There is no shortcut to visualizing three-dimensional structures of this type. It might be helpful to sketch slices through the cube of Table 2.1 with the ions drawn full scale. Many more exercises of this type will be given in Chapter 3.

EXAMPLE 2.8

Estimate the coordination number for the cation in each of these ceramic oxides: Al_2O_3, B_2O_3, CaO, MgO, SiO_2, and TiO_2.

SOLUTION

From Appendix 2, $r_{Al^{3+}} = 0.057$ nm, $r_{B^{3+}} = 0.02$ nm, $r_{Ca^{2+}} = 0.106$ nm, $r_{Mg^{2+}} = 0.078$ nm, $r_{Si^{4+}} = 0.039$ nm, $r_{Ti^{4+}} = 0.064$ nm, and $r_{O^{2-}} = 0.132$ nm.

For Al_2O_3,

$$\frac{r}{R} = \frac{0.057 \text{ nm}}{0.132 \text{ nm}} = 0.43,$$

for which Table 2.1 gives

$$\text{CN} = 6.$$

For B_2O_3,

$$\frac{r}{R} = \frac{0.02 \text{ nm}}{0.132 \text{ nm}} = 0.15, \text{ giving CN} = 2.^*$$

---

[*] The actual CN for is 3 and for CaO is 6. Discrepancies are due to a combination of uncertainty in the estimation of ionic radii and bond directionality due to partially covalent character.

For CaO,

$$\frac{r}{R} = \frac{0.106\text{ nm}}{0.132\text{ nm}} = 0.80, \text{ giving CN} = 8.$$

For MgO,

$$\frac{r}{R} = \frac{0.078\text{ nm}}{0.132\text{ nm}} = 0.59, \text{ giving CN} = 6.$$

For SiO_2,

$$\frac{r}{R} = \frac{0.039\text{ nm}}{0.132\text{ nm}} = 0.30, \text{ giving CN} = 4.$$

For TiO_2,

$$\frac{r}{R} = \frac{0.064\text{ nm}}{0.132\text{ nm}} = 0.48, \text{ giving CN} = 6.$$

PRACTICE PROBLEM 2.4

(a) Make a sketch similar to that shown in Figure 2.4 illustrating Mg and O atoms and ions in MgO. **(b)** Compare the electronic configurations for the atoms and ions illustrated in part (a). **(c)** Show which noble gas atoms have electronic configurations equivalent to those illustrated in part (a). (See Example 2.4.)

PRACTICE PROBLEM 2.5

(a) Using the ionic radii data in Appendix 2, calculate the coulombic force of attraction between the $Mg^{2+} - O^{2-}$ ion pair. **(b)** What is the repulsive force in this case? (See Examples 2.5 and 2.6.)

PRACTICE PROBLEM 2.6

Calculate the minimum radius ratio for a coordination number of **(a)** 4 and **(b)** 6. (See Example 2.7.)

PRACTICE PROBLEM 2.7

In the next chapter, we will see that MgO, CaO, FeO, and NiO all share the NaCl crystal structure. As a result, in each case the metal ions will have the same coordination number (6). The case of MgO and CaO is treated in Example 2.8. Use the radius ratio calculation to see if it estimates CN = 6 for FeO and NiO.

2.3 The Covalent Bond

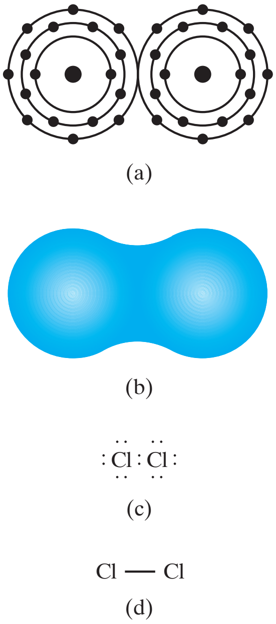


FIGURE 2.13 *The covalent bond in a molecule of chlorine gas,* Cl_2*, is illustrated with (a) a planetary model compared with (b) the actual electron density, (c) an electron-dot schematic, and (d) a bond-line schematic.*

While the ionic bond is nondirectional, the **covalent bond** is highly directional. The name *covalent* derives from the cooperative sharing of valence electrons between two adjacent atoms. **Valence electrons** are those outer orbital electrons that take part in bonding.[*] Figure 2.13 illustrates the covalent bond in a molecule of chlorine gas (Cl_2) with (a) a planetary model compared with (b) the actual **electron density**, which is clearly concentrated along a straight line between the two Cl nuclei. Common shorthand notations of electron dots and a bond line are shown in parts (c) and (d), respectively.

Figure 2.14a shows a bond-line representation of another covalent molecule, ethylene (C_2H_4). The double line between the two carbons signifies a **double bond**, or covalent sharing of two pairs of valence electrons. By converting the double bond to two single bonds, adjacent ethylene molecules can be covalently bonded together, leading to a long-chain molecule of *polyethylene* (Figure 2.14b). Such **polymeric molecules** (each C_2H_4 unit is a *mer*) are the structural basis of polymers. In Chapter 11, these materials will be discussed in detail. For now, it is sufficient to realize that long-chain molecules of this type have sufficient flexibility to fill three-dimensional space by a complex coiling structure. Figure 2.15 is a two-dimensional schematic of such a "spaghetti-like" structure. The straight lines between C and C and between C and H represent strong, covalent bonds. Only weak, secondary bonding occurs between adjacent sections of the long molecular chains. It is this secondary bonding that is the "weak link" that leads to the low

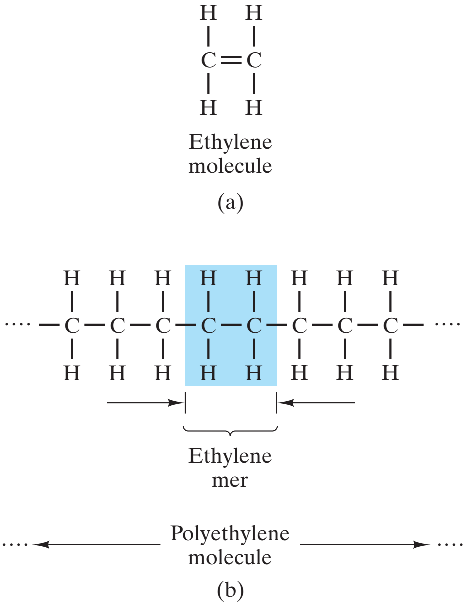


FIGURE 2.14 *(a) An ethylene molecule* (C_2H_4) *is compared with (b) a polyethylene molecule* $-\!\!\left(C_2H_4\right)\!\!-_n$ *that results from the conversion of the* C=C *double bond into two* C−C *single bonds.*

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[*] Remember that, in ionic bonding, the valence of Na^+ was +1 because one electron had been transferred to an anion.

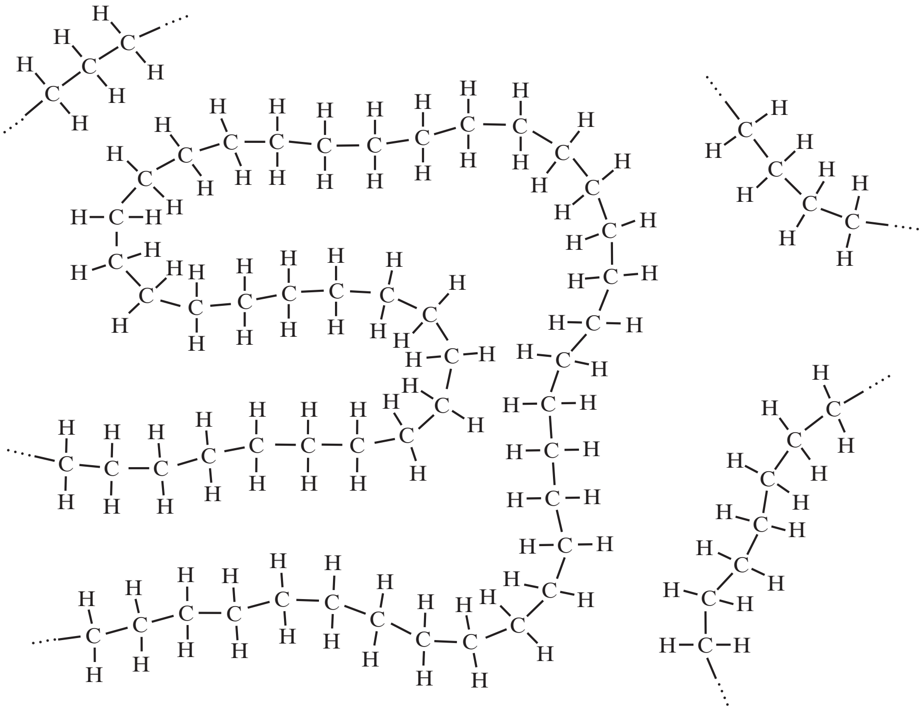


FIGURE 2.15 *Two-dimensional schematic representation of the "spaghetti-like" structure of solid polyethylene.*

strengths and low melting points for traditional polymers. By contrast, diamond, with exceptionally high hardness and a melting point of greater than 3,500°C, has covalent bonding between each adjacent pair of C atoms (Figure 2.16).

It is important to note that covalent bonding can produce coordination numbers substantially smaller than predicted by the radius ratio considerations of ionic bonding. For diamond, the radius ratio for the equally sized carbon atoms is $r/R = 1.0$, but Figure 2.16 shows that the coordination number is 4 rather than 12, as predicted in Table 2.1. In this case, the coordination number for carbon is determined by its characteristic *sp*3 hybridization bonding in which the four outershell electrons of the carbon atom are shared with adjacent atoms in equally spaced directions (see Section 2.1).

In some cases, the efficient packing considerations shown in Table 2.1 are in agreement with covalent bonding geometry. For example, the basic structural unit in silicate minerals and in many commercial ceramics and glasses is the SiO_4^{4-} tetrahedron shown in Figure 2.17. Silicon resides just below carbon in group IV A of the periodic table and exhibits similar chemical behavior. Silicon forms many compounds with fourfold coordination. The SiO_4^{4-} unit maintains this bonding configuration, but simultaneously has strong ionic character, including agreement with Table 2.1. The radius ratio ($r_{Si^{4+}}/r_{O^{2-}} = 0.039\text{ nm}/0.132\text{ nm} = 0.295$) is in the correct range ($0.225 < r/R < 0.414$) to produce maximum efficiency of ionic coordination with CN = 4. In fact, the Si–O bond is roughly one-half ionic (electron transfer) and one-half covalent (electron sharing) in nature.

The bonding force and bonding energy curves for covalent bonding look similar to those shown in Figure 2.8 for ionic bonding. The different nature of the two types of bonding implies, of course, that the ionic force equations (2.1 and 2.2) do not apply. Nonetheless, the general terminology of bond energy and bond length apply in both cases (Figure 2.18). Table 2.2 summarizes values of bond energy and bond length for major covalent bonds.

Another important characteristic of covalent solids is the **bond angle**, which is determined by the directional nature of valence electron sharing. Figure 2.19 illustrates the bond angle for a typical carbon atom, which tends to form four equally spaced bonds. This tetrahedral configuration (see Figure 2.17) gives a bond angle of 109.5°. The bond angle can vary slightly depending on the species to which the bond is linked, double bonds, and so on. In general, bond angles involving carbon are close to the ideal 109.5°.

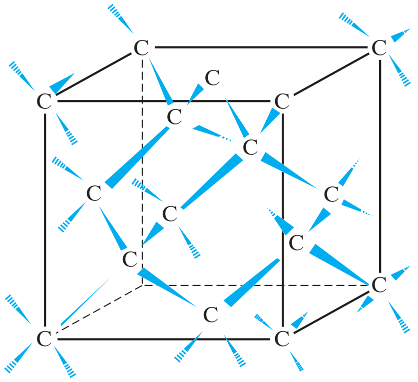


FIGURE 2.16 *Three-dimensional structure of bonding in the covalent solid, carbon (diamond). Each carbon atom (C) has four covalent bonds to four other carbon atoms. (This geometry can be compared with the diamond-cubic structure shown in Figure 3.20.) In this illustration, the bond-line schematic of covalent bonding is given a perspective view to emphasize the spatial arrangement of bonded carbon atoms.*

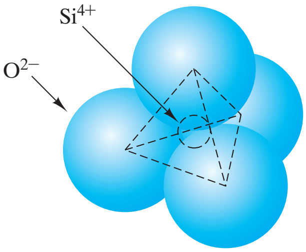


FIGURE 2.17 *The* SiO_4^{4-} *tetrahedron represented as a cluster of ions. In fact, the* Si–O *bond exhibits both ionic and covalent character.*

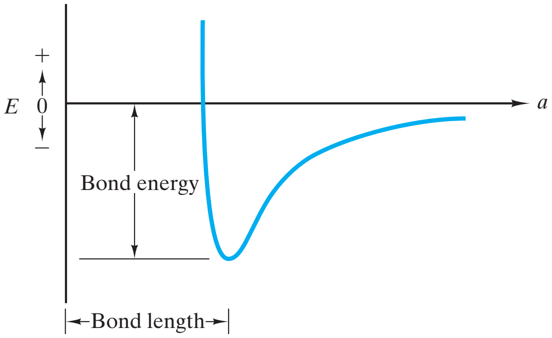


FIGURE 2.18 *The general shape of the bond-energy curve and associated terminology apply to covalent as well as ionic bonding. (The same is true of metallic and secondary bonding.)*

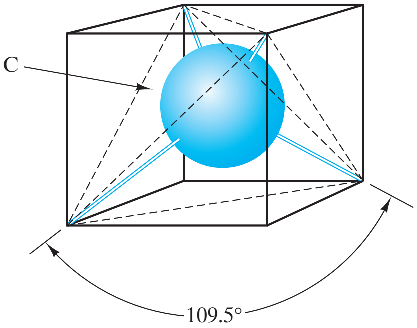


FIGURE 2.19 *Tetrahedral configuration of covalent bonds with carbon. The bond angle is 109.5°.*

TABLE 2.2

Bond Energies and Bond Lengths for Representative Covalent Bonds

Bond	Bond energy[a]		Bond length, nm
	kcal/mol	kJ/mol	
C−C	88[b]	370	0.154
C=C	162	680	0.130
C≡C	213	890	0.120
C−H	104	435	0.110
C−N	73	305	0.150
C−O	86	360	0.140
C=O	128	535	0.120
C−F	108	450	0.140
C−Cl	81	340	0.180
O−H	119	500	0.100
O−O	52	220	0.150
O−Si	90	375	0.160
N−H	103	430	0.100
N−O	60	250	0.120
F−F	38	160	0.140
H−H	104	435	0.074

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

[b] All values are negative for forming bonds (energy is released) and positive for breaking bonds (energy is required).

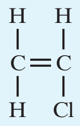
Source: L. H. Van Vlack, *Elements of Materials Science and Engineering,* 4th ed., Addison-Wesley Publishing Co., Inc., Reading, MA, 1980.

EXAMPLE 2.9

Sketch the polymerization process for polyvinyl chloride (PVC). The vinyl chloride molecule is C_2H_3Cl.

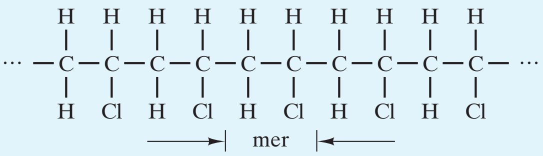
SOLUTION

Similar to the schematic shown in Figure 2.14, the vinyl chloride molecule would appear as



$$\begin{array}{ccc} \mathrm{H} & & \mathrm{H} \\ | & & | \\ \mathrm{C} & = & \mathrm{C} \\ | & & | \\ \mathrm{H} & & \mathrm{Cl} \end{array}$$

Polymerization would occur when several adjacent vinyl chloride molecules connect, transforming their double bonds into single bonds:



$$\cdots-\begin{array}{c}H\\|\\C\\|\\H\end{array}-\begin{array}{c}H\\|\\C\\|\\Cl\end{array}-\begin{array}{c}H\\|\\C\\|\\H\end{array}-\begin{array}{c}H\\|\\C\\|\\Cl\end{array}-\begin{array}{c}H\\|\\C\\|\\H\end{array}-\begin{array}{c}H\\|\\C\\|\\Cl\end{array}-\begin{array}{c}H\\|\\C\\|\\H\end{array}-\begin{array}{c}H\\|\\C\\|\\Cl\end{array}-\begin{array}{c}H\\|\\C\\|\\H\end{array}-\begin{array}{c}H\\|\\C\\|\\Cl\end{array}-\cdots$$

EXAMPLE 2.10

Calculate the reaction energy for the polymerization of polyvinyl chloride in Example 2.9.

SOLUTION

In general, each C═C is broken to form two single C─C bonds:

$$C{=}C \rightarrow 2C{-}C.$$

By using data from Table 2.2, the energy associated with this reaction is

$$680\ \text{kJ/mol} \rightarrow 2(370\ \text{kJ/mol}) = 740\ \text{kJ/mol}.$$

The reaction energy is then

$$(740 - 680)\text{kJ/mol} = 60\ \text{kJ/mol}.$$

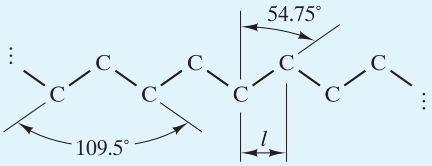
Note. As stated in the footnote in Table 2.2, the reaction energy is released during polymerization, making this a spontaneous reaction in which the product, polyvinyl chloride, is stable relative to individual vinyl chloride molecules. Since carbon atoms in the backbone of the polymeric molecule are involved rather than side members, this reaction energy also applies for polyethylene (Figure 2.14) and other "vinyl"-type polymers.

EXAMPLE 2.11

Calculate the length of a polyethylene molecule, $\left(\!-C_2H_4-\!\right)_n$, where $n = 500$.

SOLUTION

Looking only at the carbon atoms in the backbone of the polymeric chain, we must acknowledge the characteristic bond angle of 109.5°:



This angle produces an effective bond length, *l*, of

$$l = (\text{C}-\text{C bond length}) \times \sin 54.75°.$$

Using Table 2.2, we obtain

$$\begin{aligned} l &= (0.154 \text{ nm})(\sin 54.75°) \\ &= 0.126 \text{ nm}. \end{aligned}$$

With two bond lengths per mer and 500 mers, the total molecule length, L, is

$$\begin{aligned} L &= 500 \times 2 \times 0.126 \text{ nm} \\ &= 126 \text{ nm} \\ &= 0.126\ \mu\text{m}. \end{aligned}$$

Note. In Chapter 12, we will calculate the degree of coiling of these long, linear molecules.

PRACTICE PROBLEM 2.8

In Figure 2.14, we see the polymerization of polyethylene $(C_2H_4)_n$, illustrated. Example 2.9 illustrates polymerization for polyvinyl chloride $(C_2H_3C1)_n$. Make a similar sketch to illustrate the polymerization of polypropylene $(C_2H_3R)_n$, where R is a CH_3 group.

PRACTICE PROBLEM 2.9

Use a sketch to illustrate the polymerization of polystyrene $(C_2H_3R)_n$, where R is a benzene group, C_6H_5.

PRACTICE PROBLEM 2.10

Calculate the reaction energy for polymerization of **(a)** propylene (see Practice Problem 2.8) and **(b)** styrene (see Practice Problem 2.9).

PRACTICE PROBLEM 2.11

The length of an average polyethylene molecule in a commercial clear plastic wrap is 0.2 μm. What is the average degree of polymerization (n) for this material? (See Example 2.11.)

2.4 The Metallic Bond

The ionic bond involves electron transfer and is nondirectional. The covalent bond involves electron sharing and is directional. The third type of primary bond, the **metallic bond**, involves electron sharing and is nondirectional. In this case, the valence electrons are said to be **delocalized electrons**; that is, they have an equal probability of being associated with any of a large number of adjacent atoms. In typical metals, this delocalization is associated with the entire material, leading to an electron cloud, or electron gas (Figure 2.20). This mobile "gas" is the basis for the high electrical conductivity in metals. (The role of electronic structure in producing conduction electrons in metals is discussed in Chapter 13.)

Again, the concept of a bonding **energy well**, or **trough**, as shown in Figure 2.18, applies. As with ionic bonding, bond angles and coordination numbers are determined primarily by efficient packing considerations, so coordination numbers tend to be high (8 and 12). Relative to the bonding energy curve, a detailed list of atomic radii for the elements is given in Appendix 2, which includes the important elemental metals. Appendix 2 also includes a list of ionic radii. Some of these ionic species are found in the important ceramics and glasses. Inspection of Appendix 2 shows that the radius of the metal ion core involved in metallic bonding (Figure 2.20) differs substantially from the radius of a metal ion from which valence electrons have been transferred.

Instead of a list of bond energies for metals and ceramics, similar to those included for covalent bonds shown in Table 2.2, data that represent the energetics associated with the bulk solid rather than isolated atom (or ion) pairs are more useful. For example, Table 2.3 lists the heats of sublimation of some common metals and their oxides (some of the common ceramic compounds). The heat of sublimation represents the amount of thermal energy necessary to turn 1 mol of solid directly into vapor at a fixed temperature. It is a good indication of the relative strength of bonding in the solid. However, caution must be used in making direct comparisons to the bond energies shown in Table 2.2, which correspond to

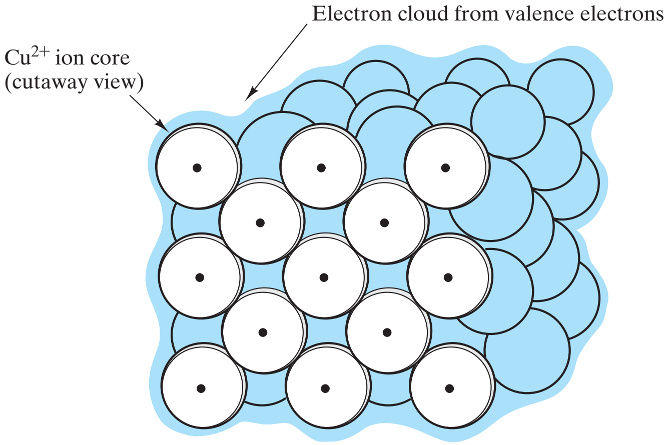


FIGURE 2.20 *Metallic bond consisting of an electron cloud, or gas. An imaginary slice is shown through the front face of the crystal structure of copper, revealing* Cu^{2+} *ion cores bonded by the delocalized valence electrons.*

TABLE 2.3

Heats of Sublimation (at 25°C) of Some Metals and Their Oxides

Metal	Heat of sublimation kcal/mol	Heat of sublimation kJ/mol	Metal oxide	Heat of sublimation kcal/mol	Heat of sublimation kJ/mol
Al	78	326			
Cu	81	338			
Fe	100	416	FeO	122	509
Mg	35	148	MgO	145	605
Ti	113	473	α-TiO	143	597
			TiO_2 (rutile)	153	639

Source: Data from *JANAF Thermochemical Tables,* 2nd ed., National Standard Reference Data Series, Natl. Bur. Std. (U.S.), *37* (1971), and Supplement in *J. Phys. Chem. Ref. Data 4*(1), 1–175 (1975).

specific atom pairs. Nonetheless, the magnitudes of energies shown in Tables 2.2 and 2.3 are comparable in range.

In this chapter, we have seen that the nature of the chemical bonds between atoms of the same element and atoms of different elements depends on the transfer or sharing of electrons between adjacent atoms. American chemist Linus Pauling systematically defined **electronegativity** as the ability of an atom to attract electrons to itself. Figure 2.21 summarizes Pauling's electronegativity values for the elements in the periodic table. We can recall from Chapter 1 that the majority of elements in the periodic table are metallic in nature (Figure 1.4). In general, the values of electronegativities increase from the left to the right side of the periodic table, with cesium and francium (in group I A) having the lowest value (0.7) and fluorine (in group VII A) having the highest value (4.0). Clearly, the metallic elements tend to have the lower values of electronegativity, and the nonmetallic elements have the higher values. Although Pauling specifically based his electronegativities on thermochemical data for molecules, we shall see in Section 4.1 that the data of Figure 2.21 are useful for predicting the nature of metallic alloys.

EXAMPLE 2.12

Several metals, such as α-Fe, have a body-centered cubic crystal structure in which the atoms have a coordination number of 8. Discuss this structure in light of the prediction of Table 2.1 that nondirectional bonding of equal-sized spheres should have a coordination number of 12.

SOLUTION

The presence of some covalent character in these predominantly metallic materials can reduce the coordination number below the predicted value. (See Example 2.8.)

I A	II A	III B	IV B	V B	VI B	VII B	VIII			I B	II B	III A	IV A	V A	VI A	VII A	0
1 H 2.1																	2 He –
3 Li 1.0	4 Be 1.5											5 B 2.0	6 C 2.5	7 N 3.0	8 O 3.5	9 F 4.0	10 Ne –
11 Na 0.9	12 Mg 1.2											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 2.21 *The electronegativities of the elements. (From Linus Pauling,* The Nature of the Chemical Bond and the Structure of Molecules and Crystals; An Introduction to Modern Structural Chemistry, *3rd ed., Cornell University Press, Ithaca, NY, 1960.)*

PRACTICE PROBLEM 2.12

Discuss the low coordination number (CN = 4) for the diamond cubic structure found for some elemental solids, such as silicon. (See Example 2.12.)

2.5 The Secondary, or van der Waals, Bond

The major source of cohesion in a given engineering material is one or more of the three primary bonds just covered. As seen in Table 2.2, typical primary bond energies range from 200 to 700 kJ/mol ($\approx$50 to 170 kcal/mol). It is possible to obtain some atomic bonding (with substantially smaller bonding energies) without electron transfer or sharing. This bonding is known as *secondary bonding,* or **van der Waals**[*] **bonding**. The mechanism of secondary bonding is somewhat similar to ionic bonding (i.e., the attraction of opposite charges). The key difference is that no electrons are transferred.[†]

Figure 2.22 illustrates how two neutral atoms can develop a weak bonding force between them by a slight distortion of their charge distributions. The

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[*] Johannes Diderik van der Waals (1837–1923), Dutch physicist, improved the equations of state for gases by taking into account the effect of secondary bonding forces. His brilliant research was first published as a thesis dissertation arising from his part-time studies of physics. The immediate acclaim for the work led to his transition from a job as headmaster of a secondary school to a professorship at the University of Amsterdam.

[†] Primary bonds are sometimes referred to as *chemical bonds*, with secondary bonds being *physical bonds*. Attraction depends on asymmetrical distributions of positive and negative charges within each atom or molecular unit being bonded. Such charge asymmetry is referred to as a **dipole**. Secondary bonding can be of two types, depending on whether the dipoles are (1) temporary or (2) permanent.

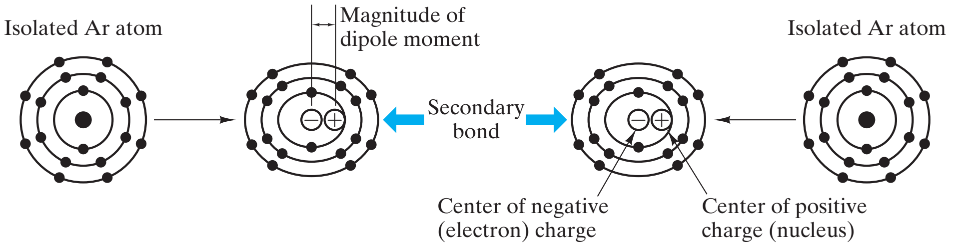


FIGURE 2.22 *Development of induced dipoles in adjacent argon atoms leading to a weak, secondary bond. The degree of charge distortion shown here is greatly exaggerated.*

example is argon, a noble gas, which does not tend to form primary bonds because it has a stable, filled outer orbital shell. An isolated argon atom has a perfectly spherical distribution of negative electrical charge surrounding its positive nucleus. However, when another argon atom is brought nearby, the negative charge is drawn slightly toward the positive nucleus of the adjacent atom. This slight distortion of charge distribution occurs simultaneously in both atoms. The result is an *induced dipole*. Because the degree of charge distortion related to an induced dipole is small, the magnitude of the resulting dipole is small, leading to a relatively small bond energy (0.99 kJ/mol or 0.24 kcal/mol).

Secondary bonding energies are somewhat greater when molecular units containing *permanent dipoles* are involved. Perhaps the best example of this is the **hydrogen bridge**, which connects adjacent molecules of water, H_2O (Figure 2.23). Because of the directional nature of electron sharing in the covalent O—H bonds, the H atoms become positive centers and the O atoms become negative centers for the H_2O molecules. The greater charge separation possible in such a **polar molecule**, a molecule with a permanent separation of charge, gives a larger **dipole moment** (product of charge and separation distance between centers of positive and negative charge) and therefore a greater bond energy (21 kJ/mol or 5 kcal/mol). The secondary bonding between adjacent polymeric chains in polymers such as polyethylene is of this type.

Note that one of the important properties of water derives from the hydrogen bridge. The expansion of water upon freezing is due to the regular and repeating alignment of adjacent H_2O molecules, as seen in Figure 2.23, which leads to a relatively open structure. Upon melting, the adjacent H_2O molecules, while retaining the hydrogen bridge, pack together in a more random and more dense arrangement.

POWERS OF 10

In Section 6.6, we shall see that secondary bonding between adjacent polymer molecules plays a critical role in understanding the nature of viscoelastic deformation in organic polymers.

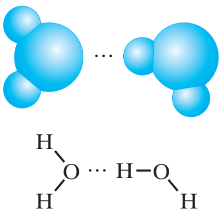


FIGURE 2.23 *Hydrogen bridge. This secondary bond is formed between two permanent dipoles in adjacent water molecules.*

EXAMPLE 2.13

A common way to describe the bonding energy curve (Figure 2.18) for secondary bonding is the "6–12" potential, which states that

$$E = -\frac{K_A}{a^6} + \frac{K_R}{a^{12}},$$

where K_A and K_R are constants for attraction and repulsion, respectively. This relatively simple form is a quantum mechanical result for this relatively simple bond type. Given $K_A = 10.37 \times 10^{-78}\ \mathrm{J \cdot m^6}$ and

$K_R = 16.16 \times 10^{-135}\ \mathrm{J \cdot m^{12}}$, calculate the bond energy and bond length for argon.

SOLUTION

The (equilibrium) bond length occurs at $dE/da = 0$:

$$\left(\frac{dE}{da}\right)_{a=a_0} = 0 = \frac{6K_A}{a_0^7} - \frac{12K_R}{a_0^{13}}.$$

Rearranging gives us

$$a_0 = \left(2\frac{K_R}{K_A}\right)^{1/6}$$

$$= \left(2 \times \frac{16.16 \times 10^{-135}}{10.37 \times 10^{-78}}\right)^{1/6} \mathrm{m}$$

$$= 0.382 \times 10^{-9}\ \mathrm{m} = 0.382\ \mathrm{nm}.$$

Note that bond energy $= E(a_0)$ yields

$$E(0.382\ \mathrm{nm}) = -\frac{K_A}{(0.382\ \mathrm{nm})^6} + \frac{K_R}{(0.382\ \mathrm{nm})^{12}}$$

$$= -\frac{(10.37 \times 10^{-78}\ \mathrm{J \cdot m^6})}{(0.382 \times 10^{-9}\ \mathrm{m})^6} + \frac{(16.16 \times 10^{-135}\ \mathrm{J \cdot m^{12}})}{(0.382 \times 10^{-9}\ \mathrm{m})^{12}}$$

$$= -1.66 \times 10^{-21}\ \mathrm{J}.$$

For 1 mol of Ar,

$$E_{\text{bonding}} = -1.66 \times 10^{-21}\ \mathrm{J/bond} \times 0.602 \times 10^{24}\ \frac{\text{bonds}}{\text{mole}}$$

$$= -0.999 \times 10^{3}\ \mathrm{J/mol}$$

$$= -0.999\ \mathrm{kJ/mol}.$$

Note. This bond energy is less than 1% of the magnitude of any of the primary (covalent) bonds listed in Table 2.2. It should also be noted that the footnote in Table 2.2 indicates a consistent sign convention (bond energy is negative).

PRACTICE PROBLEM 2.13

The bond energy and bond length for argon are calculated (assuming a “6–12” potential) in Example 2.13. Plot E as a function of a over the range 0.33 to 0.80 nm.

PRACTICE PROBLEM 2.14

Using the information from Example 2.13, plot the van der Waals bonding force curve for argon (i.e., F versus a over the same range covered in Practice Problem 2.13).

2.6 Materials—The Bonding Classification

A dramatic representation of the relative bond energies of the various bond types of this chapter is obtained by comparison of melting points. The **melting point** of a solid indicates the temperature to which the material must be subjected to provide sufficient thermal energy to break its cohesive bonds. Table 2.4 shows representative examples used in this chapter. A special note must be made for polyethylene, which is of mixed-bond character. As discussed in Section 2.3, the secondary bonding is a weak link that causes the material to lose structural rigidity above approximately 120°C. This is not a precise melting point, but instead is a temperature above which the material softens rapidly with increasing temperature. The irregularity of the polymeric structure (Figure 2.15) produces variable secondary bond lengths and, therefore, variable bond energies. More important than the variation in bond energy is the average magnitude, which is relatively small. Even though polyethylene and diamond each have similar C−C covalent bonds, the absence of secondary-bond weak links allows diamond to retain its structural rigidity more than 3,000°C beyond polyethylene.

We have now seen four major types of atomic bonding consisting of three primary bonds (ionic, covalent, and metallic) and secondary bonding. It has been traditional to distinguish the three fundamental structural materials (metals, ceramics/glasses, and polymers) as being directly associated with the three types of primary bonds (metallic, ionic, and covalent, respectively). This is a useful concept, but we have already seen in Sections 2.3 and 2.5 that polymers owe their behavior to both covalent and secondary bonding. We also noted in Section 2.3 that some of the most important ceramics and glasses have strong covalent as well as ionic character. Table 2.5 summarizes the bonding character associated with the five fundamental types of engineering materials together with some representative examples. Remember that the mixed-bond character for ceramics and glasses referred to both ionic and covalent nature for a given bond (e.g., Si—O), whereas the mixed-bond character for polymers referred to different bonds being covalent (e.g., C—H) and secondary (e.g., between chains). The relative contribution of different bond types can be graphically displayed in the form of a tetrahedron of bond types (Figure 2.24) in which each apex of the tetrahedron

TABLE 2.4

Comparison of Melting Points for Some of the Representative Materials

Material	Bonding type	Melting point (°C)
NaCl	Ionic	801
C (diamond)	Covalent	~3,550
$-(C_2H_4)-_n$	Covalent and secondary	~120[a]
Cu	Metallic	1,084.87
Ar	Secondary (induced dipole)	−189
H_2O	Secondary (permanent dipole)	0

[a] Because of the irregularity of the polymeric structure of polyethylene, it does not have a precise melting point. Instead, it softens with increasing temperature above 120°C. In this case, the 120°C value is a "service temperature" rather than a true melting point.

TABLE 2.5

Bonding Character of the Five Fundamental Types of Engineering Materials

Material type	Bonding character	Example
Metal	Metallic	Iron (Fe) and the ferrous alloys
Ceramics and glasses	Ionic/covalent	Silica (SiO_2): crystalline and noncrystalline
Polymers	Covalent and secondary	Polyethylene $\left(C_2H_4\right)_n$
Semiconductors	Covalent or covalent/ionic	Silicon (Si) or cadmium sulfide (CdS)

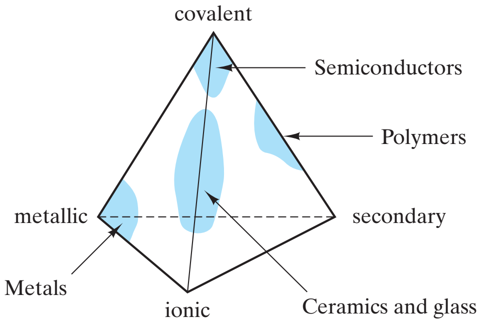


FIGURE 2.24 *Tetrahedron representing the relative contribution of different bond types to the five fundamental categories of engineering materials (the four structural types plus semiconductors).*

represents a pure bonding type. In Chapter 13, we shall add another perspective on materials classification, electrical conductivity, which will follow directly from the nature of bonding and is especially helpful in defining the unique character of semiconductors.

Summary

One basis for the classification of engineering materials is atomic bonding. While the chemical identity of each atom is determined by the number of protons and neutrons within its nucleus, the nature of atomic bonding is determined by the behavior of the electrons that orbit the nucleus.

There are three kinds of strong, or primary, bonds responsible for the cohesion of solids. First, the ionic bond involves electron transfer and is nondirectional. The electron transfer creates a pair of ions with opposite charge. The attractive force between ions is coulombic in nature. An equilibrium ionic spacing is established due to the strong repulsive forces associated with attempting to overlap the two atomic cores. The nondirectional nature of the ionic bond allows ionic coordination numbers to be determined strictly by geometrical packing efficiency (as indicated by the radius ratio). Second, the covalent bond involves electron sharing and is highly directional, which can lead to relatively low coordination numbers and more open atomic structures. Third, the metallic bond involves sharing of delocalized electrons, producing a non-directional bond. The resulting electron cloud or gas results in high electrical conductivity. The nondirectional nature results in relatively high coordination numbers, as in ionic bonding. In the absence of electron transfer or sharing, a weaker form of bonding is possible. This secondary bonding is the result of attraction between either temporary or permanent electrical dipoles.

The classification of engineering materials acknowledges a particular bonding type or combination of types for each category. Metals involve metallic bonding. Ceramics and glasses involve ionic bonding, but usually in conjunction with a strong covalent character. Polymers typically involve strong covalent bonds along polymeric chains, but have weaker secondary bonding between adjacent chains. Secondary bonding acts as a weak link in the structure, giving characteristically low strengths and melting points. Semiconductors are predominantly covalent in nature, with some semiconducting compounds having a significant ionic character. These five categories of engineering materials are, then, the fundamental types. Composites are a sixth category and represent combinations of the first four fundamental types and have bonding characteristics appropriate to their constituents.

Key Terms

anion (45)
atomic mass (40)
atomic mass unit (39)
atomic number (40)
atomic radius (49)
Avogadro's number (40)
bond angle (59)
bond length (47)
bonding energy (49)
bonding force (47)
cation (45)
coordination number (49)
coulombic attraction (46)
covalent bond (57)
delocalized electron (63)
dipole (65)
dipole moment (66)
double bond (57)
electron (39)
electron density (57)
electron orbital (40)
electronegativity (64)
energy level (41)
energy trough (63)
energy well (63)
gram-atom (40)
group (40)
hard sphere (49)
hybridization (42)
hydrogen bridge (66)
ion (45)
ionic bond (44)
ionic radius (49)
isotope (40)
melting point (68)
metallic bond (63)
mole (40)
neutron (39)
nucleus (39)
orbital shell (45)
periodic table (40)
polar molecule (66)
polymeric molecule (57)
primary bond (42)
proton (39)
radius ratio (50)
repulsive force (47)
secondary bond (40)
soft sphere (49)
valence (47)
valence electron (57)
van der Waals bond (65)

References

Virtually any introductory textbook on college-level chemistry will be useful background for this chapter. Good examples are the following:

Brown, T. L., H. E. LeMay, Jr., B. E. Bursten, C. Murphy, and **P. Woodward,** *Chemistry—The Central Science with Mastering Chemistry®*, 12th ed., Prentice-Hall, Upper Saddle River, NJ, 2012.

Oxtoby, D. W., H. P. Gillis, and **A. Campion,** *Principles of Modern Chemistry,* 7th ed., Cengage, Independence, KY, 2011.

Petrucci, R. H., F. G. Herring, J. D. Madura, and **C. Bissonnette,** *General Chemistry—Principles and Modern Applications with Mastering Chemistry®*, 10th ed., Prentice-Hall, Upper Saddle River, NJ, 2011.

Problems

Beginning with this chapter, a set of problems will be provided at the conclusion of each chapter of the book. Instructors may note that there are few of the subjective, discussion-type problems that are so often used in materials textbooks. I strongly feel that such problems are generally frustrating to students who are being introduced to materials science and engineering. As such, I shall concentrate on objective problems. For this reason, no problems were given in the general, introductory chapter, Chapter 1. A few points about the organization of problems should be noted. All problems are clearly related to the appropriate chapter section. Also, some Practice Problems for each section were already given following the solved examples within that section. These problems are intended to provide a carefully guided journey into the first calculations in each new area and could be used by students for self-study. Answers are given for nearly all of the Practice Problems following the appendices. The solutions to all practice problems will be available on the Instructors Resource Center. The following problems are increasingly challenging. Problems not marked with a bullet are relatively straightforward but are not explicitly connected to an example. Those problems marked with a bullet (•) are intended to be relatively challenging. Answers to odd-numbered problems are given following the appendices.

Section 2.1 • Atomic Structure

2.1 A gold O-ring is used to form a gastight seal in a high-vacuum chamber. The ring is formed from an 80-mm length of 2.0-mm-diameter wire. Calculate the number of gold atoms in the O-ring.

2.2 Common aluminum foil for household use is nearly pure aluminum. A box of this product at a local supermarket is advertised as giving 77 ft^2 of material (in a roll 306 mm wide by 23.3 m long). If the foil is 0.4 mil (10.16 μm) thick, calculate the number of atoms of aluminum in the roll.

2.3 In a metal-oxide-semiconductor (MOS) device, a thin layer of SiO_2 (density $= 2.20\ \text{Mg/m}^3$) is grown on a single crystal chip of silicon. How many Si atoms and how many O atoms are present per square millimeter of the oxide layer? Assume that the layer thickness is 200 nm.

2.4 A box of clear plastic wrap for household use is polyethylene, $\left(C_2H_4 \right)_n$ with density $= 0.910\ \text{Mg/m}^3$. A box of this product contains 106 ft^2 of material (in a roll 304 mm wide by 32.5 m long). If the wrap is 0.2 mil (5.08 μm) thick, calculate the number of carbon atoms and the number of hydrogen atoms in this roll.

2.5 An Al_2O_3 *whisker* is a small single crystal used to reinforce metal-matrix composites. Given a cylindrical shape, calculate the number of Al atoms and the number of O atoms in a whisker with a diameter of 1 μm and a length of 23 μm. (The density of Al_2O_3 is $3.97\ \text{Mg/m}^3$.)

2.6 An optical fiber for telecommunication is made of SiO_2 glass (density $= 2.20\ \text{Mg/m}^3$). How many Si atoms and how many O atoms are present per millimeter of length of a fiber 6 μm in diameter?

2.7 Forty grams of magnesium filings are to be oxidized in a laboratory demonstration. **(a)** How many O_2 molecules would be consumed in this demonstration? **(b)** How many moles of O_2 does this represent?

2.8 Naturally occurring gallium has an atomic weight of 69.723. Its principal isotopes are ^{69}Ga and ^{71}Ga. What is the abundance (in atomic percent) of each isotope?

2.9 A copper penny has a mass of 3.50 g. Assuming pure copper, how much of this mass is contributed by **(a)** the neutrons in the copper nuclei and **(b)** electrons?

2.10 The orbital electrons of an atom can be ejected by exposure to a beam of electromagnetic radiation. Specifically, an electron can be ejected by a photon with energy greater than or equal to the electron's binding energy. Given that the photon energy (E) is equal to hc/λ, where h is Planck's constant, c the speed of light, and λ the wavelength, calculate the maximum wavelength of radiation (corresponding to the minimum energy) necessary to eject a 1*s* electron from a ^{12}C atom. (See Figure 2.3.)

2.11 Once the 1*s* electron is ejected from a ^{12}C atom, as described in Problem 2.10, there is a tendency for one of the $2(sp^3)$ electrons to drop into the 1*s* level. The result is the emission of a photon with an energy precisely equal to the energy change associated with the electron transition. Calculate the wavelength of the photon that would be emitted from a ^{12}C atom. (You will note various examples of this concept throughout the text in relation to the chemical analysis of engineering materials.)

2.12 The mechanism for producing a photon of specific energy is outlined in Problem 2.11. The magnitude of photon energy increases with the atomic number of the atom from which emission occurs. (This increase is due to the stronger binding forces between the negative electrons and the positive nucleus as the numbers of protons and electrons increase with atomic number.) As noted in Problem 2.10, $E = hc/\lambda$, which means that a higher-energy photon will have a shorter wavelength. Verify that higher atomic number materials will emit higher-energy, shorter-wavelength photons by calculating E and λ for emission from iron (atomic number 26 compared to 6 for carbon), given that the energy levels for the first two electron orbitals in iron are at $-7{,}112$ eV and -708 eV.

Section 2.2 • The Ionic Bond

2.13 Make an accurate plot of F_c versus a (comparable to that shown in Figure 2.6) for a $Mg^{2+}-O^{2-}$ pair. Consider the range of a from 0.2 to 0.7 nm.

2.14 Make an accurate plot of F_c versus a for a $Na^{+}-O^{2-}$ pair.

2.15 So far, we have concentrated on the coulombic force of attraction between ions. But like ions repel each other. A nearest neighbor pair of Na^+ ions in Figure 2.5 are separated by a distance of $\sqrt{2}a_0$, where a_0 is defined in Figure 2.7. Calculate the coulombic force of *repulsion* between such a pair of like ions.

2.16 Calculate the coulombic force of attraction between Ca^{2+} and O^{2-} in CaO, which has the NaCl-type structure.

2.17 Calculate the coulombic force of repulsion between nearest-neighbor Ca^{2+} ions in CaO. (Note Problems 2.15 and 2.16.)

2.18 Calculate the coulombic force of repulsion between nearest-neighbor O^{2-} ions in CaO. (Note Problems 2.15, 2.16, and 2.17.)

2.19 Calculate the coulombic force of repulsion between nearest-neighbor Ni^{2+} ions in NiO, which has the NaCl-type structure. (Note Problem 2.17.)

2.20 Calculate the coulombic force of repulsion between nearest-neighbor O^{2-} ions in NiO. (Note Problems 2.18 and 2.19.)

2.21 SiO_2 is known as a *glass former* because of the tendency of SiO_4^{4-} tetrahedra (Figure 2.17) to link together in a noncrystalline network. Al_2O_3 is known as an intermediate glass former due to the ability of Al^{3+} to substitute for Si^{4+} in the glass network, although Al_2O_3 does not by itself tend to be noncrystalline. Discuss the substitution of Al^{3+} for Si^{4+} in terms of the radius ratio.

2.22 Repeat Problem 2.21 for TiO_2, which, like Al_2O_3, is an intermediate glass former.

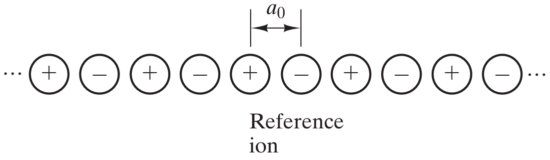
2.23 The coloration of glass by certain ions is often sensitive to the coordination of the cation by oxygen ions. For example, Co^{2+} gives a blue-purple color when in the fourfold coordination characteristic of the silica network (see Problem 2.21) and gives a pink color when in a sixfold coordination. Which color from Co^{2+} is predicted by the radius ratio?

2.24 One of the first nonoxide materials to be produced as a glass was BeF_2. As such, it was found to be similar to SiO_2 in many ways. Calculate the radius ratio for Be^{2+} and F^-, and comment.

2.25 A common feature in high-temperature ceramic superconductors is a Cu−O sheet that serves as a superconducting plane. Calculate the coulombic force of attraction between a Cu^{2+} and an O^{2-} within one of these sheets.

2.26 In contrast to the calculation for the superconducting Cu−O sheets discussed in Problem 2.25, calculate the coulombic force of attraction between a Cu^{2+} and an O^{2-}.

•2.27 For an ionic crystal, such as NaCl, the net coulombic bonding force is a simple multiple of the force of attraction between an adjacent ion pair. To demonstrate this concept, consider the hypothetical, one-dimensional "crystal" shown:



(a) Show that the net coulombic force of attraction between the reference ion and all other ions in the crystal is

$$F = AF_c,$$

where F_c is the force of attraction between an adjacent ion pair (see Equation 2.1) and A is a series expansion.

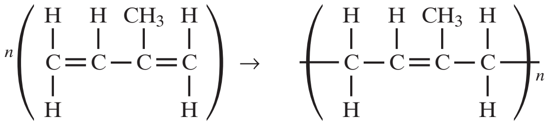
(b) Determine the value of A.

2.28 In Problem 2.27, a value for A was calculated for the simple one-dimensional case. For the three dimensional NaCl structure, A has been calculated to be 1.748. Calculate the net coulombic force of attraction, F, for this case.

Section 2.3 • The Covalent Bond

2.29 Calculate the total reaction energy for polymerization required to produce the roll of clear plastic wrap described in Problem 2.4.

2.30 Natural rubber is polyisoprene. The polymerization reaction can be illustrated as

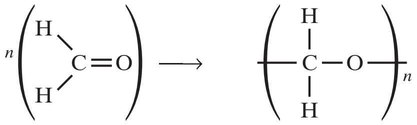


$$n\,(\mathrm{CH_2{=}CH{-}C(CH_3){=}CH_2}) \rightarrow (\mathrm{{-}CH_2{-}CH{=}C(CH_3){-}CH_2{-}})_n$$

Calculate the reaction energy (per mole) for polymerization.

2.31 Neoprene is a synthetic rubber, polychloroprene, with a chemical structure similar to that of natural rubber (see Problem 2.30), except that it contains a Cl atom in place of the CH_3 group of the isoprene molecule. **(a)** Sketch the polymerization reaction for neoprene, and **(b)** calculate the reaction energy (per mole) for this polymerization. **(c)** Calculate the total energy released during the polymerization of 1 kg of chloroprene.

2.32 Acetal polymers, which are widely used for engineering applications, can be represented by the following reaction, the polymerization of formaldehyde:

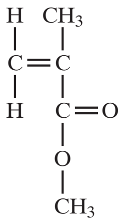


Calculate the reaction energy for this polymerization.

2.33 The first step in the formation of phenolformaldehyde, a common phenolic polymer, is shown in Figure 12.6. Calculate the net reaction energy (per mole) for this step in the overall polymerization reaction.

2.34 Calculate the molecular weight of a polyethylene molecule with $n = 600$.

2.35 The monomer upon which a common acrylic polymer, polymethyl methacrylate, is based is

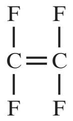


Calculate the molecular weight of a polymethyl methacrylate molecule with $n = 400$.

2.36 Bone "cement," used by orthopedic surgeons to set artificial hip implants in place, is methyl methacrylate polymerized during the surgery. The resulting polymer has a relatively wide range of molecular weights. Calculate the resulting range of molecular weights if $200 < n < 700$. (Note Problem 2.35.)

2.37 Orthopedic surgeons notice a substantial amount of heat evolution from polymethyl methacrylate bone cement during surgery. Calculate the reaction energy if a surgeon uses 25 g of polymethyl methacrylate to set a given hip implant. (Note Problems 2.35 and 2.36.)

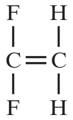
2.38 The monomer for the common fluoroplastic, polytetrafluoroethylene, is



$$\mathrm{CF_2{=}CF_2}$$

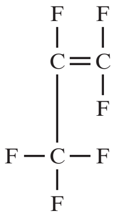
(a) Sketch the polymerization of polytetrafluoroethylene. **(b)** Calculate the reaction energy (per mole) for this polymerization. **(c)** Calculate the molecular weight of a molecule with $n = 900$.

2.39 Repeat Problem 2.38 for polyvinylidene fluoride, an ingredient in various commercial fluoroplastics, that has the monomer



$$\mathrm{CF_2{=}CH_2}$$

2.40 Repeat Problem 2.38 for polyhexafluoropropylene, an ingredient in various commercial fluoroplastics, that has the monomer



Section 2.4 • The Metallic Bond

2.41 In Table 2.3, the heat of sublimation was used to indicate the magnitude of the energy of the metallic bond. A significant range of energy values is indicated by the data. The melting point data in

Appendix 1 are another, more indirect indication of bond strength. Plot heat of sublimation versus melting point for the five metals of Table 2.3, and comment on the correlation.

2.42 In order to explore a trend within the periodic table, plot the bond length of the group II A metals (Be to Ba) as a function of atomic number. (Refer to Appendix 2 for necessary data.)

2.43 Superimpose on the plot generated for Problem 2.42 the metal-oxide bond lengths for the same range of elements.

2.44 To explore another trend within the periodic table, plot the bond length of the metals in the row Na to Si as a function of atomic numbers. (For this purpose, Si is treated as a semimetal.)

2.45 Superimpose on the plot generated for Problem 2.44 the metal-oxide bond lengths for the same range of elements.

2.46 Plot the bond length of the metals in the long row of metallic elements (K to Ga).

2.47 Superimpose on the plot generated for Problem 2.46 the metal-oxide bond lengths for the same range of elements.

•2.48 The heat of sublimation of a metal, introduced in Table 2.3, is related to the ionic bonding energy of a metallic compound discussed in Section 2.2. Specifically, these and related reaction energies are summarized in the Born–Haber cycle, illustrated next. For the simple example of NaCl,

$$\begin{tikzcd}
\text{Na (solid)} + \frac{1}{2}\text{Cl}_2\text{ (g)} \arrow[r] \arrow[d, "\Delta H_f^\circ"] & \text{Na (g)} + \arrow[d] & \text{Cl (g)} \arrow[d] \\
\text{NaCl (solid)} & \text{Na}^+\text{ (g)} + \arrow[l] & \text{Cl}^-\text{ (g)}
\end{tikzcd}$$

Given the heat of sublimation to be 100 kJ/mol for sodium, calculate the ionic bonding energy of sodium chloride. (Additional data: ionization energies for sodium and chlorine = 496 kJ/mol and −361 kJ/mol, respectively; dissociation energy for diatomic chlorine gas = 243 kJ/mol; and heat of formation, ΔH_f°, of NaCl = −411 kJ/mol.)

Section 2.5 • The Secondary, or van der Waals, Bond

2.49 The secondary bonding of gas molecules to a solid surface is a common mechanism for measuring the surface area of porous materials. By lowering the temperature of a solid well below room temperature, a measured volume of gas will condense to form a monolayer coating of molecules on the porous surface. For an 80-g sample of fused copper catalyst, a volume of 8×10^3 mm^3 of nitrogen (measured at standard temperature and pressure, 0°C and 1 atm) is required to form a monolayer upon condensation. Calculate the surface area of the catalyst in units of m^2/kg. (Take the area covered by a nitrogen molecule as 0.162 nm^2 and recall that, for an ideal gas, $pV = nRT$, where n is the number of moles of the gas.)

2.50 Repeat Problem 2.49 for a highly porous silica gel that has a volume of 1.34×10^7 mm^3 of N_2 gas [at standard temperature and pressure (STP)] condensed to form a monolayer.

2.51 Small-diameter noble gas atoms, such as helium, can dissolve in the relatively open network structure of silicate glasses. (See Figure 1.8b for a schematic of glass structure.) The secondary bonding of helium in vitreous silica is represented by a heat of solution, ΔH_s, of −3.96 kJ/mol. The relationship between solubility, S, and the heat of solution is

$$S = S_0 e^{-\Delta Hs/(RT)},$$

where S_0 is a constant, R is the gas constant, and T is the absolute temperature (in K). If the solubility of helium in vitreous silica is 5.51×10^{23} atoms/(m$^3 \cdot$ atm) at 25°C, calculate the solubility at 240°C.

2.52 Due to its larger atomic diameter, neon has a higher heat of solution in vitreous silica than helium. If the heat of solution of neon in vitreous silica is −6.70 kJ/mol and the solubility at 25°C is 9.07×10^{23} atoms/(m$^3 \cdot$ atm), calculate the solubility at 250°C. (See Problem 2.51.)