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 ($Z_i$) and decreases with increasing separation, $r_{12}$, according to Coulomb’s Law:

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

• 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.

$$ F_R = \lambda e^{-r/\rho} \quad \text{where} \quad \lambda \text{ and } \rho \text{ are experimentally determined constants.} $$

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

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

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.
Ionic Bonding Model (continued)

Calculate force of attraction \( (F_A) \) between Ca\(^{2+}\) and O\(^{2-}\) ions with their centers separated by 1.25 nm

- Crystals such as salts and ceramics are ionically bound.
- Non-directional, Na\(^+\) will attract any adjacent Cl\(^-\) equally in all directions.
- Ionic bonding occurs when \( f > 0.5 \); large EN difference (far L and R columns on Periodic table.)
- Why is melting point of CaF\(_2\) > CaCl\(_2\) > 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 LiCl (\( r_o = 2.57 \text{Å} \)) and 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?
13.3. The melting points of AB ionic crystals increase with $z^2/d$.

13.4. The correlation between $z^2/d^4$ 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**

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**Give up electrons**

**Acquire electrons**

Take Ionic Bonding Model a Step Further and Apply it to Crystal Structures

• 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 ($r_o$):

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

(1)

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, $\alpha$:

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

(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:

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

(3)

• $1.25 \leq \alpha \leq 1.76$, $\alpha$ 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 $\alpha$’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.]

$\Rightarrow$ 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):

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