**1.3 BONDING IN CERAMICS:**

The properties and the way its atoms are arranged are determined primarily by the nature and directionality of interatomic bonds. If the bond is strong, those are the *primary bonds*. The primary bonds may be ionic, covalent, or metallic.

Van der Waals and hydrogen bonds are *secondary bonds*, and they are weaker than the primary bonds. Ceramics contain two types of primary bonds—ionic and covalent. There a few ceramics that contain a third type of primary bond (e.g., the metallic bond). For example, in Fe3C, the bond is partly ionic.

Ionic compounds generally form between very active metallic elements and active nonmetals. Thus, the metals mostly involved in the formation of ceramics by ionic bonding are those from groups IA, IIA, and part of IIIA, as well as some of the transition metals. Moreover, the most active nonmetals of groups VII A and VIA form ionic bonding. For covalent bonding to occur, ionic bonding should be unfavorable to form. This unfavorability can be semi-quantified using a scale of relative *electronegativity*. Pauling proposed this scale.

**1.3-1 Ionic Bonding**

Ionic bonding gives rise to ionically bonded solids.

**1.3-1-1 Ionically Bonded Solids**

The stability of ionically bonded solids depends on the lattice energy. The greater the lattice energy, the more stable the solid will be. The stability in turn determines the melting temperature, thermal expansion, and stiffness of the solid. More stable solids will possess greater melting points, less thermal expansion, and greater stiffness.

***\* Lattice Energy Calculations***

To calculate the lattice energy, let us consider a common ionic solid NaCl. To confirm that NaCl is a predominantly ionic solid, we can find its Δx value. Putting the values for the electronegativity of Cl and Na in the equation for calculating Δx, we get Δx = 3.16−0.93 = 2.13, which is very high, showing that NaCl is predominantly ionic bonded. Figure 1.5 a shows the model of a NaCl unit cell. It shows that the centrally placed Cl ion is surrounded by six Na ions. That means the central anion is attracted to six Na+ cations at a distance r0 (Figure 1.5b). It is repelled by 12 Cl− anions at a distance √2r0 (Figure 1.5c), and attracted to eight Na+ cations at √3r0 (Figure 1.5d), and so on.



***FIGURE 1.5 (a) Schematic of the NaCl structure; (b) the first six nearest neighbors at a distance of r0 are attracted to the central anion; (c) the second 12 nearest neighbors at a distance of √2r0 are repelled; (d) the third eight nearest neighbors are attracted.***

Summing up electrostatic interactions, we can write that:

Where z1 and z2 are the net charges on the ions, n is the *Born exponent* that lies between 6 and 12, r0 is the equilibrium interatomic distance. The third term in parentheses is an alternating series that converges to some value α, called the *Madelung constant*. The total electrostatic attraction for 1 mol of NaCl in which there are twice the Avogadro’s number NAV of ions but only NAV bonds is:

Here, Elatt is the lattice energy of an ionic solid. For NaCl, it can be calculated to be equal to −750 kJ/mol.

***\* Born–Haber Cycle***

In the derivation of the expression for calculating the lattice energy, we have assumed that the ionic solid is made up of ions attracted to each other by coulombic attractions. To test this model, we can use the Born–Haber cycle. This cycle is based on the first law of thermodynamics. As we know, this law states that energy can neither be created nor destroyed. The cycle devised for NaCl is shown in Figure 1.6. For this cycle, the following equation is valid, following the first law of thermodynamics:

**ΔHform(exo) = Evap(endo) + Eion(endo) + Ediss(endo) + EEA(exo) + Elatt(exo)**

Here, ΔHform is the enthalpy of formation for NaCl; Evap and Eion are the sublimation and ionization energies, respectively, for 1 gram atom of Na atoms; and Ediss and EEA are the dissociation energy and electron affinity, respectively, for 1 gram atom of Cl atoms. The exo/endo indicate whether the energy involved is exothermic/endothermic, respectively. Exothermic energy is indicated by the − sign and endothermic by the + sign.

***FIGURE 1.6 The Born–Haber cycle.***

***\* Pauling’s Rules***

Pauling’s rules are used to interpret the majority of the ionic structures. The *first rule* states that a coordination polyhedron of anions formed is formed about each cation. The cation–anion distance is equal to the sum of their radii. The coordination number is determined by the ratio of the radii of the two ions. This relation between the coordination number and radii ratio is based on the stability of the resulting structure. This is illustrated in Figure 1.7.

In a two-dimensional representation, Figure 1.7a is a stable structure, because the repulsive force due to similarly charged ions is lesser than the attractive force between the oppositely charged ions. This is obvious because the similarly charged ions are not in contact, whereas the oppositely charged ions are touching each other. Figure 1.7b is less stable because the repulsive force has increased owing to the contact between the similarly charged ions. Figure 1.7c is unstable because of the greater repulsive force compared to the attractive force by virtue of the noncontact between the oppositely charged ions. The relation between the coordination number and the range of cation-to-anion radius ratio is shown in Table 1.1. Figure 1.8 shows the resulting structures for various coordination numbers.

The *second rule* describes a basis for evaluating local electrical neutrality. It states that, in a stable structure, the total strength of the bonds reaching an anion from the surrounding cations should be equal to the charge of the anion. The strength of an ionic bond donated from a cation to an anion is the formal charge on the cation divided by its coordination number.



***FIGURE 1.7 Stable and unstable coordination configuration (a) Stable, (b) Stable, and (c) Unstable.***

***TABLE 1.1 Relation between Coordination Number and Range of Cation-to-Anion Radius Ratio***

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***FIGURE 1.8 Polyhedra for different coordination numbers.***

The *third rule* further concerns the linkage of the cation coordination polyhedral.

In a stable structure, the corners, rather than the edges and especially the faces of coordination polyhedra, tend to be shared. If an edge is shared, it tends to be shortened. The *fourth rule* says that polyhedra formed about the cations of low coordination number and high charge tend especially to be linked by corner sharing. The *fifth rule* states that the number of different constituents in a structure tends to be small.