BSc 1st Semester NEP-2020 based Syllabus
Chemistry Unit III (Unit III: Chemical bonding I (ionic interaction))

Contents: General characteristics of ionic compounds; lattice and solvation energy; Born Lande equation; Kapustinski equation, Madelung constant, Born Haber cycle for lattice energy calculation

Introduction:

In chemistry, an ionic compound is a chemical compound composed of ions held together by electrostatic forces termed ionic bonding. The compound is neutral overall, but consists of positively charged ions called cations and negatively charged ions called anions. Individual ions within an ionic compound usually have multiple nearest neighbours, so are not considered to be part of molecules, but instead part of a continuous three - dimensional network, usually in a crystalline structure.

General Property:

1. Ionic compounds have high melting points and high boiling points. High temperatures are required to overcome the attraction between the positive and negative ions in ionic compounds. Therefore, a lot of energy is required to melt ionic compounds or cause them to boil.
2. They have higher enthalpies of fusion and vaporization than molecular compounds.
3. They are hard and brittle. Ionic crystals are hard because the positive and negative ions are strongly attracted to each other and difficult to separate, however, when pressure is applied to ionic crystal then ions of like charge may be forced closer to each other. The electrostatic repulsion can be enough to split the crystal, which is why ionic solids also are brittle.
4. They conduct electricity when they are dissolved in water. When ionic compounds are dissolved in water, the dissociated ions are free to conduct electric charge through the solution. Molten ionic compounds (molten salts) also conduct electricity.
5. They are good insulators. Although they conduct in molten form or in aqueous solution, ionic solids do not conduct electricity very well because the ions are bound so tightly to each other.
6. Ionic compounds form crystal structure.

Lattice Energy (U):

The lattice energy of a crystalline solid is a measure of the energy released when 1 mole of the crystalline substance is formed from the free gaseous ions. This is also the energy required to split 1 mole of the crystalline substance into the free gaseous ions. It is a measure of the cohesive forces that bind ions. Lattice energy is relevant to many practical properties including solubility, hardness, and volatility.

$$MX(s) = M^+(g) + X^-(g)$$

The lattice enthalpy is equal to the lattice energy at $T = 0$; at normal temperatures they differ by only a few kilojoules per mole, and the difference is normally neglected.

Calculation of Lattice Energy:

Born-Lande Equation:

First, consider a simple one-dimensional model of a solid consisting of a long line of uniformly spaced alternating cations and anions, with r the distance between their centres. If the charge numbers of the ions have the values Z_+ and Z_- (+1 and −1, for NaCl, or +2 and −1, for $CaCl_2$). The potential energy of attraction between the cation and anion is given by

$$E_{coul} = \frac{z_+ z_- e^2}{4\pi\varepsilon_0 r^2} \qquad (1)$$

There are also repulsions arising from the overlap of the atomic orbitals of the ions and the role of the Pauli principle. These repulsions are taken into account by supposing that, because wavefunctions decay exponentially with distance at large distances from the nucleus, and repulsive interactions depend on the overlap of orbitals, the repulsive contribution to the potential energy has the form

$$E_{rep} = \frac{B}{r^n} \qquad (2)$$

Here B is Born exponent and n is constant for a particular type of crystal.

Total Lattice energy

$$U = E_{coul} + E_{rep}$$

$$U = \frac{z_+ z_- e^2}{4\pi\varepsilon_0 r^2} + \frac{B}{r^n} \text{ ---------------(3)}$$

At $r = r_o$,

$$\frac{dU}{dr} = 0$$

$$\frac{dU}{dr} = \frac{d}{dr}\left(\frac{z_+ z_- e^2}{4\pi\varepsilon_0 r_0} + \frac{B}{r_0{}^n}\right) = 0$$

$$\Rightarrow - \frac{z_+ z_- e^2}{4\pi\varepsilon_0 r_0{}^2} - \frac{nB}{r_0{}^{n+1}} = 0$$

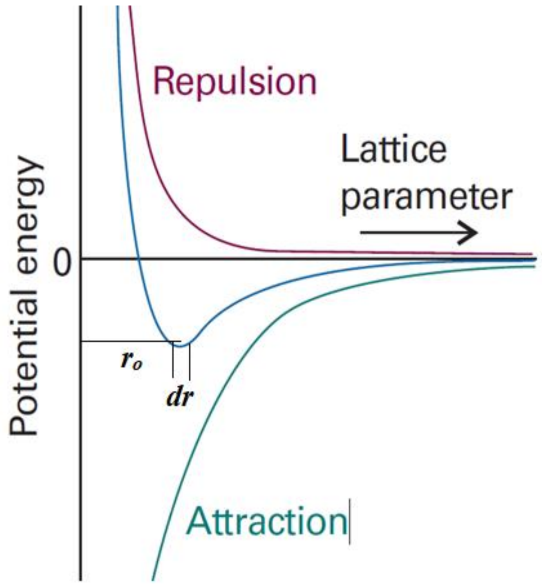
$$\Rightarrow \frac{nB}{r_0{}^{n+1}} = - \frac{z_+ z_- e^2}{4\pi\varepsilon_0 r_0{}^2}$$

$$\Rightarrow nB = - \frac{z_+ z_- e^2 r_0{}^{n+1}}{4\pi\varepsilon_0 r_0{}^2}$$

$$\Rightarrow B = - \frac{z_+ z_- e^2 r_0{}^{n-1}}{4\pi\varepsilon_0 n}$$

Substituting value of B on equation (3),

$$U_o = \frac{z_+ z_- e^2}{4\pi\varepsilon_0 r_0} - \frac{z_+ z_- e^2 r_0{}^{n-1}}{4\pi\varepsilon_0 n r_0{}^n}$$



The contributions to the total potential energy of an ionic crystal.

$$U_o = \frac{z_+ z_- e^2}{4\pi\varepsilon_0 r_0} - \frac{z_+ z_- e^2}{4\pi\varepsilon_0 n r_0}$$

$$U_o = \frac{z_+ z_- e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right) \qquad (4)$$

Equation 4 gives the energy considering only one pair of ions in the crystal. To consider the interaction between the neighbouring ion with similar charges, a parameter called Madelung's constant A is introduced to the above equation. So the equation 4 becomes

$$U_o = \frac{A z_+ z_- e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right) \qquad (5)$$

For 1 mole of crystal,

$$U_o = \frac{A N_A z_+ z_- e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right) \qquad (6)$$

Equation 6 is called Born Lande equation.

Kapustinskii equation

$$U_o = \frac{n z_+ z_- e^2}{d_0}\left(1 - \frac{d}{d_0}\right)K \qquad (7)$$

where $K = 1.20200\times10^{-4}$ J·m·mol^{-1}

$d = 3.45\times10^{-11}$ m

do = radius of cation + radius of anion

n is the number of ions in the empirical formula,