Review: Ionic Bonding Model

**Ionic** – charge is transferred from the more metallic (low EN) atom to the non-metallic (high EN) atom forming oppositely charged species, the cation (+) and anion (-).

The electrostatic interaction between the two ions, $F_{12}$, forms the bond, and increases with increasing ion charge ($Z_e$) and decreases with increasing separation, $r_{12}$, according to Coulomb’s Law:

$$ F_A = -\frac{k_o Z_1 e Z_2 e}{r_{12}^2} \quad k_o = \frac{1}{4\pi\varepsilon_0} $$

The attractive bonding forces are coulombic that is positive and negative ions attract one another. $F_A$ increases as ions approach.

However bond length is never zero because $F_R$ counteracts, due to overlapping of similarly charged (-ve) electric fields from each ion, as well as an attempt to bring (+ve) nuclei together.

$$ F_R = \lambda e^{-r/\rho} $$

where $\lambda$ and $\rho$ are experimentally determined constants.

For two ions the attractive energy $E_A$ is a function of the interatomic distance:

$$ E_A = \frac{A}{r} \quad A = k_o(Z_1 e)(Z_2 e) $$

and repulsive energy $E_R$ is

$$ E_R = \frac{B}{r^n} \quad n \text{ is } \sim 8 $$

$E_N$ (net) potential energy is sum of $E_A + E_R$ or the net potential energy between 2 adjacent ions.
Calculate force of attraction \( (F_a) \) between \( \text{Ca}^{2+} \) and \( \text{O}^{2-} \) ions with their centers separated by 1.25 nm.

- Crystals such as salts and ceramics are ionically bound.
- **Non-directional**, \( \text{Na}^+ \) will attract any adjacent \( \text{Cl}^- \) equally in all 3 directions.
- Ionic bonding occurs when \( f > 0.5 \); large EN difference (far L and R columns on Periodic table.)
- **Why is melting point of \( \text{CaF}_2 \) > \( \text{CaCl}_2 \) > \( \text{CaBr}_2 \) ?**

The **lattice energy**, similar to bond energy, is the energy required to separate all of the ions (cation and anion) in a crystal to infinity. Thus, it’s a measure of the crystal’s bond strength.

- Why would \( \text{LiCl} \) \( (r_o=2.57\text{Å}) \) and \( \text{SrO} \) \( (r_o=2.58\text{Å}) \) have approximately the same interionic spacing and the same crystal structure (rocksalt), but have different lattice energies of \( E_o=9\text{eV} \) and \( E_o=33\text{eV} \), respectively?
Relationship between Melting Point & Elastic Modulus and Lattice Energy (Force)

13.3. The melting points of AB ionic crystals increase with \( \frac{z^2}{d} \).

13.4. The correlation between \( \frac{z^2}{d^4} \) and the elastic modulus, \( c_{44} \), for various AB compounds with a NaCl structure. Data from J. J. Gilman, Progress in Ceramic Science 1 (1961): 146–94.

From Materials Science – an Intermediate Text by William F. Hosford
Examples of Ionic Bonding

- Predominant bonding in **Ceramics**

To compute the total electrostatic contribution to the lattice energy, $E$, we must sum both the attractive and repulsive interactions between all of the ions of nearest neighbor distance ($r_o$):

$$E_A = -M \frac{ke^2}{r_o}$$

where $M$ is the Madelung constant, which is a relationship of the distance of the ions from one another due to a specific type of crystal. It depends on the geometric arrangement of the constituent ions in the crystal structure. “See class handout and Table 7.9 in Rohrer for values.”

For binary structures, it is common to use a reduced Madelung constant, $\alpha$:

$$\alpha = \frac{2M}{(n_1+n_2)|Z_1Z_2|}$$

where $n_1$ and $n_2$ are stoichiometry of cation and anion. For NaCl, $n_1=n_2=Z_1=Z_2=1$

The reduced Madelung constant leads to a convenient expression for the total electrostatic energy which separates the chemical parameters such as charge ($Z$), stoichiometry ($n$) and ionic distance/sizes ($r_o$) from the structural information in the Madelung constant:

$$E_A = -\frac{ke^2\alpha(n_1+n_2)Z_1Z_2}{2r_o}$$

1.25 ≤ $\alpha$ ≤ 1.76, $\alpha$ generally increases with increasing coordination number of the structure, e.g.

$\alpha_{\text{CsCl}} > \alpha_{\text{NaCl}} > \alpha_{\text{ZnS}}$.

Also, compounds with layered structures (more directional bonding), e.g. CdCl$_2$ and V$_2$O$_5$ have lower α’s which implies the electrostatic contribution to the bonding is diminished while the covalent contribution is increased. [SiF$_4$: $\alpha=1.25$ since low CN & covalent.]

We still need to include the repulsive energy ($E_R$) contribution, we will return to this later since we need to discuss the Lennard-Jones portion of the energy.
Example Calculation of Madelung Constant

For NaCl (Rocksalt crystal structure):

*From Handout “Materials Science – an Intermediate Text by William F. Hosford”*