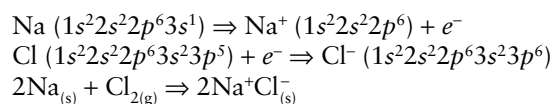# 3 Chemical Bonding

The forces responsible for chemical combination of atoms are of two main types. There are those forces which arise between electrically charged species, repulsive if the charges are similar, attractive if dissimilar. … The second type of force may be called an exchange force and these can be described in terms of the Schrödinger wave equation…. A little reflection will reveal that we understand neither – all we have is two ways of describing different situations, and in all probability the origin of both forces is the same.

Fyfe (1964)

Chemical compounds are formed by the combination of two or more atoms (or ions), and the formation of a stable compound occurs when the combination results in a lower energy than the total energy of the separated atoms (or ions). Interatomic (or interionic) net attractive forces that hold atoms (or ions) in solids together are called *chemical bonds*.

Chemical bonds usually involve only the *valence electrons* (*s* and *p* electrons in the outermost orbitals) of an atom. Physical and chemical properties of all substances depend on the character of the chemical bonds that hold them together.

Much of the bonding in solids of geochemical interest can be described in terms of two end-member types: (i) *ionic* (or *electrovalent*) *bonds* that exist because of electrostatic attraction between cations and anions formed by transfer of one or more electrons between atoms; and (ii) *covalent bonds* that arise because of sharing of electrons between atoms that results from overlap of orbitals from the two atoms. For example, the ionic bonding in NaCl results from the electrostatic attraction between a Na^+ cation formed by the loss of a valence electron from the $3s$ orbital of the Na atom ($1s^2 2s^2 2p^6 3s^1$) and a Cl^- anion formed by incorporation of that electron into the $3p$ orbital of the Cl atom ($1s^2 2s^2 2p^6 3s^2 3p^5$) (Fig. 3.1a):

$$Na\ (1s^2 2s^2 2p^6 3s^1) \Rightarrow Na^+\ (1s^2 2s^2 2p^6) + e^-$$
$$Cl\ (1s^2 2s^2 2p^6 3s^2 3p^5) + e^- \Rightarrow Cl^-\ (1s^2 2s^2 2p^6 3s^2 3p^6)$$
$$2Na_{(s)} + Cl_{2(g)} \Rightarrow 2Na^+Cl^-_{(s)}$$

The NaCl molecule itself is electrically neutral because its structure contains a Na^+ cation for every Cl^- anion. Sodium and chlorine atoms combine readily because of the large difference in their first ionization potential and electron affinity (see section 2.4). Covalent bonding, on the other hand, arises from sharing of electrons. The covalent bonding in Cl_2, for example, may be viewed as resulting from the sharing of a pair of electrons between two Cl atoms, each of which contributes one electron to the shared pair (Fig. 3.1b). Atoms can share one, two, or three electron pairs, forming, respectively, single, double, and triple covalent bonds. All bonds between atoms of different elements have some degree of both ionic and covalent character.

Compounds containing predominantly ionic bonding are called *ionic compounds*, and those that are held together mainly by covalent bonds are called *covalent compounds*. This difference in bonding accounts for the differences in some properties associated with simple ionic and covalent compounds (Table 3.1). Other types of bonds that will be discussed briefly in this chapter include *metallic bonds, Van der Waals bonds*, and *hydrogen bonds*.
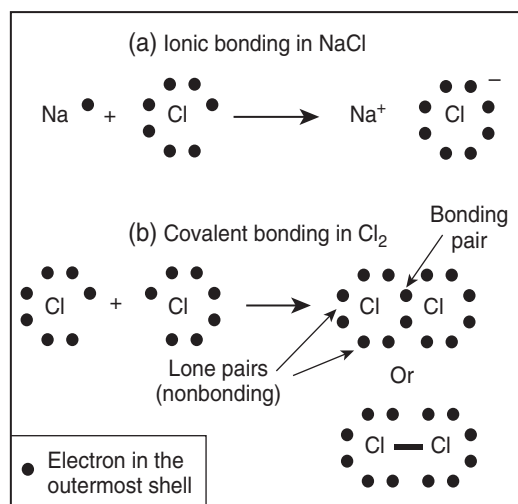
Fig. 3.1 Lewis dot representation of (a) ionic bonding (solid NaCl) and (b) covalent bonding (Cl_2 gas). In this kind of illustration, the chemical symbol of the element includes the inner complete shells of electrons, and the valence electrons (i.e., electrons in the outermost occupied *s* and *p* orbitals) are represented by dots. The single covalent bond in Cl_2 is represented by the two dots of the "bonding pair" or by a single line representing that pair; any pair of unshared electrons in the same orbital, which does not participate in the formation of covalent bonds, are referred to as a "lone pair."

3.1 Ionic bonding

3.1.1 Ionic radii

The potential energy of a system (E_p) comprised of two oppositely charged ions (e.g., Na^+ and Cl^-), each with its electron cloud around the nucleus, approaching each other is given by (Fyfe, 1964):

$$E_p = -\frac{e^2}{R} + \frac{be^2}{R^n} \qquad (3.1)$$

where R is the interionic distance (i.e., distance between the centers of the two ions, which are assumed to be hard spheres), b is a constant, and n is an integer with values between 8 and 12. The term $-e^2/R$ represents the coulombic attraction between the opposite net charges ($\pm e$), and the term e^2/R^n arises out of the repulsion caused by interpenetration of the electron clouds and by the repulsion between the nuclei of the ions. As R gets smaller, the attraction term (which, by convention, is assigned a negative sign) becomes more negative, indicating lower potential energy and thus increased stability. The repulsion (which, by convention, is assigned a positive sign) contributes little to E_p for large values of R, but its contribution increases very rapidly when R becomes smaller than a critical value R_0, which is the equilibrium interionic distance at which the isolated ion pair is most stable (Fig. 3.2). When the two ions are separated by the distance R_0, we have a stable *ionic bond* formed between them. The value of R_0, the *bond length*, can be determined from the fact that it corresponds to the minimum value of E_p and occurs when $dE/dR = 0$. (When the cation is associated with more than one anion, as in a crystal, repulsion between the anions makes R_0 somewhat larger.) The curve for E_p in Fig. 3.2 is typical of all atomic–molecular systems, and it is the basis of the concepts of interionic distance and *ionic radius*, and the premise that to a first approximation ions have a more or less constant ionic size. Strictly speaking, the electron density distribution around a nucleus does not have a spherical symmetry, as implied by the term "ionic radius." A more appropriate term, according to Gibbs *et al.* (1992), is "bonded radius," which refers to the distance between the center of one atom to the point of minimum electron density in the direction between two nuclei. The outer extent of an atom in other directions is usually different because of a different distribution of electrons (i.e., the atom is not spherical). The bonded radius can be measured from electron distribution maps. However, we continue to rely on the concept of ionic radii because the approach has been quite successful in explaining most of the ionic crystal structures.

Table 3.1 Some properties of ionic and covalent compounds.

| Property	Ionic compounds	Covalent compounds
Participating elements	Commonly between two elements with quite different electronegativities[1], usually a metal and a nonmetal	Commonly between two elements with similar electronegativities[1], usually nonmetals. Homonuclear molecules (such as Cl_2 comprised of only one element) are covalent
Melting point	They are solids with high melting points (typically > 400°C). Ionic compounds do not exist as gases in nature	They are gases, liquids, or solids with low melting points (typically < 300°C)
Solubility	Many are soluble in polar solvents such as water, and most are insoluble in nonpolar solvents such as carbon tetrachloride (CCl_4).	Many are insoluble in polar solvents, and most are soluble in nonpolar solvents such as carbon tetrachloride (CCl_4)
Electrical conductivity	Molten compounds and aqueous solutions are good conductors of electricity because they contain charged particles (ions)	Due to lack of charged particles, liquid and molten compounds do not conduct electricity, and aqueous solutions are usually poor conductors of electricity

[1] See section 3.6.5.
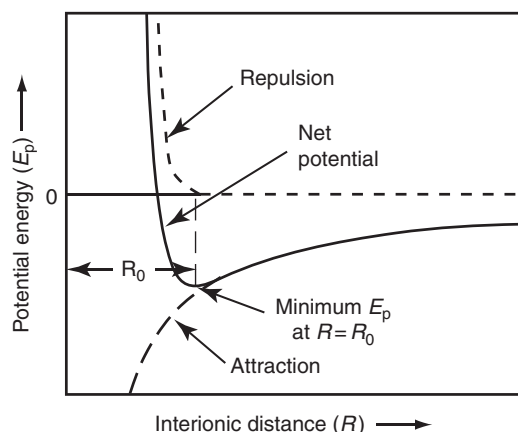
Fig. 3.2 Variation of the potential energy (E_p) of a system consisting of a singly charged cation and a singly charged anion as a function of interionic distance. The equilibrium interionic distance (R_0) is marked by the minimum value of E_p, when $dE/dR = 0$. For $R > R_0$, E_p is essentially determined by the coulombic attraction between the opposite charges and for $R < R_0$ by the repulsion between the nuclei and the electron clouds.

For the discussion below, we assume a model of pure ionic bonding arising out of a geometric framework of ions represented by hard spheres of constant radius. But how do we determine the radius of each ion? Actually, it is not possible to measure the radius of individual ions in a solid, but we can measure the interionic distance between centers of two ions in a solid from its cell dimensions determined with X-ray diffraction techniques, and then determine the radius of individual ions through some manipulation (Companion, 1964). For the purpose of illustration, let us suppose that Fig. 3.3 represents the packing in LiCl and KCl crystals as revealed by X-ray diffraction data. It is reasonable to expect that Li$^+$, with only two electrons, is a very small cation and assume that the packing in LiCl be largely determined by the much larger Cl$^-$ anions (each containing 18 electrons) touching each other. In this case, the radius of the Cl$^-$ ion (r_{Cl^-}) is one-half of the measurable interionic distance d_1. We can now determine the radius of K$^+$ ion from the measured interionic distance d_2 in a KCl crystal: $r_{K^+} = d_2 - r_{Cl^-}$. It turns out that the ionic radii calculated by this strategy are reasonably constant from compound
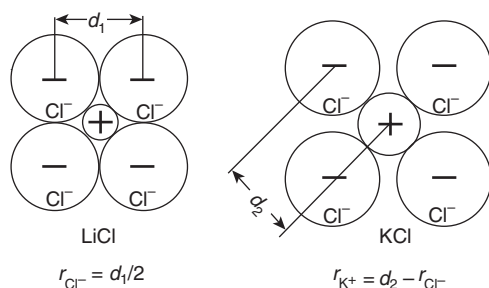

Fig. 3.3 Strategy for determining ionic radii from packing of ions (assumed to be hard spheres) in LiCl and KCl.

to compound and, carried over the entire Periodic Table, this has enabled the setting up a self-consistent set of average ionic radii (Fig. 3.4).

As expected, ionic radii of cations and anions vary with atomic number. The radius of a given ion is also a function of the *coordination number*, the number of nearest neighbors of the ion in a crystalline structure (see section 3.1.2). Some general trends for ionic radii (expressed in Å) with octahedral (or six-fold) coordination (Fig. 3.4), the most common kind of coordination for most ions in silicate minerals, are summarized below:

(1) Cations are smaller than anions, the only exceptions being the five largest cations (Rb$^+$, Cs$^+$, Fr$^+$, Ba^{2+}, and Ra^{2+}), which are larger than F$^-$, the smallest anion.

(2) Within an *isoelectronic series* – a series of ions with the same number of electrons – ionic radius decreases with increasing atomic number because of increased nuclear attraction for the electron cloud. For example,

$$r_{Si^{4+}}(0.48) < r_{Al^{3+}}(0.54) < r_{Mg^{2+}}(0.72) < r_{Na^+}(1.02)$$
$$< r_{F^-}(1.33) < r_{O^{2-}}(1.40)$$

(3) On the other hand, in the lanthanide (or rare-earth) series characterized by cations with 3+ charge, the ionic radius decreases with increasing atomic number, from 1.13 for La^{3+} to 0.94 for Lu^{3+}. This so-called *lanthanide contraction* can be attributed to the influence of the increasing nuclear charge.

(4) Within a family of ions, such as the alkali metals or the halogens, the ionic size increases as we go down the Periodic Table. For example,

$$r_{Li^+}(0.76) < r_{Na^+}(1.02) < r_{K^+}(1.38) < r_{Rb^+}(1.52)$$
$$< r_{Cs^+}(1.67) < r_{Fr^+}(1.80)$$

$$r_{F^-}(1.33) < r_{Cl^-}(1.81) < r_{Br^-}(1.96) < r_{I^-}(2.20)$$

This variation is a consequence of adding electrons with their most probable distance farther from the nucleus.

(5) In the case of cations of the same element, ionic radius decreases with increase in ionic charge because of a decrease in the number of electrons. For example,

$$r_{Fe^{3+}}(0.73) < r_{Fe^{2+}}(0.78)$$
$$r_{Mn^{4+}}(0.62) < r_{Mn^{3+}}(0.73) < r_{Mn^{2+}}(0.83)$$
$$r_{Ti^{4+}}(0.61) < r_{Ti^{3+}}(0.72) < r_{Ti^{2+}}(0.87)$$
$$r_{U^{6+}}(0.81) < r_{U^{4+}}(0.97)$$

The opposite is true for anions, although anions with variable charge are not common.

3.1.2 Coordination number and radius ratio

How do ions fit together to produce different crystal structures? The fundamental constraint is that, for a given set of ions, the most stable arrangement is the one that has the

IONIC RADII (Å) (octahedral coordination)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H Very small																	2 He
3 Li$^+$ 0.76	4 Be^{2+} 0.27*											5 B^{3+} 0.11*	6 C^{4+} 0.15*	7 N^{5+} 0.13	8 O^{2-} 1.40	9 F$^-$ 1.33	10 Ne
11 Na$^+$ 1.02	12 Mg^{2+} 0.72											13 Al^{3+} 0.54	14 Si^{4+} 0.26*	15 P^{5+} 0.17*	16 S^{-2} 1.84	17 Cl$^-$ 1.81	18 Ar
19 K$^+$ 1.38	20 Ca^{2+} 1.00	21 Sc^{3+} 0.75	22 Ti^{4+} 0.61	23 V^{5+} 0.54	24 Cr^{3+} 0.62	25 Mn^{2+} 0.83	26 Fe^{2+} 0.78	27 Co^{2+} 0.75	28 Ni^{2+} 0.69	29 Cu^{2+} 0.73	30 Zn^{2+} 0.74	31 Ga^{3+} 0.62	32 Ge^{4+} 0.73	33 As^{3+} 0.58	34 Se^{2-} 1.98	35 Br$^-$ 1.96	36 Kr
37 Rb$^+$ 1.52	38 Sr^{2+} 1.18	39 Y^{3+} 0.90	40 Zr^{4+} 0.72	41 Nb^{5+} 0.64	42 Mo^{4+} 0.65	43 Te^{6+} 0.56	44 Ru^{3+} 0.76	45 Rh^{3+} 0.75	46 Pd^{2+} 0.86	47 Ag$^+$ 0.94	48 Cd^{2+} 0.95	49 In^{3+} 0.80	50 Sn^{4+} 0.69	51 Sb^{5+} 0.60	52 Te^{6+} 0.56	53 I$^-$ 2.20	54 Xe
55 Cs$^+$ 1.67	56 Ba^{2+} 1.35	57–71 Lanth	72 Hf^{4+} 0.71	73 Ta^{5+} 0.64	74 W^{6+} 0.60	75 Re^{4+} 0.63	76 Os^{4+} 0.71	77 Ir^{4+} 0.71	78 Pt^{4+} 0.71	79 Au$^+$ 1.37	80 Hg^{2+} 1.02	81 Tl^{3+} 0.67	82 Pb^{2+} 1.19	83 Bi^{3+} 1.03	84 Po^{6+} 0.67	85 At^{7+} 0.62	86 Rn
87 Fr$^+$ 1.80	88 Ra^{2+} 1.43	89–103 Actin	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112						

	Lanthanides	57 La^{3+} 1.13	58 Ce^{3+} 1.09	59 Pr^{3+} 1.08	60 Nd^{3+} 1.06	61 Pm^{3+} 1.04	62 Sm^{3+} 1.04	63 Eu^{3+} 1.03	64 Gd^{3+} 1.02	65 Tb^{3+} 1.00	66 Dy^{3+} 0.99	67 Ho^{3+} 0.98	68 Er^{3+} 0.97	69 Tm^{3+} 0.96	70 Yb^{3+} 0.95	71 Lu^{3+} 0.94
	Actinides	89 Ac^{3+} 1.18	90 Th^{4+} 1.08	91 Pa^{4+} 0.98	92 U^{4+} 0.97	93 Np^{4+} 0.95	94 Pu^{4+} 0.88	95 Am^{4+}	96 Cm^{4+}	97 Bk^{4+}	98 Cf^{4+}	99 Es	100 Fm	101 Md	102 No	103 Lr

* Tetrahedral coordination

Fig. 3.4 Ionic radii of ions in octahedral coordination. Å = 10^{-10} m. Sources of data: compilations by Krauskopf and Bird (1995), and Faure (1991).

lowest potential energy. The general rules that need to be observed for attaining maximum stabilization of a crystal structure are as follows:

(1) The crystal structure must be electrically neutral, that is, the cation: anion ratio must be such that the positive charges are exactly balanced by the negative charges.
(2) The cation–anion separation must be close to the equilibrium interionic distance (R_0 in Fig. 3.2) for the compound under consideration.
(3) The arrangement of the ions must be in a regular pattern, with as many cations around anions as possible and as far away from each other as possible; analogous restrictions apply to the anions. In other words, we may treat the ions as spherical balls and pack them as closely as

possible, subject to the constraints of electrical neutrality of the structure and minimum interionic distance. In a given three-dimensional close packing of spheres, the number of oppositely charged nearest neighbors surrounding an ion is called its *coordination number* (*CN*). If an ion *A*, for example, is surrounded by four ions of *B*, $CN_A = 4$ (tetrahedral coordination); if *A* is surrounded by six ions of *B*, $CN_A = 6$ (octahedral coordination), and so on. As discussed below, coordination number is an important consideration in crystal chemistry.

Generally, cations are smaller than anions, so the number of anions that can be packed around the smaller cations determines crystal structures. The combined influence of cations and anions on coordination number can be predicted from a consideration of the magnitudes of their radii
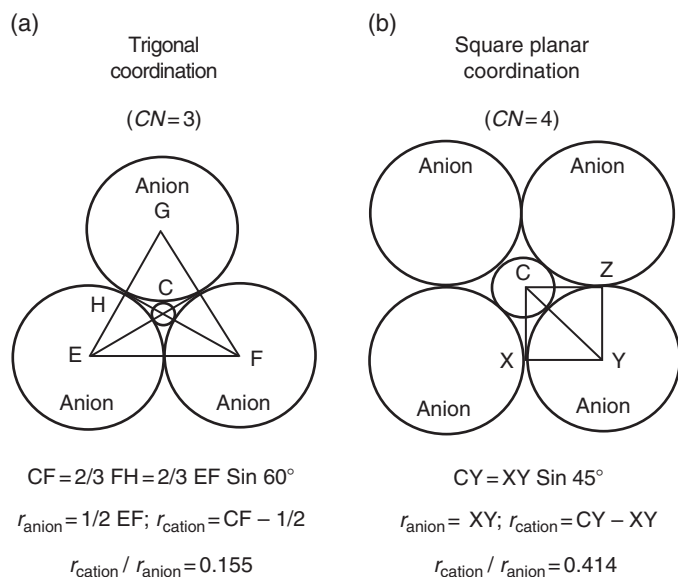
(a)

Trigonal coordination

($CN=3$)

CF = 2/3 FH = 2/3 EF Sin 60°

$r_{anion} = 1/2$ EF; $r_{cation} =$ CF − 1/2

$r_{cation} / r_{anion} = 0.155$

(b)

Square planar coordination

($CN=4$)

CY = XY Sin 45°

$r_{anion} =$ XY; $r_{cation} =$ CY − XY

$r_{cation} / r_{anion} = 0.414$

Fig. 3.5 Critical radius ratios for (a) threefold (trigonal) and (b) fourfold (square planar) coordinations.

expressed as the *radius radio (RR)*. For a cation in a binary ionic solid, *RR* is defined as

$$\text{Radius ratio } (RR) = \frac{r_c}{r_a} \qquad (3.2)$$

where r_c and r_a are ionic radius of the cation and the anion, respectively. Evidently, as the cation becomes larger relative to the anion, a larger number of anions may fit around the cation. In other words, the *CN* of the cation is likely to increase as *RR* increases.

Accepting a model based on close packing of spheres, we can easily calculate the *critical radius ratios* (i.e., the limiting values of the radius ratio) for different geometrical arrangements of the spheres. The smallest value of *CN* is 2, which represents the situation when the cation is so small that it is possible to pack only two anions around it if anion–cation contact is to be maintained. As the size of the cation increases relative to that of the anion, it becomes possible to place three anions in mutual contact around the cation (i.e., *CN* = 3) when *RR* reaches a critical value of 0.155 (Fig. 3.5a). With increasing size of the cation relative to that of the anion, the *CN* changes to higher values. The calculated critical radius ratios for different possible symmetries are: 0.155–0.225 for *CN* = 3 (trigonal coordination); 0.225–0.414 (Fig. 3.5b) for *CN* = 4 (tetrahedral or square planar coordination); 0.414–0.732 for *CN* = 6 (octahedral coordination); 0.732–1.0 for *CN* = 8 (body-centered cubic coordination); and > 1.0 for *CN* = 12 (edge-centered cubic coordination) (Fig. 3.6). Other coordination numbers, such as 5, 7, 9, 10, and 11, do exist but are quite uncommon because such coordination polyhedra cannot be

Critical radius ratio	Cation coordination number (CN)	Symmetry of anions around the cation	Sketch of symmetry	Example
< 0.155	2	Linear		HF_2
0.155 – 0.225	3	Trigonal planar (Corners of an equilateral triangle)		CO_3^{2-}
0.225 – 0.414	4	Tetrahedral (Corners of a tetrahedron)		ZnS
0.014 – 0.732	4	Square planar (Corners of a regular square)		$Ni(CN)_4^{2-}$
0.014 – 0.732	6	Octahedral (Corners of a regular octahedron)		NaCl
0.732 – 1.00	8	Body-centered cubic (corners of a cube)		CsCl
> 1.00	12	Edge-centered cubic (mid–points of cube edges)		

● Cation
○ Anion

Fig. 3.6 The effect of critical radius ratios on coordination number and possible geometrical arrangements of ions in ionic crystals. ZnS (sphalerite) itself is not an ionic compound but its name is given to the structure because it is the most common compound in which this geometrical arrangement occurs (Evans, 1966).

extended into infinite, regular three-dimensional arrays (Greenwood, 1970). In mineral structures, the most common anion is O^{2-}, which has an ionic radius of 1.40 Å, and the ionic radii of most common cations are between 0.60 and 1.10 Å. Thus, the radius ratios with oxygen in minerals mostly lie between 0.43 and 0.79, suggesting that the most frequent coordination number in minerals is 6. This is why Fig. 3.4 lists ionic radii for octahedral coordination rather than for tetrahedral or cubic coordination. Examples of some ionic crystal structures characterized by different coordinations are presented in Fig. 3.7.

Many cations in silicate minerals occur exclusively in a particular coordination with oxygen, but some occur in more than one coordination, to some extent controlled by the temperature and pressure of crystallization. For example, the radius ratio of Al^{3+} bonded to O^{2-} is 0.54 Å/1.40 Å = 0.386, which is very close to the theoretical boundary of 0.414 between *CN* = 4 and *CN* = 6. Thus, in silicate minerals formed

(a)

ZnS – Tetrahedral coordination

(b)

NaCl – Octahedral coordination

(c)

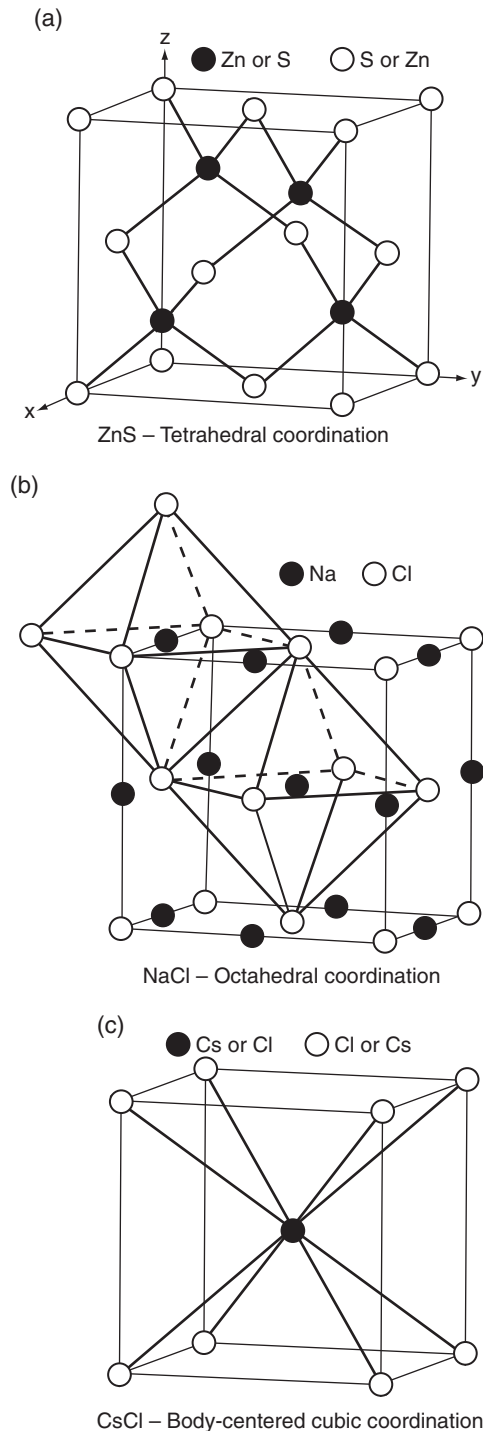CsCl – Body-centered cubic coordination

Fig. 3.7 Examples of some ionic crystal structures characterized by different coordinations: (a) ZnS (tetrahedral); (b) NaCl (octahedral); and (c) CsCl (body-centered cubic). It should be stressed that such illustrations of crystal structures represent only the geometry of arrangement of the centers of the ions or the mean positions of the vibrating nuclei; the electron density is concentrated near the nuclei and along directions to near neighbors. (From *An Introduction to Crystal Chemistry*, 2nd edition, by R.C. Evans, Figure 3.04, p. 35, Figure 3.02, p. 33, and Figure 3.03, p. 34; Copyright 1966, Cambridge University Press. Reproduced with permission of the publisher.)

at high temperatures or low pressures, Al^{3+} tends to assume tetrahedral coordination and substitute for Si^{4+}, whereas in minerals formed at low temperatures or high pressures, Al^{3+} tends to occur in octahedral coordination.

Crystal structures are often more complicated than what can be predicted on the basis of radius ratios. An important complicating factor is the degree of covalence (electron sharing) in many dominantly ionic minerals, resulting in distortion of the electronic charge density around ions (*polarization*) (see section 3.6.5).

3.1.3 *Lattice energy of ideal ionic crystals*

The stability of ionic compounds is optimized by close packing of oppositely charged ions together in extended arrays. The three-dimensional arrangement of atoms or ions in a crystal is commonly referred to as (crystal) *lattice*. Every lattice is associated with a certain amount of stabilization energy, which is called the (crystal) *lattice energy*. *The lattice energy* (U_L) *of a perfectly ionic crystal is defined as the amount of energy required at absolute zero (i.e., −273°C) to convert one mole of the solid into its constituent ions at infinite separation in the gas phase*:

$$M_a X_b(s) \Rightarrow aM^{b+}(g) + bX^{a-}(g) \ (U_L) \tag{3.3}$$
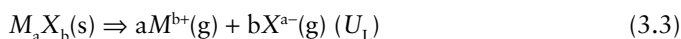
The lattice energy for NaCl, for example, is 786 kJ mol^{-1}; that is, it would require 786 kJ of energy per mole of NaCl to produce infinite separation of Na$^+$ and Cl$^-$ ions in the gas phase. We can also conclude that one mole of solid NaCl compound is 786 kJ lower in energy, and thus more stable, than a mixture of one mole each of the constituent ions.

For 1 gram-mole of a binary compound, the lattice energy can be calculated directly from the properties of the ions by means of the following equation, originally derived by Born and Landé (see Box 3.1):

$$U_L = M_c A \frac{z_c \, z_a \, e^2}{R} \left(1 - \frac{1}{n}\right) \tag{3.4}$$

where z_c and z_a are the charges on cations and anions (expressed as a multiple of the electron charge e), R is the cation–anion interionic distance, n is a constant for the particular crystal structure, A is the Avogadro's number, and M_c is a numerical quantity called the *Madelung constant*, the value of which depends on the crystal structure (Table 3.2). From experimental studies of compressibility, it is known that for most ionic crystals n has a value between 8 and 12. Suggested values of n for some common solids are: LiF, 5.9; LiCl, 8.0; LiBr, 8.7; NaCl, 9.1; NaBr, 9.5. By convention, the lattice energy is considered positive because energy is consumed for separation of the ions. The energy released during

<hr>

Box 3.1 Expression for the lattice energy of an ionic crystal

The electrostatic potential energy (E_p) associated with a cation–anion pair in an ionic crystal can be described by a relation of the form (Fyfe, 1964)

$$E_p = -\frac{z_c\, z_a\, e^2}{R} + \frac{be^2}{R^n} \qquad (3.5)$$

where z_c and z_a are the charges on cations and anions (expressed as a multiple of the electron charge e), R is the interionic distance separating the ions, and b and n are constants characteristic of the crystal structure. As in equation (3.1), the first term in equation (3.5) represents normal coulombic attraction and the second term repulsion. The potential energy of an entire crystal, which is obtained by adding together all such interactions over the three-dimensional lattice of the entire crystal, is (for derivation see Fyfe, 1964, pp. 48–49):

$$E_{p\,(crystal)} = -M_c \frac{z_c\, z_a\, e^2}{R}\left(1 - \frac{1}{n}\right) \qquad (3.6)$$

where M_c is a numerical quantity called the *Madelung constant*, the value of which depends on the crystal structure (Table 3.2). To obtain the lattice energy of 1 gram-mole of a crystal, this energy must be multiplied by Avogadro's number (A), the number of molecules in one mole of a substance. The lattice energy (U_L) of a crystal is defined as $-AE_{p(crystal)}$, so that

$$U_L = -AE_p = M_c A \frac{z_c\, z_a\, e^2}{R}\left(1 - \frac{1}{n}\right) \qquad (3.4)$$

Note that U_L decreases with increasing R, and approaches zero as R approaches infinity.

Table 3.2 Madelung constants for selected types of crystal structures.

Structure type	Madelung constant	Coordination (anion) : Coordination (cation)	Solid compound
NaCl type	1.747	6:6	Halite
CsCl type	1.747	8:8	CsCl
ZnS type	1.638	4:4	Sphalerite
CaF$_2$ type	2.519	8:4	Flourite
TiO$_2$ type	2.408	6:3	Rutile
Al$_2$O$_3$ type	4.172	6:4	Corundum

Source of data: Lide (1998).

the reverse process, the formation of a crystal from its widely separated constituent ions, called the *energy of crystallization* (E_{cryst}), is assigned a negative sign (i.e., $U_L = -E_{cryst}$). Equation (3.4) does not include the contribution due to the van der Waals forces of attraction between the ions (see section 3.8),

but the correction arising out of this weak force is very small – for example, less than about $12\,kJ\,mol^{-1}$ for the alkali halides (Evans, 1966).

The Born–Landé equation, strictly speaking, applies only to binary compounds, but it enables us to make some qualitative statements regarding the lattice energy of more complex substances. For a particular structure type, lattice energies are greater the higher the charge on the ions, the smaller the ions, and the closer the packing (Mason, 1966).

For crystals of the same structure, with ions of the same charge, the lattice energy varies as the interionic distance: $U_{LiCl} < U_{NaCl} < U_{KCl}$.

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Example 3–1: Calculation of the lattice energy and the energy of crystallization of one mole of NaCl crystals using equation (3.5)

Given: radius of Na$^+$ (r_{Na^+}) = 1.02 Å; radius of Cl$^-$ (r_{Cl^-}) = 1.81 Å; $A = 6.02 \times 10^{23}$; $e = 4.80 \times 10^{-10}$ coulombs; $n = 9$; and $M = 1.747$

$R = 1.02\ \text{Å} + 1.81\ \text{Å} = 2.83\ \text{Å} = 2.83 \times 10^{-8}\,\text{cm}$

$$
\begin{aligned}
U_L(\text{NaCl}) &= M_c A \frac{z_c z_a e^2}{R}\left(1 - \frac{1}{n}\right) \\
&= (1.747)(6.02 \times 10^{23}) \\
&\quad \frac{(1)(1)(4.80 \times 10^{-10})^2}{2.83 \times 10^{-8}}\left(1 - \frac{1}{9.1}\right) \\
&= 10.517 \times 8.141 \times 0.890 \times 10^{-11} \\
&= 76.201 \times 10^{11}\ \text{ergs mol}^{-1} \\
&= (76.201 \times 10^{11})(2.389 \times 10^{-11})\ \text{kcal mol}^{-1} \\
&= 182\ \text{kcal mol}^{-1} = 761\ \text{kJ mol}^{-1}
\end{aligned}
$$

$E_{cryst}(\text{NaCl}) = -U_L(\text{NaCl}) = -761\,\text{kJ mol}^{-1}$

It is impossible to measure precisely the lattice energy of a crystal directly, but it can be estimated from more readily measurable quantities by applying *Hess's Law of Heat Summation*, which says that the heat of a reaction (exothermic or endothermic) is the same whether it occurs in one step or a series of steps. The energy cycle used in this approach to calculate lattice energy is known as the *Born–Haber cycle*, which is illustrated in Example 3–2 for NaCl. Lattice energies of selected solid halides, estimated by application of the Born–Haber cycle, are listed in Table 3.3.

<hr>

Example 3–2: Estimation of the lattice energy of 1 mole of NaCl crystal using the Born–Haber cycle approach

The estimate of lattice energy obtained by the application of Born–Haber cycle will vary somewhat, depending on the reactions chosen for the cycle; the cycle depicted in Fig. 3.8 will suffice to illustrate the concept.

Table 3.3 Estimated lattice energies (U_L) of selected solid compounds (halides).

Solid	(U_L) kJ mol⁻¹	Solid	(U_L) kJ mol⁻¹	Solid	(U_L) kJ mol⁻¹	Solid	(U_L) kJ mol⁻¹
LiF	1036	LiCl	853	LiBr	807	LiI	757
NaF	923	NaCl	786	NaBr	747	NaI	704
KF	821	KCl	715	KBr	682	KI	649
RbF	785	RbCl	689	RbBr	660	RbI	630
CsF	740	CsCl	659	CsBr	631	CsI	604
MgF_2	2957	$MgCl_2$	2526	$MgBr_2$	2440	MgI_2	2327
AlF_3	5215	$AlCl_3$	5492	$AlBr_3$	5361	AlI_3	5218

Source of data: Lide (1998).

I_{Na}= Ionization potential of sodium = 495.9 kJ mol⁻¹

E_{Cl}= Electron affinity of chlorine = 348.3 kJ mol⁻¹

S_{Na}= Heat of sublimation of sodium = 108.8 kJ mol⁻¹

D_{Cl}= Heat of dissociation of chlorine = 236.0 kJ mol⁻¹

Q_{NaCl}= Heat of formation of NaCl = − 411.3 kJ mol⁻¹

U_{NaCl}= Lattice energy of NaCl
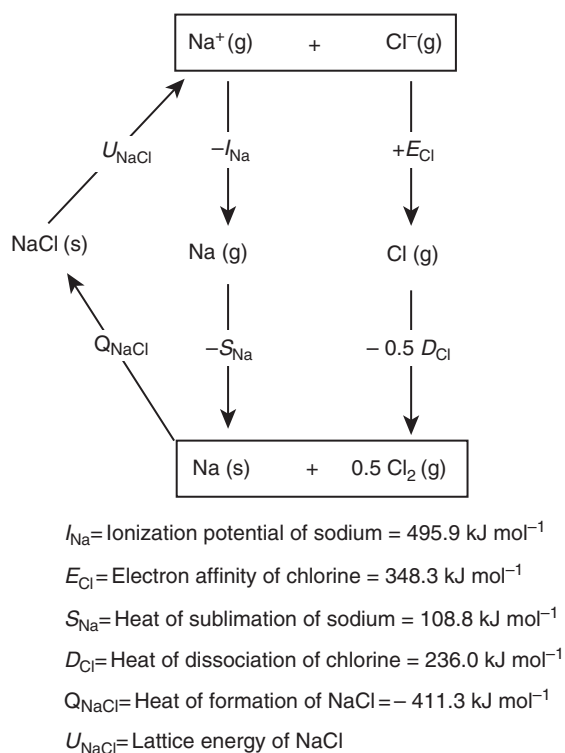
Fig. 3.8 Born–Haber cycle for estimation of the lattice energy of solid NaCl. Sources of data: Fyfe (1964); Evans (1966).

The reactions included in this Born–Haber cycle are:

Reaction	Heat of reaction (kJ mol⁻¹)
$Na^+(g) + e^- = Na$ (g)	$(-I_{Na}) = 495.9$
$Cl^-(g) = Cl$ (g) $+ e^-$	$(+E_{Cl}) = 348.3$
Na (g) = Na (s)	$(-S_{Na}) = 108.8$
Cl (g) = $0.5Cl_2$(g)	$(-0.5D_{Cl}) = 236.0$
Na (s) + 0.5 Cl_2 (g) = NaCl (s)	$(+Q_{NaCl}) = -411.3$

Addition of the above equations gives

$$Na^+(g) + Cl^-(g) = NaCl (s) \qquad [-U_L(NaCl) \text{ or } E_{cryst}(NaCl)]$$

Rearranging and substituting the given energy values, we get the lattice energy of NaCl:

$$U_{L(NaCl)} = I_{Na} + S_{Na} + 0.5D_{Cl} − Q_{NaCl} − E_{Cl}$$
$$= 495.9 + 108.8 + 118.0 + 411.3 − 348.3 = 785.7 \text{ kJ mol}^{-1}$$

Note that the estimated value of $U_{L\,(NaCl)}$ is very close to that obtained in Example 3–1.

To a first approximation, the lattice energy of a crystal may be viewed as representing the binding energy of the ions in the crystal. The magnitude of the lattice energy, therefore, has significant influence on certain physical properties, such as melting point and solubility, of a solid. Melting points of solids with similar crystal structures tend to increase with increasing lattice energy. For example, the melting point of NaCl ($U_L \approx 760$ kJ mol⁻¹) is 801°C, but that of MgO ($U_L \approx 3790$ kJ mol⁻¹), which also has a simple cubic crystal structure, is 2800°C. The higher melting point is partly due to a smaller cation–anion distance in the MgO structure, but primarily due to its much higher lattice energy (Companion, 1964). This is to be expected as $E_{p\,(crystal)}$ (and consequently U_L) increases fourfold when the ionic charge increases from 1 to 2 (equations 3.4 and 3.6).

Lattice energy is one of many factors that determine the solubility of a salt in water (see Chapter 7). When a salt, such as NaCl, dissolves in water, it dissociates into Na^+ and Cl^- ions, both of which become dispersed in the solution:

$$NaCl (s) \xrightarrow{H_2O} Na^+_{aq} + Cl^-_{aq} \qquad (3.7)$$

The lattice energy of a salt gives a rough indication of the solubility of a salt in water because it reflects the energy that must be supplied to separate the cations in the salt from its anions. It follows that solubility of salts should decrease with increasing lattice energy. Thus, from the data in Table 3.3, we may predict that halides of alkaline earth metals are less soluble than those of alkali metals, and aluminum halides are even less so. Similarly, the solubility of NaOH ($U_L = 900$ kJ mol⁻¹)

is very high (420 g L^{-1}), but that of $Mg(OH)_2$ (U_L = 3006 kJ mol^{-1}) is very low (0.009 g L^{-1}), and $Al(OH)_3$ (U_L = 5627 kJ mol^{-1}) is essentially insoluble in water.

3.2   Crystal structures of silicate minerals

Assuming a model of pure ionic bonding, the basic unit for building crystal structures of silicate minerals is considered to be the *silicon–oxygen tetrahedron* (SiO_4^{4-}), which is comprised of four O^{2-} anions at the four corners of a tetrahedron and the much smaller Si^{4+} cation filling the interstitial space at the center of the tetrahedron, giving the unit a net charge of −4 (Fig. 3.9). In essence, silicate structures (except those formed at extremely high pressures) consist of linked silicon–oxygen
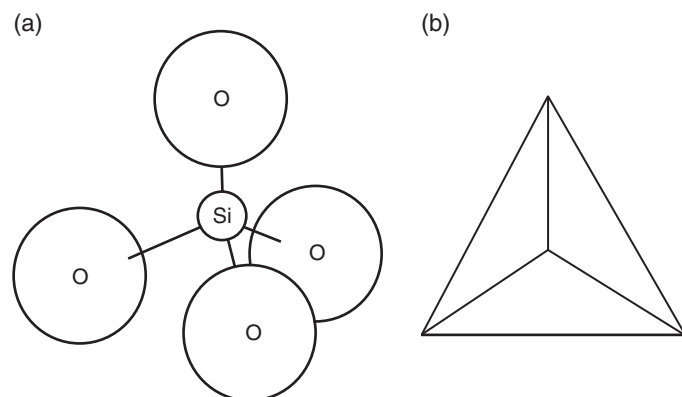
Fig. 3.9 The silicon–oxygen tetrahedron, the basic building block for crystal structures of silicate minerals: (a) A model of the tetrahedron using rods to depict the ionic bonds that connect the central Si^{4+} cation to the four O^{2-} anions positioned at the corners; (b) A commonly used graphical representation of the tetrahedron.

tetrahedra and cations as can be accommodated by the structure to achieve electrical neutrality. The different structural classes of silicate minerals result from the various ways in which the silicon–oxygen tetrahedra are linked to each other (Table 3.4). The tetrahedra may exist as isolated units, with no shared oxygen, or may be linked by sharing one, two, three, or four oxygen ions, as illustrated in Fig. 3.10. The bonds between silicon and oxygen within SiO_4^{4-} units are so strong that the dimensions and shape of the tetrahedra remain nearly constant irrespective of what the rest of a silicate structure may be.

3.3   Ionic substitution in crystals

Most rock-forming minerals are dominantly ionic compounds, and they are seldom pure phases. Deviation of the chemical composition of a mineral from its ideal chemical formula occurs due to incorporation of minor amounts of foreign ions into the lattice, primarily by ionic substitutions governed by similarities in size and charge of the ions involved. The ability of different elements to occupy the same lattice position in a particular crystal structure is called *diadochy*. For example, Mg, Fe, Mn, and Sr are diadochic in the structure of calcite because they can substitute for Ca in this structure. The concept of diadochy, if used rigorously, always applies to a particular crystal structure. Two elements may be diadochic in one mineral and not in another (Mason, 1966).

3.3.1   Goldschmidt's rules

It is well known from experience that there exists a preferential association, or *geochemical coherence*, between certain elements in natural assemblages because ions of such elements substitute easily for each other in minerals. The Norwegian

Table 3.4 Structural classification of silicate minerals.

Silicate class	Linkage of tetrahedra	Repeat unit	Si:O ratio	Example of silicate mineral
Nesosilicates	Independent tetrahedra (no sharing of oxygen ions)	SiO_4^{4-}	1:4	Forsterite (olivine) [Mg_2SiO_4]
Sorosilicates	Two tetrahedra sharing one oxygen ion	$Si_2O_7^{6-}$	2:7	Åkermanite [$Ca_2MgSi_2O_7$]
Cyclosilicates (ring structures)	Closed rings of tetrahedra, each sharing two oxygen ions	SiO_3^{2-}	1:3	Beryl [$Al_2Be_3Si_6O_{18}$]
Inosilicates (single chains)	Continuous single chains of tetrahedra, each sharing two oxygen ions	SiO_3^{2-}	1:3	Enstatite (pyroxene) [$MgSiO_3$]
Inosilicates (double chains)	Continuous double chains of tetrahedra, alternately sharing two and three oxygen ions	$Si_4O_{11}^{6-}$	4:11	Anthophyllite (amphibole) [$Mg_7(Si_4O_{11})_2(OH)_2$]
Phylosilicates (sheet structures)	Continuous sheets of tetrahedra, each sharing three oxygen ions	$Si_2O_5^{2-}$	2:5	Phlogopite (mica) [$KMg_3(AlSi_3O_{10})(OH)_2$]
Tektosilicates (framework structures)	Continuous framework of tetrahedra, each sharing four oxygen ions	SiO_2	1:2	Albite (plagioclase feldspar) [$Na(AlSi_3)O_8$]

Nesosilicate	Sorosilicate	Cyclosilicate

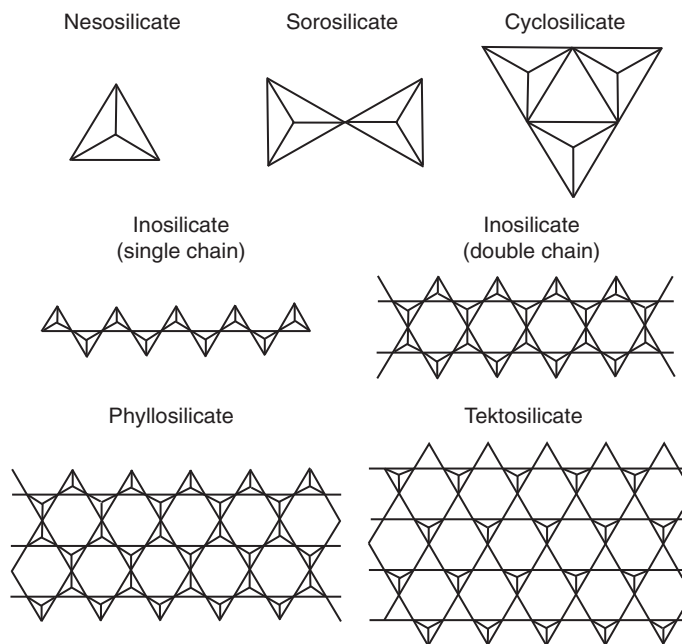| Inosilicate (single chain)	Inosilicate (double chain)

Phyllosilicate	Tektosilicate

Fig. 3.10 Different patterns of silicon–oxygen tetrahedra linkages for the various structural classes of silicate minerals listed in Table 3.4. The sketch is a two-dimensional representation of crystal structures that are three-dimensional. In all cases, except the tektosilicate, the apexes of all the tetrahedra are pointing upward. The tektosilicate structure consists of layers of hexagonal rings of tetrahedra with alternate rows of apexes pointing in opposite directions, and the upward-pointing apexes of a given layer coincide with the downward-pointing apexes of the layer above it. Thus, all four oxygens of each tetrahedron of the tektosilicate are shared with oxygens of other tetrahedra in the structure.

geochemist V.M. Goldschmidt (1888–1947) was the first to propose a series of rules governing the mutual replacement (diadochy) of ions in magmatic minerals, on the assumption that the bonding in these minerals was purely ionic. He considered that between two ions capable of diadochy, the one that makes the larger contribution to the energy of the crystal structure is incorporated preferentially. *Goldschmidt's rules of substitution* may be summarized as follows:

(1) If two ions have the same radius and the same charge, they would enter into solid solution in a given mineral with equal ease, in amounts roughly proportional to their abundances. The ionic radii must not differ by more than 15%; substitution is limited or rare if the radii differ by 15% to 30%, and nonexistent if the difference is more than 30%. Examples are the common substitution of Ta^{5+} (0.64 Å) for Nb^{5+} (0.64 Å), Hf^{4+} (0.71 Å) for Zr^{4+} (0.72 Å), Ga^{3+} (0.62 Å) for Al^{3+} (0.54 Å), and Fe^{2+} (0.78 Å) for Mg^{2+} (0.72 Å) in many silicate minerals. In such cases, the minor element is said to be *camouflaged* in the crystal structure (Shaw, 1953).

(2) When two ions possessing the same charge but different radii compete for a particular lattice site, the ion with the smaller radius would be incorporated preferentially because the smaller ion forms a stronger ionic bond. During magmatic crystallization, for example, the earlier formed olivine tends to be enriched in Mg^{2+} (0.72 Å) relative to Fe^{2+} (0.78 Å).

(3) When two ions having similar radii but different charges compete for a particular lattice site, the ion with the higher charge would be incorporated preferentially because the ion with higher charge forms a stronger ionic bond. If the substituting ion has a higher charge than the ion in the lattice being substituted, it is said to be *captured* by the crystal structure; if the substituting ion has a lower charge, it is said to be *admitted* by the crystal structure. For example, the K-feldspar structure captures Ba^{2+} (1.35 Å) for replacement of K^+ (1.38 Å), and the biotite structure admits Li^+ (0.76 Å) for replacement of Mg^{2+} (0.72 Å).

(4) Ions whose charges differ by one unit may substitute for one another provided electrical neutrality of the crystal is maintained by *coupled (or compensatory) substitution*. Example: concurrent substitution of Na^+ (1.02 Å) by Ca^{2+} (1.00 Å) and of Si^{4+} (0.26) Å by Al^{3+} (0.47 Å) in plagioclase feldspars:

$$NaAlSi_3O_8 + Ca^{2+} + Al^{3+} \Rightarrow CaAl_2Si_2O_8 + Na^+ + Si^{4+} \quad (3.8)$$
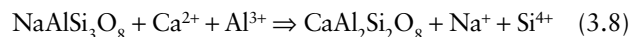
In general, very little or no substitution takes place when the difference in charge on the ions is > 1, even if the size is appropriate. Zr^{4+} (0.72 Å) does not substitute for Mg^{2+} (0.72 Å) nor Cr^{3+} (0.62 Å) for Li^+ (0.76 Å); this is probably because of the difficulty in achieving charge balance by compensatory substitutions.

3.3.2   *Ringwood's rule*

Over the years the generalizations embodied in the Goldschmidt's rules have been found to be fraught with many exceptions. Moreover, some ion pairs of similar size and charge, such as Mg^{2+} (0.72 Å) and Ni^{2+} (0.69 Å), show only a moderately close association, whereas a few ion pairs, for example Sr^{2+} (1.18 Å) and Hg^{2+} (1.02 Å), show virtually no geochemical coherence. Obviously, there are other properties that are also important in predicting geochemical associations.

A major limitation in the application of Goldschmidt's rules is the assumption of pure ionic bonding because most minerals have a significant component of covalent bonding. Ringwood (1955) suggested that substitution may be limited, even when the size and charge criteria are satisfied, if the competing ions have different electronegativities (see section 3.6.5) and, therefore, form bonds of different strengths. For example, Cu^{2+} (0.73 Å) rarely substitutes for Mg^{2+} (0.72 Å) because of the large difference in electronegativity (1.90 versus 1.31), although it should from the consideration of charge and size. Si^{4+} (0.26 Å; electronegativity = 1.9) and

Ge^{4+} (0.73 Å; electronegativity = 2.01), on the other hand, show strong geochemical coherence because of almost identical values of electronegativity, despite a large difference in ionic radius. Ringwood's rule states that between two cations satisfying the criteria of charge and size for diadochic substitution in a crystal structure, preference will be for the one with lower electronegativity because it forms a more ionic, stronger bond. In most cases, the difference in electronegativity required before elements obey this rule is about 0.1. For example, Pb^{2+} (1.19 Å; electronegativity = 1.8) does not substitute easily for K^+ (1.38 Å; electronegativity = 0.82) in potash–bearing minerals and hence becomes concentrated in the residual magma.

It should be evident that the extent of ionic substitution is determined by the nature of the crystal structure and how similar the ions are in terms of size, charge, and electronegativity. Other factors that affect the extent of substitution are the temperature and pressure at which the substitution takes place, elevated temperatures and lower pressures favoring increased substitution. Higher temperatures promote greater atomic vibration and open structures, which are easier to distort locally to accommodate cations of different sizes. Thus, the concentration of minor and trace elements in minerals (e.g., of Fe in sphalerite, ZnS) provides a potential means of determining the temperatures of mineral formation (geothermometry; see section 6.5). Pressure at the time of substitution has the opposite effect, but is much less important (except at very high pressures) because most minerals are quite incompressible.

Although the rules discussed above can be applied to explain to a certain extent the distribution of elements during many geochemical processes (especially magmatic crystallization and metamorphic recrystallization), their application is limited because of numerous exceptions, especially when the transition elements are involved (Burns and Fyfe, 1967; Burns, 1973). The order of uptake of the transition-metal ions by minerals formed by magmatic crystallization is better explained by the crystal-field theory.

3.4   Crystal-field theory

Crystal-field theory was developed originally by the physicists Hans Bethe and John Hasbrouck van Vleck in the 1930s to explain the absorption spectra of the transition metals such as Ni, Co, Fe, Ti, etc. At its present state of development, the theory can be applied to account for some magnetic properties, colors, hydration enthalpies, and spinel structures ("normal" versus "inverse" spinels) of transition metal complexes (Burns and Fyfe, 1967; Burns, 1973, 1993).

Crystal-field theory describes the effects of electrostatic fields on the energy levels of the valence electrons (electrons in the outermost orbitals) of a transition-metal when it is surrounded by negatively charged ligands in a crystal structure. (A *ligand* is an ion, a molecule, or a molecular group that

binds to another chemical entity to form a larger complex.) The ligands are assumed to be point negative charges sited on the Cartesian axes, and the bonding entirely ionic. The more comprehensive *ligand-field theory*, which is too complicated to be discussed here, treats the metal-ligand interaction as a covalent bonding interaction involving overlap between the *d*-orbitals of the metals and the ligand-donor orbitals.

3.4.1   Crystal-field stabilization energy

Transition elements are characterized by incompletely filled inner *d* or *f* orbitals. Let us consider the first transition series involving 3*d* orbitals. Electronic structures of this transition series are of the general form [Ar core $(1s^2 2s^2 2p^6 3s^2 3p^6)3d^{1 \text{ to } 10} 4s^{1 \text{ or } 2}$], and ions are formed when the 4*s* electrons, and in some cases 3*d* electrons, are removed from the metal atom. When such an ion is surrounded by ligands, for example, in octahedral coordination (i.e., coordinated to six identical ligands), the increased repulsion between the anions and the electrons of the 3*s* orbital, which has a spherical symmetry, results simply in raising the energy level of 3*s* electrons. The 3*p* orbitals of the metal pointing directly towards the point charges of anions are also raised to a higher energy level because of increased repulsion between the ligands and 3*p* electrons, but remain degenerate.

The main effect of the ligands on the transitional-metal ion arises from interaction with 3*d* electrons. In a free (isolated) transition-metal ion, the 3*d* orbitals ($3d_{z^2}$, $3d_{x^2-y^2}$, $3d_{xy}$, $3d_{xz}$, $3d_{yz}$; see Table 2.2 and Fig. 2.6) are fivefold degenerate – i.e., they are energetically equivalent and the *d* electrons have equal probability of being located in any of the five 3*d* orbitals. When the same ion is placed in a crystal, for example in an octahedral coordination, the five 3*d* orbitals do not experience exactly the same kind of interaction because they do not have the same spatial configuration relative to the ligands. The $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals (designated as e_g symmetry group) have lobes that point directly towards the point charges of the ligands, whereas the $3d_{xy}$, $3d_{xz}$, $3d_{yz}$ orbitals (designated as t_{2g} symmetry group) have lobes that point between the negative charges. This results in a greater electrostatic repulsion for the e_g electrons than the t_{2g} electrons. The 3*d* orbitals can no longer remain degenerate, and they split into two groups that have different levels of energy (Fig. 3.11a). The energy separation between t_{2g} and e_g orbitals is termed the *crystal-field splitting parameter* and denoted by Δ_o (the "o" stands for an octahedral coordination). Energy is lowered by 2/5 Δ_o for the three t_{2g} orbitals and raised by 3/5 Δ_o for the two e_g orbitals relative to the mean energy of an unperturbed ion (Fig. 3.11a). Each electron in a t_{2g} orbital lowers the energy of the transition-metal ion, and thus increases its stability, by 2/5 Δ_o, whereas each electron in the e_g orbital diminishes the stability by 3/5 Δ_o relative to a hypothetical nontransitional-metal ion of the same size and charge. The resultant net energy, which depends on the number of electrons and how they fill the
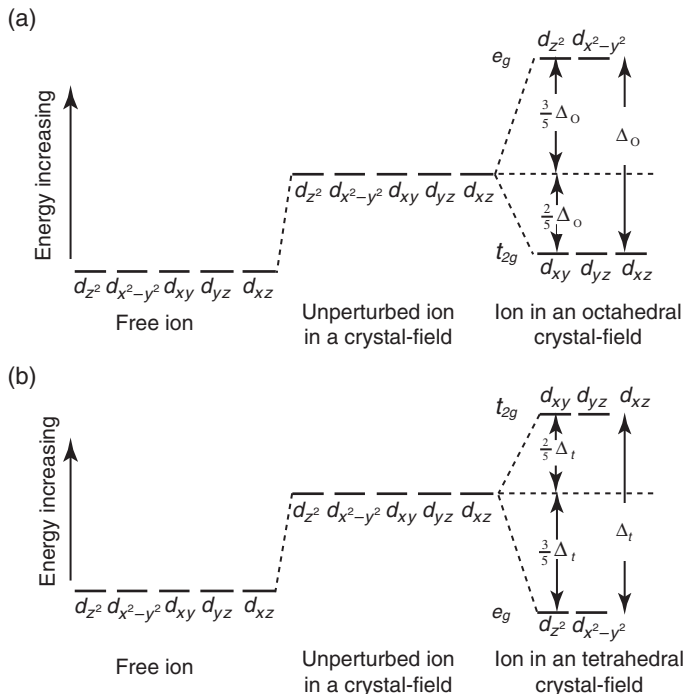
(a)

(b)

Fig. 3.11 Schematic energy level diagram for 3d orbitals of a transition-metal ion (not to scale): (a) octahedral coordination in a crystal; (b) tetrahedral coordination in a crystal. Δ_o = crystal-field splitting parameter for octahedral coordination; Δ_t = crystal-field splitting parameter for tetrahedral coordination; $\Delta_t = 4/9\ \Delta_o$.

orbitals, is called *crystal-field stabilization energy* (CFSE), the magnitude of which can be estimated from absorption spectra measurements.

Let us examine how the 3d orbitals are filled by electrons in an octahedral field (Fig. 3.12), the most common type of coordination between transition-metal ions and ligands in silicate minerals. As per Hund's rule of maximum multiplicity (see Section. 2.3.1), ions possessing one, two, or three 3d electrons (e.g., Ti^{3+}, V^{3+}, and Cr^{3+}, respectively) can have only one electronic configuration, each with 3d electrons occupying different t_{2g} orbitals, with parallel orientation of their spins. The CFSE for these three cases, respectively, are: $2/5\ \Delta_o$; $2/5\ \Delta_o + 2/5\ \Delta_o = 4/5\ \Delta_o$; and $4/5\ \Delta_o + 2/5\ \Delta_o = 6/5\ \Delta_o$. Ions carrying four, five, six, or seven 3d electrons (e.g., Mn^{3+}, Fe^{3+}, Fe^{2+}, and Co^{2+}, respectively) present a choice between two states: a weak-field (or high-spin) state; and a strong-field (or low-spin) state. In the high-spin state, two electrons occupy e_g orbitals without pairing before the rest are paired in t_{2g} orbitals. No energy is expended by pairing of electrons in t_{2g} orbitals already filled with unpaired electrons, but the CFSE is reduced by $3/5\ \Delta_o$ for every electron in e_g orbitals. Thus, the calculated CFSEs for this state with four, five, six, and seven 3d electrons, respectively, are: $6/5\ \Delta_o - 3/5\ \Delta_o = 3/5\ \Delta_o$; $3/5\ \Delta_o - 3/5\ \Delta_o = 0$; $0 + 2/5\ \Delta_o = 2/5\ \Delta_o$; and $2/5\ \Delta_o + 2/5\ \Delta_o = 4/5\ \Delta_o$. In the low-spin state, it is energetically more favorable for the electrons to fill
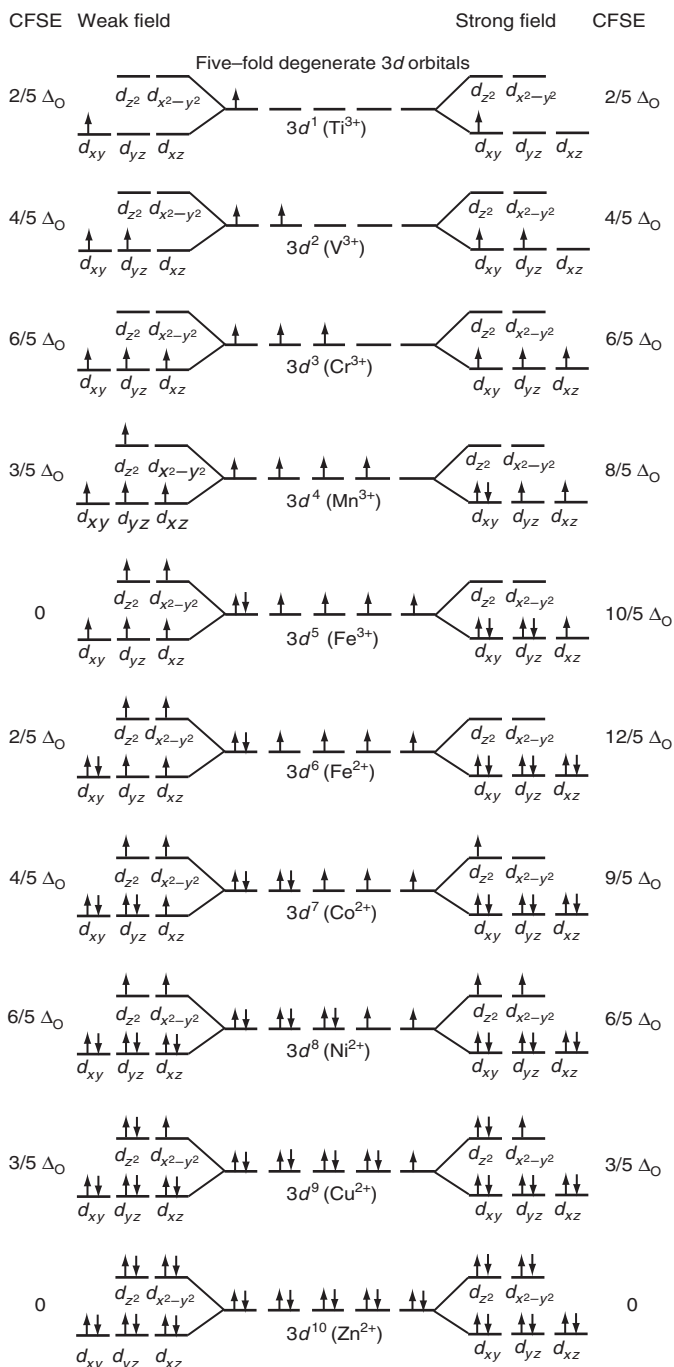

Fig. 3.12 Filling of electrons in 3d orbitals of 3d transition elements in octahedral coordination in a crystal and the resulting values of CFSE for strong-field (low-spin) and weak-field (high-spin) configurations (not to scale). Δ_o = octahedral crystal-field splitting parameter; CFSE = crystal-field stabilization energy. The calculated CFSE must be reduced by the energy required to pair two electrons in a t_{2g} orbital. Source of data: Burns and Fyfe (1967).

lower-energy t_{2g} orbitals before e_g orbitals, and the calculated CFSEs for this state with four, five, six, and seven $3d$ electrons, respectively, are: $6/5\,\Delta_o + 2/5\,\Delta_o = 8/5\,\Delta_o$, $8/5\,\Delta_o + 2/5\,\Delta_o = 10/5\,\Delta_o$, $10/5\,\Delta_o + 2/5\,\Delta_o = 12/5\,\Delta_o$, and $12/5\,\Delta_o - 3/5\,\Delta_o = 9/5\,\Delta_o$. Finally, each ion with eight, nine, or ten electrons (e.g., Ni^{2+}, Cu^{2+}, and Zn^{2+}, respectively) possesses only one electronic configuration in which t_{2g} and e_g orbitals are filled as shown in Fig. 3.12, along with calculated CFSEs that are identical for both low-spin and high-spin states. The distinction between low-spin and high-spin states is important in understanding magnetic properties of transition-metal compounds. For instance, pyrite is diamagnetic (i.e., weakly repelled by magnetic fields), indicating a low-spin configuration, $(t_{2g})^6$, of Fe^{2+}; ferromagnesian silicates, on the other hand, are paramagnetic (i.e., weakly attracted to magnetic fields), indicating a high-spin configuration, $(t_{2g})^4(e_g)^2$ (Burns and Fyfe, 1967).

The electronic configurations of $3d$ transition-metals in tetrahedral coordination, and the corresponding CFSEs, can be worked out the same way as explained above for octahedral coordination, remembering that in a tetrahedral field the $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals are more stable (i.e., have a lower energy) than the $3d_{xy}$, $3d_{xz}$, $3d_{yz}$ orbitals (Fig. 3.11b). The tetrahedral crystal-field splitting parameter, Δ_t, is smaller than Δ_o. For the same transition-metal cation in a tetrahedral coordination with identical ligands and identical metal-ligand interatomic distances, $\Delta_t = 4/9\,\Delta_o$. The difference between Δ_o and Δ_t, referred to as the *octahedral site-preference energy* parameter, is useful for the interpretation of cation distributions in mineral-forming processes and crystal structures.

3.4.2 Nickel enrichment in early-formed magmatic olivine

It is well documented that Ni in mafic and ultramafic igneous rocks is contained mainly in olivine, the earliest silicate mineral to crystallize from a basaltic magma, followed next in importance by orthopyroxene and then by clinopyroxene. Furthermore, there is a positive correlation between the Mg : Fe ratio and Ni concentration in these minerals, the forsterite-rich members of the olivine series, for example, being richer in Ni than fayalite-rich members. In the older literature, this correlation has been attributed to the substitution of Ni^{2+} (0.69 Å) for Mg^{2+} (0.72 Å) according to Goldschmidt's rules for ionic substitution (camouflage), but this is not consistent with Ringwood's rule because of the much higher electronegativity of Ni (1.88 compared to 1.31 for Mg). Ringwood (1955) argued that the dominant geochemical characteristic of Ni is its camouflage by Fe^{2+} (0.78 Å) in silicate crystals, as should be expected from their almost identical electronegativities (1.83 for Fe compared to 1.88 for Mg), but the smaller size of Ni^{2+} facilitates its preferential entry into early crystals.

Burns and Fyfe (1964, 1966, 1967) invoked the crystal-field theory to explain the Ni enrichment of early magmatic crystals. Absorption spectra of transition-metal compounds and their

melts are similar, indicating that ions receive comparable CFSE in the two phases. Moreover, heats of fusion are generally small, one to three orders of magnitude lower than lattice energies, indicating that bond energies in solid and liquid phases are comparable. In silicate melts of basaltic and granitic compositions, transition-metal ions occupy both tetrahedral and octahedral sites, but almost exclusively octahedral sites in silicate minerals crystallizing from such magmas, and the magnitude of the octahedral site-preference energy parameter gives an indication of the relative affinity of an ion in a magma for a silicate crystal. The predicted orders of uptake arranged in terms of the octahedral site-preference energy (in kcal mol^{-1}) are:

Divalent cations: Ni (20.6) > Cu (15.2) > Co (7.4) > Fe (4.0) > Mn (0)

Trivalent cations: Cr (37.7) > Co (19.0) > V (12.8) > Ti (6.9) > Fe (0)

Thus, Ni^{2+} and Cr^{3+}, which have the largest values of the octahedral site-preference energy, should be expected to be readily accommodated by early-formed olivine and spinel. Cu^{2+} in the above list is an exception; presumably it prefers more deformable sites in a magma and is taken up by late-stage minerals (Burns and Fyfe, 1967).

3.4.3 Colors of transition-metal complexes

Crystal-field effects are the most common origin of color in transition-metal compounds and many minerals. If the $3d$ orbitals of a transition-metal ion in a molecule have been split into two sets as described above, absorption of a photon of energy in the visible or infrared region of the electromagnetic spectrum (see Fig. 13.1) can cause one or more electrons to jump momentarily from a lower energy orbital to a higher energy orbital, thus creating an excited transient-metal ion. The difference in energy between the ground state and the excited state is equal to the energy of the absorbed photon. Only specific wavelengths of light (or colors) are absorbed, and the substance takes on the color of the transmitted light, which is the complementary color of the absorbed light (Table 3.5).

Table 3.5 Wavelength absorbed and color observed.

Wavelength (λ) absorbed	Color observed
400 nm (violet)	Green-yellow ($\lambda = 560$ nm)
450 nm (blue)	Yellow ($\lambda = 600$ nm)
490 nm (blue-green)	Red ($\lambda = 620$ nm)
570 nm (yellow-green)	Violet ($\lambda = 410$ nm)
580 nm (yellow)	Dark blue ($\lambda = 430$ nm)
600 nm (orange)	Blue ($\lambda = 450$ nm)
650 nm (red)	Green ($\lambda = 520$ nm)
1 nm = 10^{-9} m = 10 Å.	

3.5 Isomorphism, polymorphism, and solid solutions

3.5.1 Isomorphism

The term *isomorphism*, which was introduced by Mitscherlich in 1819, means "equal form." In practice, *two substances are called isomorphous if they have similar crystal structures but different chemical formulas*. A typical pair is sodium nitrate ($NaNO_3$) and calcium carbonate ($CaCO_3$), which have almost identical crystal structure but very different physical properties such as hardness and solubility. Isomorphism is widespread among minerals of the spinel group, the garnet group, the pyroxene group, and the amphibole group. The basis of isomorphism is the similarity in ionic size relations of the different ions, leading to the same coordination and the same structure type. Replacement of cations or anions in a crystal lattice should be termed "substitution" or "solution" rather than isomorphous replacement (Fyfe, 1964).

3.5.2 Polymorphism

The term *polymorphism*, meaning "many forms", applies to *two or more substances (elements or compounds) that have the same or closely similar chemical formulas but different crystal structures*. The difference among the various structural forms may involve cation coordination, arrangement of the ions, or the nature of bonding. Polymorphism is quite common among minerals. Some familiar examples are the polymorphs of $CaCO_3$ (calcite, trigonal; aragonite, orthorhombic), FeS_2 (pyrite, cubic; marcasite, orthorhombic), C (diamond, cubic; graphite, hexagonal), and Al_2SiO_5 (andalusite, orthorhombic; sillimanite, orthorhombic; kyanite, triclinic). The polymorphs have discernibly different physical and chemical properties, and different pressure–temperature stability fields (see Figs 4.12, 6.4 and 7.10), the high-temperature modifications generally showing a higher crystallographic symmetry.

The transformation from one polymorph to another may be *displacive* or *reconstructive*, or of the *order-disorder* type. Transformations, such as from low-quartz to high-quartz ("low" and "high" denoting, respectively, lower and higher crystallographic symmetry) are displacive because there is very little difference in energy of the two polymorphs so that the change can be accomplished quite readily by minor displacement of the ions. The transformation of graphite to diamond, on the other hand, is an example of reconstructive transformation; it is much slower and more difficult, because it involves the formation of a new crystal structure with reconstructed bonds. In general, higher pressure favors polymorphs with high densities and large coordination numbers (e.g., calcite = aragonite; sillimanite = kyanite), whereas higher temperature favors polymorphs with low densities and small coordination numbers (e.g., quartz = tridymite; kyanite = sillimanite).

A crystal structure is said to be "disordered" if the constituent ions (or atoms) are randomly distributed among crystallographically equivalent sites (sites that are the same in terms of crystallographic symmetry), and "ordered" if the distribution is not random. Perfect ordering occurs only at absolute zero temperature; the degree of ordering gradually decreases with increasing temperature, and the crystal structure becomes completely disordered above a certain temperature characteristic of the structure and composition of the crystal. Between these two end-states of perfect order and complete disorder, there may be stable states of varying degrees of disorder, each of which may be considered a separate polymorph. The three polymorphs of $KAlSi_3O_8$ (potassium feldspar) – microcline, orthoclase, and sanidine – are an important example of order–disorder relationship with respect to the three Si^{4+} ions and one Al^{3+} ion, which occupy four tetrahedral sites that differ slightly in size and nearest neighbor configuration. Microcline is the low-temperature, ordered (triclinic) form of $KAlSi_3O_8$ in which Al^{3+} ions occupy one kind of site and three Si^{4+} ions the other three; orthoclase is the medium-temperature, partially ordered form (pseudomonoclinic); and sanidine is the high-temperature, disordered form (monoclinic) characterized by more random distribution of the Si^{4+} and Al^{3+} ions.

3.5.3 Solid solutions

A *solid solution* is a solution in the solid state of one or more solutes in a solvent whose crystal structure remains unchanged by addition of the solutes. Almost all minerals are solid solutions to varying degrees. The range of compositions produced by solid solution in a given mineral is known as a *solid solution series* and its compositional extremes as *end members*. A solid solution series may be *continuous*, in which case all intermediate members are possible (e.g., the olivine solid solution series with Mg_2SiO_4 and Fe_2SiO_4 as end members) or *discontinuous*, in which case only a restricted range of composition between the end members is found (e.g., the limited solid solution between ZnS and FeS).

Solid solution should not be confused with isomorphism, because they are distinct concepts (Mason, 1966). Isomorphism is neither necessary to, nor sufficient for, solid-solution formation. Many isomorphous substances show little solid solution (e.g., calcite, $CaCO_3$ and smithsonite, $ZnCO_3$), and extensive solid solution may occur between components that are not isomorphous (e.g., FeS and ZnS, which have very different crystal structures).

There are three kinds of solid solutions based on the mechanism that causes their chemical composition to vary (Fig. 3.13):

(1) *Substitutional solid solution* (Fig. 3.13a), in which one or more kinds of ions or atoms are substituted by other kinds. This is the most common type in the realm of minerals. A very good example is the binary olivine solid solution series, $(MgFe)_2SiO_4$, that spans all intermediate compositions ranging from the magnesium end-member Mg_2SiO_4 (forsterite) to the iron end-member Fe_2SiO_4 (fayalite) because of diadochic substitution of Mg^{2+} by Fe^{2+}, which carry the same charge and have similar ionic size. Another familiar
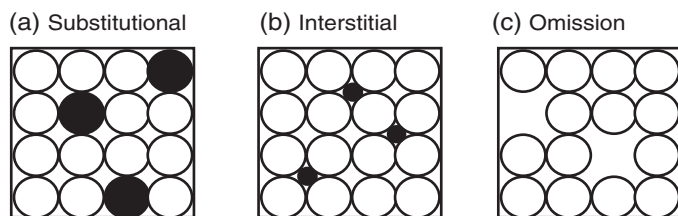
Fig. 3.13 Schematic representation of the three kinds of solid solutions: (a) substitutional solid solution; (b) interstitial solid solution; and (c) omission solid solution.

example is the plagioclase solid solution series characterized by progressive coupled substitution of Na^+ and Si^{4+} by Ca^{2+} and Al^{3+} (equation 3.8).

(2) *Interstitial solid solution* (Fig. 3.13b), in which foreign ions or atoms are added to fill unoccupied interstitial crystal sites (❑) that exist between ions or ion groups. An example of interstitial solid solution is the incorporation of Na^+ into the structure of cristobalite (a high-temperature polymorph of quartz) to compensate for the charge imbalance created by the replacement of a small amount of Si^{4+} by Al^{3+}. Minerals such as beryl ($Be_3Al_2Si_6O_{18}$), whose structures provide large openings, are particularly susceptible to interstitial substitution. Beryl contains large channel-like cavities that can be occupied by relatively large monovalent cations, the charge balance being maintained by coupled substitution of Al^{3+} or Be^{2+} for Si^{4+} in tetrahedral sites:

❑ $+ Si^{4+} \Leftrightarrow Al^{3+} + (K^+, Rb^+, Cs^+)$ or ❑ $+ Si^{4+} \Leftrightarrow Be^{2+}$ $+ 2(K^+, Rb^+, Cs^+)$
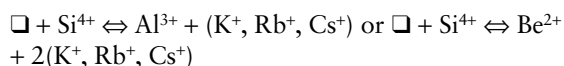
This type of solid solution is very common in metals, which easily accommodate small atoms such as H, C, B, and N.

(3) *Omission solid solution* (Fig. 3.13c), in which some ion sites that are normally occupied remain vacant. The best example of such a solid solution – actually a type of crystal defect – is the monosulfide mineral pyrrhotite whose chemical analysis always shows more sulfur than its theoretical proportion in FeS. It is now well established that this discrepancy is due to a deficiency of Fe, not an excess of S, in the crystal structure, so that the generalized chemical formula of pyrrhotite is written as $Fe_{1-x}S$, where x varies between 0 and 0.125. The electrical neutrality in this structure is maintained by the replacement of three Fe^{2+} by only two Fe^{3+} leaving one site vacant: $3Fe^{2+} \Rightarrow 2Fe^{3+} + $ ❑.

The extent of solid solution between given solutes and solvent depend on the factors that affect the degree of substitution (see section 3.3). The favorable factors include: similar ionic size, charge, and electronegativity; flexibility of the solvent crystal structure to accommodate local strains (by bending bonds rather than by stretching or compressing them); and high temperature and low pressure. Thermodynamic aspects of solutions, including solid solutions, will be discussed in Chapter 5.

3.6   Covalent bonding

3.6.1   *Valence bond theory versus molecular orbital theory*

Soon after the application of quantum mechanics to the hydrogen atom, scientists began applying quantum mechanics to molecules, starting with the H_2 molecule. The treatment of covalent bonding, based on the principles of quantum mechanics, has developed in two distinct, but mutually consistent, forms: the *valence bond theory,* and the *molecular orbital theory*. In the valence bond approach, covalent bonds between two atoms A and B are formed by the sharing of valence electrons of opposite spin, resulting from interaction between atomic orbitals (AOs) that contain these electrons. In the molecular orbital approach, we start with the nuclei of the two atoms and feed all the electrons of the molecule into *molecular orbitals* (MOs) that are constructed by appropriate combination of atomic orbitals of about the same energy. Thus, atomic orbitals are associated with a single atom (or ionic species), whereas molecular orbitals are associated with the molecule as a whole. It is assumed that electrons would fill molecular orbitals following the same principles as followed by electrons for filling atomic orbitals:

(1) The molecular orbitals are filled in a way that yields the lowest potential energy for the molecule.
(2) Each molecular orbital can accommodate a maximum of two electrons of opposite spin (Pauli's exclusion principle).
(3) Orbitals of equal energy are half filled with electrons having parallel spin before they begin to pair up with electrons of opposite spin (Hund's rule).

The molecular orbital approach is more powerful because the orbitals reflect the geometry of the molecule to which they are applied. The downside is that it is a more difficult concept to visualize.

The essence of covalent bonding can be explained by the formation of the simplest of all molecules, the homonuclear diatomic H_2 molecule. An isolated H atom has the ground-state electron configuration $1s^1$, and the probability density for this one electron is distributed spherically about the H nucleus. When two hydrogen atoms approach each other, the electron charge clouds represented by the two $1s$ atomic orbitals begin to merge (which is referred to as *overlap* of atomic orbitals), and the electron charge density begins to shift. Due to the attraction between the electron of one H atom and the positively charged nucleus of the other H atom, the overlap gradually increases with decrease in the internuclear distance (R) between the two atoms. How close to each other the two atoms can get is determined by the short-range repulsion between the two positively charged nuclei. The merger reaches its limit when the potential energy of the system (E_p) reaches a minimum; this is the position of closest approach of the two atoms and it defines the equilibrium internuclear distance (R_0). At this point, we have formed a H_2 molecule consisting of two
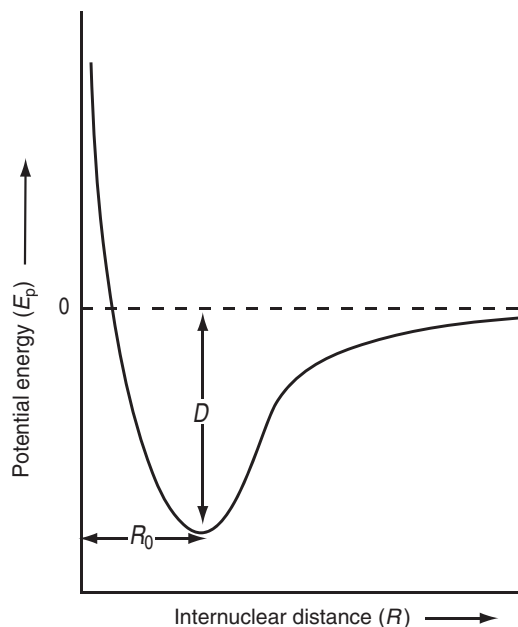
Fig. 3.14 Potential energy (E_p) diagram for the diatomic molecule H_2. For large values of internuclear distance (R), the potential energy of the system, which consists of two isolated hydrogen atoms, is arbitrarily assigned a value of zero. R_0 represents the equilibrium internuclear distance at which the potential energy reaches a minimum and the system attains maximum stability; at smaller values of R, the strong repulsion between the nuclei causes the potential energy to rise sharply. For the formation of a covalent H_2 molecule, $R_0 = 0.74$ Å, and the corresponding minimum potential energy is -435 kJ mol^{-1} (which corresponds to -7.23×10^{-19} kJ per H_2 molecule). The energy D closely approximates the experimental dissociation energy of the molecule into its component atoms in their ground states.

nuclei held together by a covalent bond comprised of two shared electrons with opposite spins. This system has a lower potential energy than the system comprised of the two isolated H atoms (Fig. 3.14), and thus is more stable. For each such covalent bond, there is a condition of optimal overlap that results in maximum bond strength (*bond energy*) at a particular internuclear distance (*bond length*).

The formation of a covalent bond between the two H atoms can be rationalized in two ways. Viewed from the perspective of the valence bond theory, the two electrons occupy the region of highest density of electron negative charge between the two nuclei, the region where the two orbitals overlap (Fig. 3.15a). Both electrons are now in the orbitals of both H atoms, and each H atom may be considered to have the stable electron configuration of He ($1s^2$). In terms of the molecular orbital theory, the two $1s$ atomic orbitals merge into a bigger electron cloud, a *molecular orbital* (MO). The MO may be visualized as the volume within which we should find a high percentage of the negative charge generated by the electrons (Fig. 3.15b). The two electrons are shared equally between the nuclei and are identified with the entire H_2 molecule, not with either of the nuclei. This sharing of the electron pair forms a covalent bond.
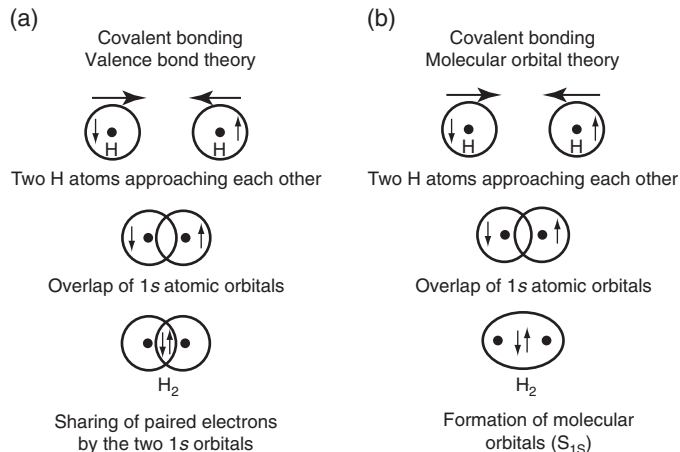

Fig. 3.15 Formation of a covalent bond in a H_2 molecule by sharing of electrons: (a) Overlap of two $1s$ atomic orbitals (valence bond theory); (b) Formation of a molecular orbital by merger of two $1s$ orbitals (molecular orbital theory).

3.6.2   *Covalent radii*

As in the case of ionic bonding (see Fig. 3.2), R_0 in Fig. 3.14 represents the sum of the covalent radii of the two H atoms, the bond length, from which the covalent radius of each atom can be determined. In the case of the H_2 molecule, the covalent radius will just be the one-half of R_0, and it is applicable only to crystal structures in which H is covalently bonded. The covalent radius of an atom varies with the number of bonds the atom has with its neighbors and the distortion of its atomic orbitals as a result of hybridization (see section 3.6.3). Tabulated values of covalent radii represent either average or idealized values.

The covalent radius of an atom, unlike its ionic radius, should not be visualized as the radius of a spherical atom; the concept of covalent radius is applicable only to interatomic distances between atoms joined by covalent bonds and not to distances between atoms of the same kind when not so joined (Evans, 1966). For example, the single-bond covalent radius of Cl atom is 0.99 Å, which is one-half of the measured Cl–Cl interatomic distance of 1.99 Å in the covalent Cl_2 molecule. In the crystal structure of solid chlorine, however, the interatomic distance between neighboring Cl atoms of different molecules, which are bound together only by weak van der Waals forces (see section 3.8), is about 3.6 Å, giving about 1.8 Å as the van der Waals radius of the Cl atom, the same as the ionic radius of Cl$^-$ in octahedral coordination. In general, the covalent radius of an element is much smaller than its ionic radius because of greater penetration of unpaired electron orbitals in covalent bonding.

3.6.3   *Hybridization of atomic orbitals*

The formation of molecular orbitals is not all that happens to atomic orbitals when atoms approach each other. Before combining across atoms, atomic orbitals that are close to

each other in energy within the same atom have the ability to combine in an additive way, forming a new set of orbitals that is at a lower total energy in the presence of the other atoms than the pure atomic orbitals would be. This process of blending of atomic orbitals is called *hybridization*, and the newly formed orbitals are called *hybrid orbitals*. (1s and 2s orbitals do not hybridize because of the large difference in their energy levels.) The number of hybrid orbitals formed always equals the number of atomic orbitals involved in the hybridization (Companion, 1964, p. 59). The hybrid orbitals of an atom (or ionic species) can overlap with orbitals on other atoms (or ions) to share electrons and form covalent bonds. The importance of hybrid orbitals lies in the fact that they usually provide a better description of the experimentally observed geometry of the molecule (or ionic species), especially for molecules formed with carbon, nitrogen, or
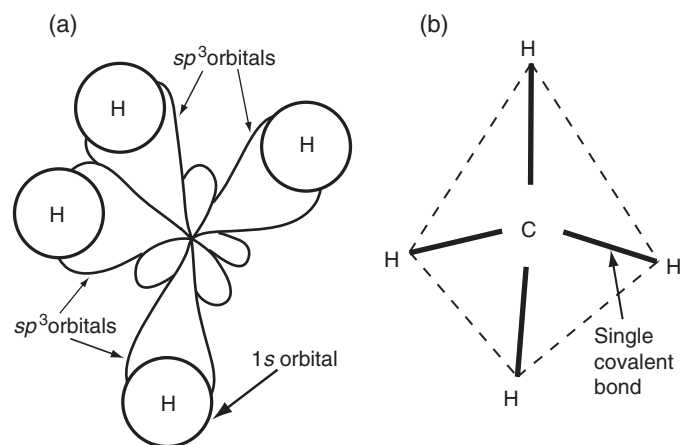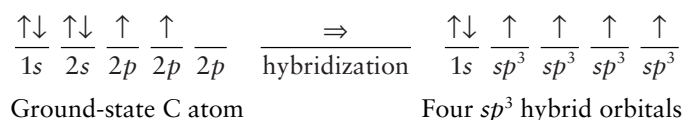
oxygen (and to a lesser extent phosphorous and sulfur). This is why the main application of hybridization lies in the field of organic chemistry.

To illustrate the concept of hybridization, let us consider the covalent bonding in CH_4 (methane gas). Experimental results tell us that the C in this compound is bonded to the four H atoms by four equivalent covalent bonds, but the ground-state electronic configuration of C ($Z = 6$), $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$, suggests that the two p orbitals with unpaired electrons should result in the formation of only two covalent bonds. This discrepancy can be resolved by invoking hybridization of the $2s$ orbital with the three $2p$ orbitals (whose energy level is not that different from that of the $2s$ orbital) to form four sp^3 hybrid orbitals, each with one unpaired electron:

$$\frac{\uparrow\downarrow}{1s}\ \frac{\uparrow\downarrow}{2s}\ \frac{\uparrow}{2p}\ \frac{\uparrow}{2p}\ \frac{}{2p} \qquad \xrightarrow[\text{hybridization}]{\Rightarrow} \qquad \frac{\uparrow\downarrow}{1s}\ \frac{\uparrow}{sp^3}\ \frac{\uparrow}{sp^3}\ \frac{\uparrow}{sp^3}\ \frac{\uparrow}{sp^3}$$

Ground-state C atom   Four sp^3 hybrid orbitals

The four sp^3 orbitals are directed in space toward the four corners of a regular tetrahedron. When four H atoms, each with an unpaired $1s$ electron, approach such a C atom, the overlap of the four $1s$ AOs of H and the four hybrid AOs of C form the CH_4 molecule with four equivalent covalent bonds. The shape of the CH_4 molecule would consequently be like that of a tetrahedron (Fig. 3.16); experiments have confirmed that is the case.

There are many types of hybridization that give rise to characteristic molecular configurations; some common configurations are listed in Table 3.6 and illustrated in Fig. 3.17.

3.6.4   Sigma (σ), pi (π), and delta (δ) molecular orbitals

There are three kinds of molecular orbitals (MOs) that are of interest to us: (i) sigma (σ) MOs; (ii) pi (π) MOs; and (c) delta (δ) MOs. Only σ MOs can be constructed from s AOs; only σ and

Fig. 3.16 Hybridization of atomic orbitals in the formation of a CH_4 molecule: (a) overlap between a carbon atom with sp^3 hybrid orbitals and four $1s$ orbitals of four H atoms; (b) the tetrahedral symmetry of the CH_4 molecule with four equivalent σ bonds.

Table 3.6 Some common hybrid orbital configurations.

Hybrid[1]	Number of bonds	Orbitals on the hybridized atom	Configuration of bonds	Examples
sp	2	$s + p$	Linear	CO_2, C_2H_2
sp^2	3	$s +$ two ps	Trigonal–planar (to corners of an equilateral triangle)	C_2H_4, C (graphite)
sp^3	4	$s +$ three ps	Tetrahedral (to corners of a regular tetrahedron)	CH_4, C (diamond)
dsp^2	4	$s +$ two $ps + d$	Square planar (to corners of a square)	$Ni(CN)_4^{2-}$
d^2sp^3	6	$s +$ three ps + two ds	Octahedral (to corners of a regular octahedron)	SF_6
d^4sp	6	$s + p +$ four ds	Trigonal prismatic (to corners of a trigonal prism)	MoS_2

[1]Hybridization at the central atom (e.g., C in CH_4 molecule).
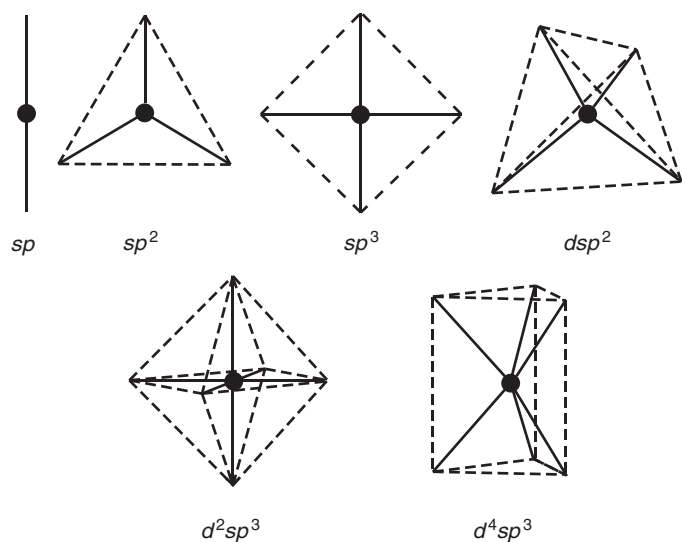
Fig. 3.17 The bond configurations corresponding to some simple hybrid orbitals. The solid dot in each represents the central atom (e.g., C in a CH$_4$ molecule) for the bonds. sp, linear; sp^2, to corners of an equilateral triangle; dsp^2, to corners of a square; sp^3, to corners of a regular tetrahedron; d^2sp^3, to corners of a regular octahedron; d^4sp, to corners of a trigonal prism. (From *An Introduction to Crystal Chemistry*, 2nd edition, by R.C. Evans, Figure 4.01, p. 60; Copyright 1966, Cambridge University Press. Reproduced with permission of the publisher.)

(a) σ molecular orbital from p_z atomic orbitals

Isolated p_z atomic orbitals

Head-on overlap of p_z orbitals

σ molecular orbital boundary diagram

(b) π molecular orbital from p_z atomic orbitals

Isolated p_z atomic orbitals

Sideways overlap of p_z orbitals

π molecular orbital boundary diagram

(c) δ molecular orbital from $d_{x^2-y^2}$ atomic orbitals

Isolated $d_{x^2-y^2}$ atomic orbitals   δ molecular orbital boundary diagram
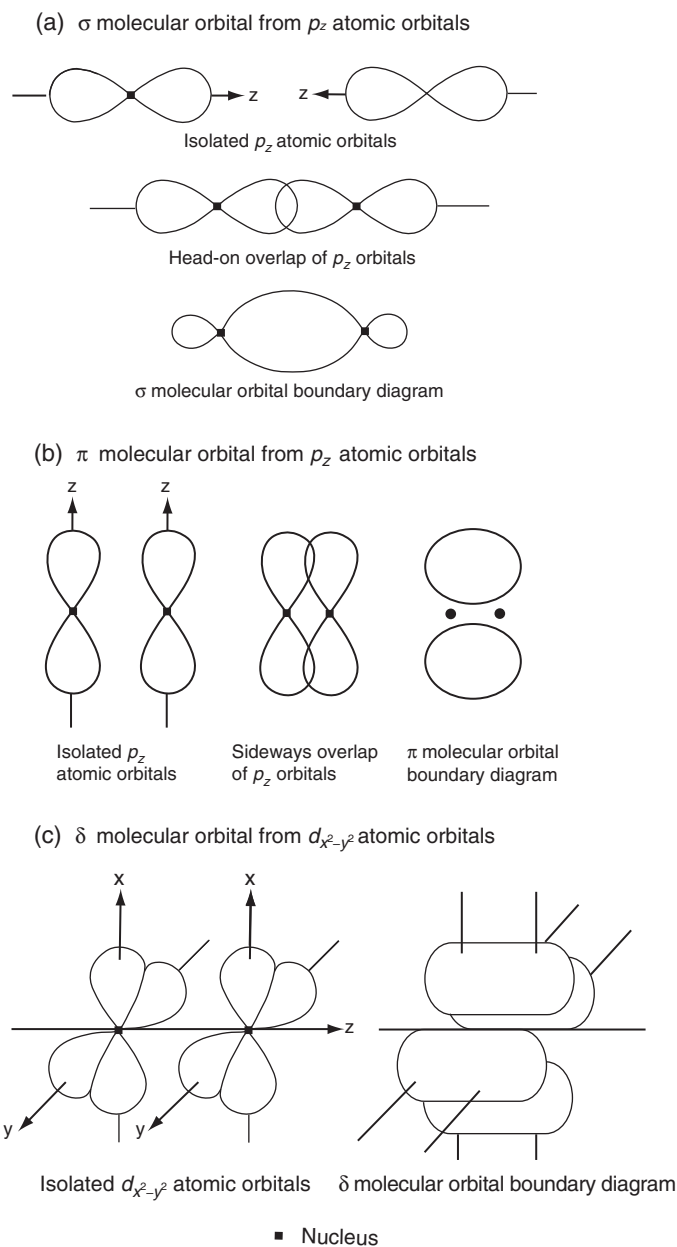
■ Nucleus

Fig. 3.18 The formation of bonding molecular orbitals: (a) σ molecular orbital by end-on overlap of two $2p_z$ atomic orbitals; (b) π molecular orbital by sideways overlap of two $2p_z$ atomic orbitals; and (c) δ molecular orbital by face-to-face overlap of two $3d_{x^2-y^2}$ atomic orbitals. For molecules larger than H$_2$, the z direction is assumed to be the internuclear axis, but the labeling of x axis and y axis is arbitrary. (After Companion, 1964.)

π MOs can be constructed from p AOs; and σ, π, and δ MOs can be constructed from d AOs (Companion, 1964). Some typical examples of molecular orbital formation are described below.

The MO formed by the overlap of s orbitals is designated as a σ MO (Fig. 3.18a), and for the H$_2$ molecule as σ_{1s^2} since it is occupied by two electrons due to the merger of two 1s AOs. The distinguishing criterion of σ MOs is that it has no nodal plane (a plane of zero electron density) containing the internuclear axis. The strongest kinds of covalent bonds are associated with σ MOs. Actually, the covalent bonding is more complicated because of the formation of complementary *bonding* and *antibonding* molecular orbitals (see Box 3.2); for simplicity only bonding MOs are shown in Fig. 3.18.

When larger atoms are involved in the formation of covalent molecules, σ MOs can also form when two p AOs overlap end-on (e.g., in a diatomic molecule such as O$_2$, F$_2$, or N$_2$), or when a p orbital in one atom interacts with an s orbital in another atom (e.g., in a molecule of HF). As can be seen in Fig. 3.18, the σ MO formed by end-on overlap of two p_z orbitals has two nodal planes (the *xy* and *xz* planes), but neither contains the internuclear axis; the π MO formed by sideways overlap of two p_z orbitals has only one nodal plane (the *xy* plane) and it contains the internuclear axis; and the δ MO formed from face-to-face overlap of two $d_{x^2-y^2}$ orbitals has two nodal planes (the *xz* and *yz* planes) each of which contains the internuclear axis.

3.6.5 *The degree of ionic character of a chemical bond: Electronegativity*

In pure ionic bonding the transferred electron(s) should be associated solely with, and distributed symmetrically around, the nucleus of the anion so formed. Pure ionic bonds, however, do not exist in nature. In reality, the coulombic attraction exerted by

Box 3.2 Bonding and antibonding molecular orbitals

The wave properties of the electron cause variation in the intensity of negative charge generated by the electron. Just as in-phase superposition of light waves leads to an increase in the light intensity and out-of-phase superposition a decrease, the intensity of the negative charge is enhanced by in-phase interaction of electron waves and decreased by out-of-phase interaction.

Let us consider the molecular orbital (MO) formation from two $1s$ atomic orbitals (AOs). The model of MO formation assumes that two $1s$ AOs can overlap in two extreme ways – in-phase and out-of-phase interaction – to form two MOs. The in-phase interaction creates an increase in the negative charge between the two nuclei, leading to an increase in the attraction between the electron and the atoms in the bond, and thus to lower potential energy, which makes it energetically preferable to the two separate $1s$ AOs. This orbital is called a *bonding molecular orbital*, and is designated as σ_{1s} in which the symbol σ (sigma) stands for the fact that the orbital is cylindrically symmetrical about the internuclear (or bond) axis (Fig. 3.19).

The out-of-phase interaction creates exactly the opposite situation, a MO of higher potential energy and, therefore, energetically less favorable compared to the separate $1s$ AOs. A molecular orbital of this type, in which the electrons tend to destabilize the bond between atoms, is called an *antibonding molecular orbital*. It is also symmetrical about the bond axis, and to distinguish it from a bonding orbital is designated with an asterisk as σ_{1s}^* (Fig. 3. 19).

Bonding and antibonding orbitals are also formed by the overlap of p and d AOs. For example, when two O atoms combine to form a O_2 molecule, the end-on overlap of the two $2p_z$ AOs generates the $\sigma_{2p(z)}$ (bonding) and $\sigma_{2p(z)}^*$ (antibonding) MOs (the z direction is assumed to be the internuclear axis). If the remaining p orbitals overlap, they must do so sideways, forming what are designated as π MOs. Thus, the sideways overlap of the two $2p_x$ AOs would generate $\pi_{2p(x)}$ (bonding) and $\pi_{2p(x)}^*$ (antibonding) MOs, and the sideways overlap of the two $2p_y$ AOs would generate another pair of $\pi_{2p(y)}$ (bonding) and $\pi_{2p(y)}^*$ (antibonding) MOs of the same potential energy.

Bonding and antibonding configuration of molecular orbitals are commonly depicted in diagrams such as Fig. 3.19 and Fig. 3.20. Figure 3.19 is for the H_2 molecule, the simplest case; Fig. 3.20 represents a generalized framework of the expected molecular orbital diagram resulting from the overlap of $1s$, $2s$, and $2p$ AOs, and is applicable to molecules such as O_2, F_2, CO, and NO. Because they meet head-on, the interaction between $2p_z$ orbitals is stronger than the interaction between $2p_x$ or $2p_y$ orbitals, which meet edge-on. As a result, the σ_{2p} orbital has a lower energy than the π_{2p} orbitals, and the σ_{2p}^* orbital has a higher energy than the π_{2p}^* orbitals.

The procedure for filling electrons in the MOs is as follows:

(1) Find out (or work out) the electronic configuration of the atoms involved (for the F atom, for example, it is $1s^2\ 2s^2\ 2p^5$).
(2) Fill the molecular orbitals from bottom to top until all the electrons are added, remembering that the number of MOs generated must equal the number of AOs being merged (because we must have the same number of places to put electrons in the molecule that we had in the atoms) and that MOs of equal energy are half-filled with parallel spin ($\uparrow$) before they are paired with opposite spin ($\uparrow\downarrow$).

The number of electrons in the bonding and antibonding MOs can be used to calculate the *bond order* (BO) and predict the stability of the covalent molecule. The bond order is defined as

Bond order (BO) = 0.5 (number of electrons in bonding MOs – number of electrons in antibonding MOs) (3.9)

Bond order values of 0, 1, 2, and 3 correspond to classical no bond, single, double, and triple bonds. If for a molecule BO = 0, the molecule is unstable; if BO > 0, the molecule is stable. The higher the bond order, the more stable is the covalent bond. We can also use the molecular orbital diagram to predict whether the molecule is paramagnetic (i.e., weakly attracted to magnetic fields) or diamagnetic (i.e., weakly repelled by magnetic fields). Molecules that contain unpaired electrons are paramagnetic; those that contain only paired electrons are diamagnetic. The H_2 molecule (see Fig. 3.19), for example, is diamagnetic and its bond order is 0.5 (2–0) = 1, indicating that it is stable.
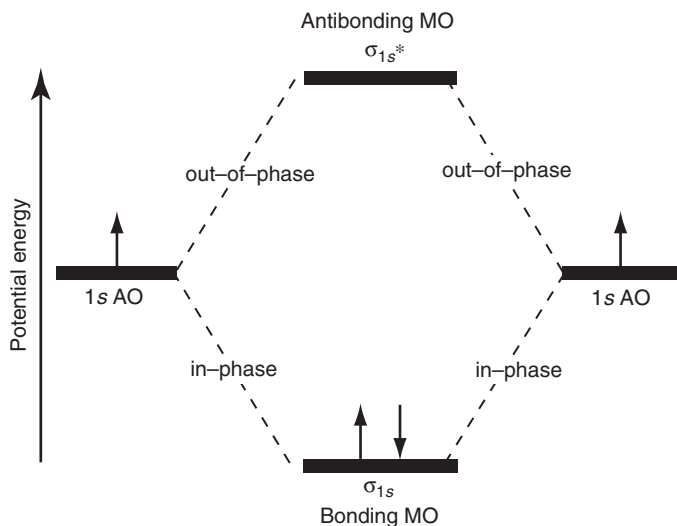

Fig. 3.19 Molecular orbital diagram for the H_2 molecule ($Z = 1$) showing sigma bonding and antibonding molecular orbitals (MO) formed from the overlap of $1s$ atomic orbitals (AO).
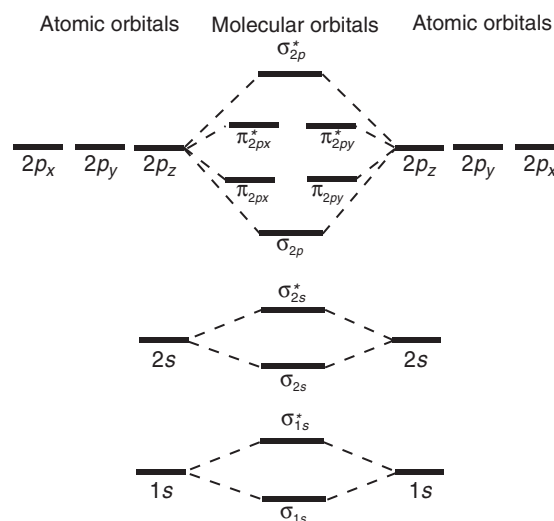
Fig. 3.20 Generalized framework of expected molecular orbital diagram from the overlap of $1s$, $2s$, and $2p$ orbitals for covalent molecules such as O_2, F_2, CO, and NO.

the neighboring cations forces the electron density of the anion to be concentrated to a small extent in the region between the nuclei. This distortion, referred to as *polarization* of the anion, results in a degree of electron sharing, or partial covalency, in any real ionic bond. The larger the *ionic potential* (charge to radius ratio) of a cation, the stronger is the polarization.

Polarization of a covalent bond occurs when the electron density becomes asymmetric around the atoms because one of the atoms exerts greater attraction on the shared electrons than the other, giving that atom a slight negative net charge (and leaving a complementary small positive charge on the other atom). This, in effect, amounts to transferring a fraction of an electron from one atom to another and imparting a degree of ionic character to the predominantly covalent bond. Such bonds, as in the *heteronuclear* diatomic molecule HF, formed by unequal sharing of electron pairs, are called *polar covalent bonds*, as opposed to *nonpolar covalent bonds*, in all *homonuclear* diatomic molecules (such as H_2, O_2, N_2, F_2, Cl_2, etc.) in which the bonding electron pairs are shared equally between the nuclei. In the case of HF, for example, the F atom (which has a higher electronegativity) attracts the shared electron pair more strongly than does the H atom. This causes a distortion of the electron density, and its small shift toward the F atom leaves the H-end of the HF molecule slightly positive and the F-end slightly negative. The polar HF molecule is commonly represented as

$$\overset{\delta+}{H} - \overset{\delta-}{F}$$

where the $\delta+$ over the H atom and the $\delta-$ over the F atom indicate that the "H-end" of the molecule is more positive relative to the "F-end," and *vice versa* (not that H has a charge of +1 and F a charge of –1). The separation of charge in a polar covalent bond creates an *electric dipole*, whose strength is expressed in terms of its *electric dipole moment* (μ), which is defined as

$$\mu = d\delta \tag{3.10}$$

where d is the distance separating the charges of equal magnitude and opposite sign, and δ is the magnitude of the charge. All molecules whose positive-charge and negative-charge centers do not coincide possess an electric dipole moment.

Realizing that there must exist a continuous progression between purely covalent bonds and dominantly ionic bonds, the American Nobel laureate Linus Pauling (1901–1974) introduced the concept of *electronegativity* in 1932 to quantitatively express the degree of ionic character of a mixed ionic–covalent bond. Electronegativity (χ) is a parameter that describes *the tendency of an atom in a molecule to attract electrons towards itself when chemically combined with another atom.* (The equivalent property of a free atom is its electron affinity – see section 2.4.1.) Thus, electronegativity, which is related to ionization potential and electron affinity, is a measure of the ability of an atom to compete for electrons with other atoms to which it is bonded. For example, the electronegativity of chlorine is higher than that of hydrogen in an HCl molecule, which means that the chlorine atom displays greater attraction for electrons than does the hydrogen atom.

Whereas the chemical applications of ionization potential are limited to elements that lose electrons to form cations, the concept of electronegativity is applicable to all kinds of elements and the bonds they form. However, unlike ionization potential, electronegativity cannot be measured and has to be calculated from other atomic or molecular properties.

Several methods of calculation have been proposed, but the most commonly used method is the one originally proposed by Pauling based on measured electric dipole moments. Pauling's electronegativity is a dimensionless quantity that is estimated on an arbitrary scale ranging from 0 (helium) to 4.1 (fluorine) (see Appendix 3). In general, electronegative values increase within a period of the Periodic Table with increasing atomic number – e.g., from $\chi = 0.98$ for Li ($Z = 3$) to $\chi = 3.98$ for F($Z = 9$) – and decrease from top to bottom within a group – e.g., from $\chi = 3.98$ for F ($Z = 9$) to $\chi = 2.2$ for At ($Z = 85$). The inert gases (He, Ne, etc.) have zero (or close to zero) electronegativity values, and the peak values belong to the halogens (F, Cl, Br, I; see Fig. 2.9). Cation-forming elements (electron donors) with low values of electronegativity, such as alkali and alkaline earth metals, are called *electropositive*; anion-forming elements (electron acceptors) characterized by high values of electronegativity, such as the halogens and oxygen ($\chi = 3.44$), are called *electronegative*.

Although electronegativity is not a precisely defined atomic property, the electronegative difference between two atoms provides a useful measure of the polarity and ionic character of the bond between them in solid compounds. The larger the electronegativity difference between two atoms, the greater is the probability of them forming an ionic bond in which the more electronegative element represents an anion and the less electronegative element a cation. Between elements with similar electronegativity values, neither has a stronger preference for electrons, and they tend to share electrons by covalent bonding. Typically, a bond is considered ionic if the electronegativity difference between the two bond-forming elements is > 2.1. Thus, the Na–Cl bond ($|\chi_{Na} - \chi_{Cl}| = |0.93–3.16| = 2.23$) should be ionic whereas the Fe–S bond ($|\chi_{Fe} - \chi_S| = |1.83–2.58| = 0.75$) should be covalent. The Mg–O bond ($\Delta\chi = 2.13$) and Ca–O bond ($\Delta\chi = 2.44$), which are common in rock-forming silicate minerals, are also ionic. However, Si–O and Al–O bonds ($\Delta\chi = 1.54$ and 1.83, respectively) in the same minerals should be considered covalent by this definition, although they are generally regarded as ionic for the purpose of silicate mineral crystal structures.

Based on the premise that elements having different electronegativities form bonds whose ionic character is proportional to the magnitude of electronegativity difference (Fig. 3.21), Linus Pauling suggested the following empirical relation to calculate the percentage ionic character of a bond (PIC) between two atoms A and B:

$$PIC_{A–B} = 16|\chi_A - \chi_B| + 3.5|\chi_A - \chi_B|^2 \tag{3.11}$$

where χ_A and χ_B are the electronegativities of the two atoms (see Appendix 3). According to this formulation, the Na–Cl bond (PIC = 53.1%) is only slightly more ionic than covalent
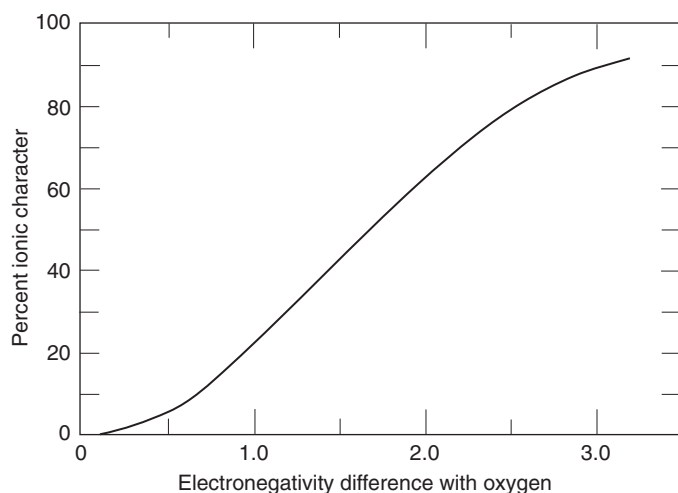
Fig. 3.21 The degree of ionic character of a single chemical bond between an element (A) and oxygen (B) as a function of the electronegativity difference $|\chi_A - \chi_B|$. An electronegativity difference of about 1.7 corresponds to a bond that is 50% ionic; bonds with larger electronegativity difference are primarily ionic, those with a smaller difference are primarily covalent, but there are exceptions. Source of data: Faure (1998).
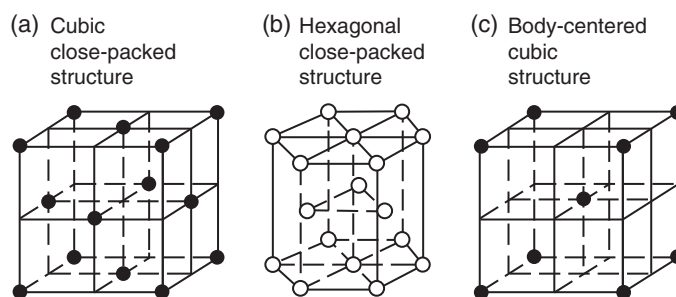

Fig. 3.22 Crystal structures of metallic elements. (a) Cubic close-packed structure (face-centered cubic), in which each atom is surrounded by 12 neighbors (e.g., Cu, Ni, Au). (b) Hexagonal close-packed structure, in which each atom is surrounded by 12 neighbors, 6 at a slightly greater distance than the other 6 (e.g., Mg, Ti, Zn). (c) Body-centered cubic structure, in which each atom is surrounded by 8 neighbors at the corners of a cube (e.g., Li, Na, Mo). Assuming the atoms to be perfect spheres, the packing efficiency (volume of the spheres occupied by the sphere/total volume) is 74.05% for both cubic and hexagonal close-packed structures; the body-centered cubic structure is not a close-packed array and its packing efficiency drops to 68.02%.

(although NaCl is often cited as a typical example of an ionic compound), the Ca–O bond (PIC = 59.9%) is mostly ionic, the Mg–O bond (PIC = 50%) is as much ionic as covalent, and the Si–O bond (PIC = 32.9%) is dominantly covalent. Thus, electronegativity alone does not provide accurate predictions about the bonding character and coordination numbers in all kinds of compounds.

Example 3.3: Calculation of the percentage ionic character of the bond between H and F in the HF molecule, using the electronegativity values and empirical relation given by Pauling

$\chi_H = 2.20$; $\chi_F = 3.98$ (Appendix 3)

$$PIC_{H-F} = 16|\chi_H - \chi_F| + 3.5|\chi_H - \chi_F|^2$$
$$= 16|2.20 - 3.98| + 3.5\,|2.20 - 3.98|^2$$
$$= (16 \times 1.78) + (3.5 \times (1.78)^2) = 28.48 + 11.09 = 39.57$$

So, the H–F bond in the HF molecule is about 40% ionic and 60% covalent.

3.7 Metallic bonds

Most metallic elements display *close-packed structures* (spheres, representing atoms, touching all their immediate neighbors), which represent the geometrically most compact arrangement of spheres in space (see Evans, 1966, fig. 5.01, p. 81). The close-packed arrangement results in crystal structures with hexagonal or cubic (face-centered and body-centered) symmetry (Fig. 3.22).

Metallic bonding is the bonding that exists among the atoms within the crystal structure of a metallic element. The bonding cannot be ionic because a metal is not composed of cations and anions. Van der Waals bonds (see section 3.8) are too weak to account for the high melting points of metals, and localized covalent bonds are unlikely in view of the fact that each atom in the crystal structure of metals has 12 to 14 near neighbors. Moreover, the bonding in metals must explain their special properties, such as electrical and thermal conductivity and malleability, which are not characteristics of ionic or covalent compounds.

Most metals have *s* electrons external to filled or partially filled inner shells – for example, the two 4*s* electrons in Ni ($1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^8$ $4s^2$). These *s* electrons are "delocalized," partly because they are most easily ionized and partly because they occupy a large volume in space relative to other electrons and present an overall low electron density to the positive nucleus (Companion, 1964). For a simple model to explain metallic bonding, it is assumed that the lattice sites in the metal crystal are occupied by the relatively small positive ionic cores (e.g., Ni^{2+}), which are surrounded by a "sea" of delocalized (loosely bound) electrons. This is why atoms or layers of atoms are allowed to slide past each other, resulting in the characteristic properties of malleability and ductility.

Metallic bonding is the electrostatic attraction between the ionic cores and the delocalized electrons. The latter are not associated with a single atom or a covalent bond; they are contained within a molecular orbital that is shared with all the ionic cores in the crystal and extends over the entire crystal in all directions with equal probability. These electrons are free

Table. 3.7 Van der Waals radius (Å) of some elements.

Element	Radius	Element	Radius	Element	Radius	Element	Radius
H (Z = 1)	1.20	N (Z = 7)	1.55	F (Z = 9)	1.35	S (Z = 16)	1.85
C (Z = 6)	1.7	O (Z = 8)	1.52	P (Z = 13)	1.9	Cl (Z = 17)	1.8

to move around throughout the crystal structure and thus are capable of conducting electricity. Without any particular direction for a net movement of electrons in the crystal structure, there is no flow of electricity in an isolated piece of metal, but a current will flow through the metal piece if it is connected to the terminals of a battery, confirming the presence of delocalized electrons. The thermal conductivity of metals arises from the fact that their loosely bound electrons can transfer heat energy at a faster rate than the tightly bound electrons in substances with covalent bonding. (There are a few nonmetals that can conduct electricity: graphite because, like metals, it has free electrons, and molten and aqueous ionic compounds because they have moving ions.)

Atomic radii of metals can be derived from measurements of their cell dimensions. In the case of metals with close-packed structures, the atomic radius is half the distance of the interatomic distance. In structures of lower coordination, such as the cubic body-centered structure of the alkali metals, a similar definition of atomic radius is applicable, but the values so obtained are not immediately comparable with those derived from close-packed structures (Evans, 1966). The radius of an isolated atom is not a meaningful concept unless the coordination is specified because a small but systematic decrease in the atomic radius occurs with decreasing coordination. In general, atomic radii of metals are comparable to their covalent radii; the corresponding ionic radii are smaller because outer electrons are stripped away during the formation of an ion and those that remain are bound closely to the nucleus.

3.8   Van der Waals bonds

As early as 1873, Johannes Diderik van der Waals (1837–1923), a Nobel laureate from the Netherlands, postulated the existence of weak attractive and repulsive forces among the molecules of a gas and attributed the observed deviations from the ideal gas law to these forces (see section 4.1.1). Although the application of his postulate was limited to correcting the gas law through empirically derived constants, it is now recognized that van der Waals bonds operate between all atoms, ions, and molecules in all solids, and add a small contribution to the binding forces in ionic and covalent solids.

The van der Waals bonds are associated with energies of only about 10–50 kJ mol^{-1}, and their effect is largely masked in any crystal structure held together by other interatomic

bonds, which are much stronger (see Table 3.7). The only solids in which the properties of the van der Waals bonds can be studied in isolation are the inert gases in the solid state to which they condense at sufficiently low temperatures. Such solids have a spatially undirected, cubic and hexagonal close-packed arrangement of atoms, similar to those found in metals (see Fig. 3.22).
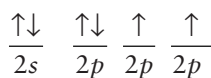
The *van der Waals radius* of an atom is the radius of an imaginary hard sphere that can be used to model the atom for many purposes. Van der Waals radii are determined from measurements of atomic spacing between pairs of unbonded but touching atoms in crystals. Some examples are listed in Table 3.7.
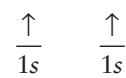
3.9   Hydrogen bond

The *hydrogen bond* is a special kind of intermolecular bond that forms between the hydrogen atom in a polar bond such as O–H and an electronegative atom such as oxygen, hydrogen, or fluorine in a neighboring molecule. The fact that the hydrogen bond is found only between the atoms of strongly electronegative elements such as fluorine, oxygen, nitrogen, and (occasionally) chlorine suggests that it must be essentially ionic in character (Evans, 1966). Hydrogen is the only element capable of forming such bonds because the H$^+$ ion is unique in terms of both its very small size and its lack of extranuclear electrons. The typical hydrogen bond, with energy in the order of about 20 kJ mol^{-1}, is considerably weaker than covalent or ionic bonds, but stronger than van der Waals bonds.

The most ubiquitous, although not completely understood, example of a hydrogen bond is found between molecules of water, which has many anomalous physical and chemical properties (such as a high boiling point compared to other covalent molecules of similar molecular weights such as CO and NO) because of this kind of bonding (see section 7.1). Let us examine how a hydrogen bond forms between water molecules.

As shown below, there are eight valence electrons involved in a molecule of water, six associated with oxygen atoms and one with each of the hydrogen atoms:

$$\frac{\uparrow\downarrow}{2s} \quad \frac{\uparrow\downarrow}{2p} \quad \frac{\uparrow}{2p} \quad \frac{\uparrow}{2p} \qquad\qquad \frac{\uparrow}{1s} \quad \frac{\uparrow}{1s}$$

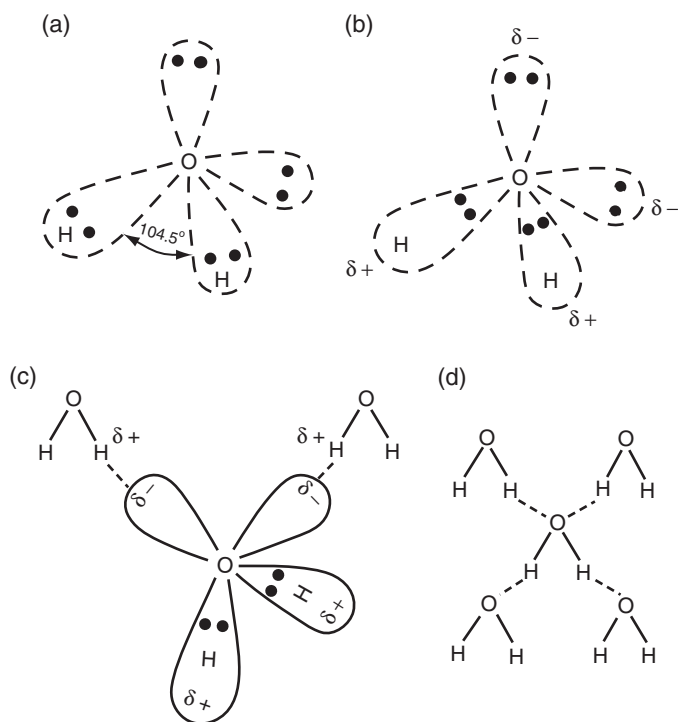Ground-state O atom   Ground state H atoms

Fig. 3.23 Structure of the water molecule and the linkage of water molecules through hydrogen bonds. (a) Tetrahedral distribution of the four pairs of electrons (two bonding pairs shared with hydrogens and two lone pairs) surrounding the oxygen in a water molecule. (b) Charge distribution in a water molecule ($\delta+$ with the hydrogens and $\delta-$ with the lone pairs). (c) Formation of hydrogen bonds between lone pairs on the oxygen and the hydrogens of neighboring molecules; (d) Linkage of a water molecule to four neighboring water molecules through hydrogen bonds. (After O'Neill, 1985.)

Two pairs of electrons are shared between the oxygen atom and two hydrogen atoms forming covalent bonds (H–O–H); the other two pairs are nonbonding or *lone pairs* because they are not shared with another atom (Fig. 3.23a). Because of repulsion between negative charges, the pairs of electrons would move as far apart as possible. The maximum separation is achieved if the four pairs are arranged in a tetrahedral configuration within the sphere of influence of the oxygen atom, one pair at each corner of the tetrahedron. The two lone pairs of electrons occupy a smaller volume and have a greater repulsive effect than the two bonding pairs, which causes the H–O–H bond angle to be reduced from the theoretical value of 109.5° for tetrahedral coordination to 104.5°.

Being more electronegative than hydrogen, oxygen attracts the shared bonding pair of electrons more strongly than does hydrogen. The result is a slight negative charge on the oxygen atom and a slight positive charge on each of the two bonding hydrogen atoms; the extra negative charge is concentrated on the two lone pairs of electrons (Fig. 3.23b). In other words, the two corners of the tetrahedron occupied by hydrogen atoms carry a positive charge, whereas the two remaining corners

carry a negative charge. We can thus picture the water molecule behaving like a dipolar molecule, with a net positive charge on one side and a net negative charge on the other. The polarity of the water molecules is responsible for its remarkable solvent properties (see section 7.1).

A hydrogen bond forms by dipole–dipole interaction when the positively charged end of a water molecule is electrostatically attracted to the negatively charged end of a neighboring water molecule (Fig. 3.23c). This electrostatic bond is called a hydrogen bond. Each water molecule can be involved in four hydrogen bonds: two hydrogen bonds to the oxygen via its lone pairs, and a hydrogen bond between each hydrogen and the oxygen in a neighboring water molecule (Fig. 3.23d). This kind of linkage creates an open structure by holding the water molecules apart in fixed positions (O'Neill, 1985).

3.10 Comparison of bond types

A comparison of the bond types associated with solids is summarized in Table 3.8, with a comparison of dissociation energies (E_D) for various bond types in Table 3.9.

3.11 Goldschmidt's classification of elements

The distribution of the elements in a gravitational field, such as that of the Earth, is controlled not by their densities or atomic weights, but by their affinities for the three major groups of phases that can be formed — metals, sulfides, and silicates. Early in the 19th century, V.M. Goldschmidt (1888–1947), the famous Norwegian geochemist, reached this conclusion on the basis of three kinds of observations: (i) the composition of chondritic meteorites (see section 12.1), which are believed to have an average composition similar to that of the primordial Earth and to have undergone similar differentiation; (ii) analyses of metal, slag (silicates), and matte (sulfides) produced during smelting of sulfide ores for metal extraction; and (iii) the compositions of naturally occurring silicate rocks, sulfide ores, and native metals. The conclusion can also be supported from a comparison of free energies of reactions involved in the formation of various alloys, sulfide compounds, and silicate compounds. The concept of free energy and the calculation of free energy change for reactions will be discussed in Chapter 4.

Based on the way in which the elements distribute themselves among iron liquid, sulfide liquid, silicate liquid, and a gas phase, Goldschmidt (1937) classified the elements into four groups (Table 3.10): (i) *siderophile* (iron-loving) elements, which prefer to form metallic alloys (e.g., Fe–Ni alloy); (ii) *chalcophile* (sulfur-loving) elements, which most easily form sulfides; (iii) *lithophile* (rock-loving) elements, which readily combine with oxygen to form silicate and oxide minerals; and (iv) *atmophile* elements, which are commonly found in a gas phase. The geochemical character of an element is

Table 3.8 Comparison of properties of solids with different kinds of bonding.

Property	Ionic	Covalent	Metallic	Van der Waals
Formation	Commonly by combination of two elements with quite different electronegativities, usually a metal and a nonmetal	Commonly by combination of two elements with similar electronegativities, usually nonmetals	Within the crystal structures of metallic elements	Present in all solids as a contributing binding force
Crystal structure	Spatially nondirected; structures of high coordination and symmetry	Spatially directed; structures of low coordination and low symmetry	Spatially nondirected; structures of high coordination and symmetry	Formally analogous to metallic bond
Mechanical strength	Strong, giving hard crystals	Strong, giving hard crystals	Variable; gliding common	Weak, giving soft crystals
Dissociation energy (see Table 3.9)	Similar values (400–1300 kJ mol^{-1})			Much smaller values (< 50 kJ mol^{-1})
Melting point	Fairly high (typically 400 to 3000°C)	High (1200–4000°C)	Variable (–39° to 3400°C)	Low
Electrical conductivity	Molten compounds and solutions in polar solvents are good conductors (because they contain mobile ions)	Molten compounds and aqueous solutions are poor conductors (because they do not contain charged particles)[1]	Good conductors (because they contain delocalized electrons)	Insulators in solid and in melt

[1] Exceptions: diamond is a good conductor of heat; graphite is a good conductor of electricity.

Table 3.9 Comparison of dissociation energies (E_D) for various bond types.

Bond type	Reaction	E_D (kJ mol^{-1})	Bond type	Reaction	E_D (kJ mol^{-1})
Ionic	$NaCl_{(s)} \Rightarrow Na^+_{(g)} + Cl^-_{(g)}$	761*	Metallic	$Na_{(s)} \Rightarrow Na_{(g)}$	109
Ionic	$NaCl_{(s)} \Rightarrow Na_{(g)} + Cl_{(g)}$	640	Metallic	$Pb_{(s)} \Rightarrow Pb_{(g)}$	194
Ionic	$CaO_{(s)} \Rightarrow Ca_{(g)} + O_{(g)}$	1075	Metallic	$Ni_{(s)} \Rightarrow Ni_{(g)}$	423
Covalent	$C_{(diamond)} \Rightarrow C_{(g)}$	720	van der Waals	$S_{(s)} \Rightarrow S_{(g)}$	13
Covalent	$H_2O_{(g)} \Rightarrow 2H_{(g)} + O_{(g)}$	932	van der Waals	$Ar_{(s)} \Rightarrow Ar_{(g)}$	6
Covalent	$SiC_{(s)} \Rightarrow Si_{(g)} + C_{(g)}$	1197	Hydrogen bond	$H_2O_{(ice)} \Rightarrow H_2O_{(g)}$	50

*The lattice energy of NaCl crystal.
Sources of data: Compilations in Fyfe (1964) and Gill (1996).

Table 3.10 Goldschmidt's geochemical classification of elements.[1]

Siderophile	Chalcophile	Lithophile	Atmophile
Fe, Co, Ni	Cu, Ag, (Au)	Li, Na, K, Rb, Cs	H, N, (C), (O)
Ru, Rh, Pd	Zn, Cd, Hg	Be, Mg, Ca, Sr, Ba, (Pb)	(F), (Cl), (Br), (I)
Re, Os, Ir, Pt, Au	Ga, In, Tl	B, Al, Sc, Y, REE	He, Ne, Ar, Kr, Xe
Mo, Ge, Sn, C, P	(Ge), (Sn), Pb	(C), Si, Ti, Zr, Hf, Th	
(Pb), (As), (W)	As, Sb, Bi	(P), V, Nb, Ta	
	S, Se, Te	O, Cr, W, U	
	(Fe), (Mo), (Re)	(Fe), Mn	
		F, Cl, Br, I	
		(H), (Tl), (Ga), (Ge), (N)	

[1] Elements in parentheses belong primarily in another class. For example, Fe is dominantly siderophile, but also behaves as a chalcophile element as well as a lithophile element.
Source of data: Goldschmidt (1937).

largely governed by the electronic configuration of its atoms and hence is closely related to its position in the Periodic Table. Comparison of Table 3.10 with the Periodic Table (Fig. 2.8) shows that in general siderophile elements are concentrated at the center of the Periodic Table, lithophile elements to the left of the center, chalcophile elements to the right, and atmophile elements to the extreme right (Krauskopf and Bird, 1955) It can also be correlated with electrode potentials (see Chapter 8): siderophile elements are mostly noble metals with low electrode potentials; lithophile elements have high electrode potentials; and chalcophile elements have intermediate values. Goldschmidt's classification also included a fifth group named *biophile* elements (such as C, H, O, N, P, S, Cl, I), which are concentrated by living organisms.

It is clear from the many overlaps among the groups in Table 3.10 that the classification scheme is not perfect. Some elements show affinity for more than one group, because the distribution of any element is dependent to some extent on temperature, pressure, and chemical environment of the system (e.g., oxygen fugacity, competing atoms, etc.). It is, however, a useful qualitative guide to the behavior of elements during geochemical processes.

3.12   Summary

1. Chemical bonds hold the atoms or ions in a crystal structure together and determine the physical and chemical properties of the crystal. There are five kinds of chemical bonds: ionic bonds, covalent bonds, metallic bonds, van der Waals bonds, and hydrogen bonds.

2. Ionic bonds arise from electrostatic attraction between cations and anions, covalent bonds from sharing of electrons between atoms, and metallic bonds from the electrostatic attraction between the ionic cores of atoms at lattice positions and the delocalized electrons. Van der Waals bonds are weak attractive and repulsive forces that operate between all atoms, ions, and molecules in all solids. The hydrogen bond is a special kind of intermolecular bond that forms between the hydrogen atom in a polar bond such as O–H and an electronegative element such as oxygen on a neighboring molecule.

3. In ionic compounds, the number of oppositely charged nearest neighbors surrounding an ion is called its coordination number (CN). The coordination number and, therefore, the geometry of packing in ionic crystals can be predicted from the radius ratio r_c/r_a, where r_c and r_a are the cation and anion radius, respectively.

4. The lattice energy (U_L) of a perfectly ionic crystal is defined as the amount of energy required at absolute zero (i.e., –273°C) to convert one mole of the solid into its constituent ions at infinite separation in the gas phase. For 1 gram-mole of a binary ionic compound it can be calculated using the equation

$$U_L = MA\frac{z_c z_a e^2}{R}\left(1 - \frac{1}{n}\right)$$

where z_c and z_a are the charges on cations and anions (expressed as a multiple of the electron charge e), R is the interionic distance separating the ions, n is a constant for the particular crystal structure, A is the Avogadro's number, and M is a numerical quantity called the Madelung constant, the value of which depends on the crystal structure.

5. The crystal structures of silicate minerals can be rationalized in terms of different patterns of linkages among silicon–oxygen tetrahedra (SiO_4^{4-}).

6. The extent of ionic substitution in minerals is governed by the nature of the crystal structure and how similar the ions are in terms of size, charge, and electronegativity. Elevated temperatures and lower pressures favor increased substitution.

7. Crystal-field theory, which describes the effects of electrostatic fields on the energy levels of the valence electrons (electrons in the outermost orbitals) of a transition-metal when it is surrounded by negatively charged ligands in a crystal structure, provides reasonable explanations for some magnetic properties, colors, hydration enthalpies, and spinel structures of transition metal complexes.

8. Isomorphism refers to substances having similar crystal structures but different chemical formulas, whereas polymorphism refers to substances having similar chemical formulas but different crystal structures.

9. A solid solution is a solution in the solid state of one or more solutes in a solvent whose crystal structure remains unchanged by addition of the solutes. Solid solutions form: by substitution of ions of one kind by another in the lattice, by interstitial accommodation of ions, or by omission of ions from the lattice leaving vacant sites.

10 Covalent bonding is best explained through the formation of bonding and antibonding molecular orbitals (σ, π, and δ) from the overlap of atomic orbitals on the atoms in the molecule.

11. Before combining across atoms, atomic orbitals that are close to each other in energy within the same atom have the ability to combine with one another to form hybrid covalent bonds. The concept of orbital hybridization is useful for explaining the bonding in some molecules such as CH_4.

12. Anomalous physical and chemical properties of water, such as its high boiling point and high solvent capacity, are due to hydrogen bonding within and between water molecules.

13. Goldschmidt classified the elements into four groups: (i) siderophile (iron-loving) elements, which prefer to form metallic alloys (e.g., Fe–Ni); (ii) chalcophile (sulfur-loving) elements, which most easily form sulfides; (iii) lithophile (rock-loving) elements, which readily combine with oxygen to form silicate and oxide minerals; and (iv) atmophile elements, which are commonly found in a gas phase. This classification scheme is not perfect, but it is a useful qualitative guide to the behavior of elements during geochemical processes.

3.13   Recapitulation

Terms and concepts

Antibonding molecular orbital
Atomic orbital
Atomic radius
Avogadro's number
Bond length
Bond order
Bonding molecular orbital
Born–Haber cycle
Close-packed crystal structures
Coordination number
Coupled substitution
Covalent bond (polar and nonpolar)
Covalent radius
Crystal-field theory
Crystal-field stabilization energy (CFSE)
Delocalized electrons
Diadochy
Diamagnetism
Dipole moment
Dissociation energy
Electric dipole moment
Electronegativity
Energy of crystallization
Geochemical coherence
Goldschmidt's classification of elements
Goldschmidt's rules of ionic substitution
Hybridization
Hydrogen bond
Ionic bond
Ionic potential
Ionic radius
Isomorphism
Lanthanide contraction
Lattice energy
Molecular orbitals (σ, π, and δ)
Madelung constant
Metallic bond
Ordered structure
Paramagnetism
Polarization
Polymorphism
Radius ratio
Rare earth elements
Silicon–oxygen tetrahedron
Solid solution
Silicate crystal structures
Valence bond theory

Van der Waals bond
Van der Waals radius

Computation techniques

- Lattice energy using the Born–Haber cycle.
- Percent ionic character of a bond.

3.14   Questions

1. Which of the following series of ions are isoelectronic? Justify your answer.
   (a) Au^+, Hg^{2+}, Tl^{3+}, and Pb^{4+}
   (b) Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}
   (c) Li^+, Be^{2+}, B^{3+}, C^{4+}, and N^{5+}

2. From the data given in Table 3.3, what generalizations can you make about the trends in variation of lattice energy?

3. Calculate the lattice energy and the energy of crystallization of 1 mole of KCl crystals using equation (3.4). Given: $n = 9$; $r_{K^+} = 1.38$, $r_{Cl^-} = 1.81$, $A = 6.02 \times 10^{23}$, $e = 4.80 \times 10^{-10}$ Coulomb, and $M_{KCl} = 1.747$.

4. Calculate the lattice energy of one mole of solid LiCl (U_{LiCl}) by constructing a Born–Haber cycle of appropriate reactions based on the heat data given below:
   First ionization potential of lithium (I_{Li}) = 520 kJ mol^{-1}
   Electron affinity of chlorine (E_{Cl}) = 348 kJ mol^{-1}
   Heat of sublimation of lithium (S_{Li}) = 159 kJ mol^{-1}
   Heat of dissociation of chlorine (D_{Cl}) = 236 kJ mol^{-1}
   Heat of formation of LiCl (Q_{LiCl}) = -409 kJ mol^{-1}
   [Hint: see Fig. 3.2 and Example 3-2.]

5. Applying the principles of molecular orbital formation, explain why oxygen forms a stable O_2 molecule whereas helium does not form a stable He_2 molecule. Is oxygen paramagnetic or diamagnetic?

6. Determine the percent ionic character of the following bonds between: (i) Na and Cl; (ii) Cl and O; and (iii) Zn and O.

7. Explain why the following substitutions are not common in minerals: Cu^+ for Na^+: Cl^- for F^-, and C^{4+} for Si^{4+}.

8. Name three elements you would expect to find in trace quantities in calcite ($CaCO_3$) substituting for Ca. Justify your answer.

9. Explain why both lithium and cesium are concentrated in the late mica minerals of pegmatites, although their ionic radii are very different.

10. Explain why boron minerals are more common than vanadium minerals in igneous and sedimentary rocks, although vanadium is a more abundant element than boron.