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CHEMICAL BONDING

Ionic Bond:

- It is formed by the complete transference of one or more electrons from the outermost energy shell (Valency shell) of one atom to the outermost energy shell of the other atom.
- The electrostatic attraction between the oppositely charged ions is called the ionic bond.

Characteristics of Ionic compounds:

- Low conductivity in solid state but good conductivity in the molten state
- High melting and boiling points.
- Ionic compounds are hard and brittle: The hard nature is due to the extraordinary stability of the ionic lattice. Brittleness is due to the fact that a slight relative displacement of the ionic layers by the application of a sufficiently high force greatly reduces the stability.
- Soluble in polar solvents with high dielectric constants:

Two charges q_1 and q_2 interact with potential energy which is directly proportional to the product of charges and inversely proportional to the distance of separation and the dielectric constant. $E = \frac{q_1 q_2}{4\pi\epsilon r}$ where r is the distance between separation of the ions and is the permittivity $\epsilon = \epsilon_r \epsilon_0$ where E_0 is the permittivity of vacuum and ϵ_r is the relative permittivity or dielectric constant of the medium. For a large value of ϵ_r i.e. a polar solvent, the interaction energy is lowered and the lattice loses its stability and the crystal breaks up and dissolves.

- Ionic bonds are non-directional in nature.

Factor influencing the formation of Ionic bond:

- Ionisation energy:** It is defined as the amount of energy required to remove the most loosely bound electron from an isolated gaseous atom of an element. The lesser the Ionisation energy, the greater is the ease of the formation of a cation, the more stable the ionic compound will be.
- Electron Affinity:** It is defined as the amount of energy released when an electron is added to an isolated gaseous atom of an element. The higher the energy released during this process, the easier will be the formation of an anion.
- Lattice Energy:** It is defined as the amount of energy released when cations and Anions are brought from infinity to their respective equilibrium sites in the crystal lattice to form one mole of the ionic compound. The higher magnitude of the lattice energy, the greater is the tendency of the formation of an ionic bond.

Lattice energy is always positive.

- The formation of a mole of an ionic solid from the constituent gaseous ions may be represented as under:

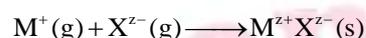
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$M^+(g) + X^-(g) \xrightarrow{-u} M^+X^-(s)$; u = lattice energy. Lattice energies can not be measured directly, but experimental values are obtained from thermodynamic data using the Born-Haber Cycle.

- It is obvious that the greater the magnitude of lattice energy of an ionic solid the greater would be its stability.
- The lattice energies of ionic solids are quite high. This is on account of strong electrostatic attraction between oppositely charged ions present in the solid. Since coulombic forces of attraction vary directly as the product of charges the higher the valency of the ions, the greater would be the lattice energy of the ionic solid. Thus, lattice energy increases as we move from uni-univalent ionic solids to uni-bivalent ionic solids and then to bi-bivalent ionic solids.

Born-Lande equations.

- The lattice energy of ionic solids can be calculated theoretically on the basis of coulombic interactions between the ions present in the crystals. Such a theoretical treatment was initiated by Born and Lande. The derivation is as follows.



- Consider the electrostatic energy of an ion pair $M^{Z+}X^{z-}$:-

$E = Z^+z^-e^2$ where, $e = 1.6 \times 10^{-19}$ coloumb, r is the distance separating the ions and ϵ_0 , the permittivity of vaccum.

- In a crystal lattice there will be a large number of interactions of the above type. To take into account these interactions, a constant called Madelung Constant is taken. The values for the Madelung constant have been calculated for all common crystal structures, by summing the contributions of all the ions in the crystal lattice. The value of the Madelung constant depends only on the geometry of the lattice. It is independent of the ionic radius and charge.
- Thus the attractive energy per mole is given by $E_c = A N_0 z^+ z^- e^2$ which is negative since Z^+ and Z^- have opposite signs. Here N_0 = Avogadro no. Thus unless there is a repulsion energy to balance the attractive coulombic energy there can be no stable lattice. Repulsion at close ranges of ions is to be expected since ions are not point charges but possess electron clouds which repel each other when the inter atomic distance becomes very small.
- Born suggested a repulsive energy term of the form B/r^n , where B is a constant that depends on the structure, and exponent n is a constant called the "Born Exponent", which may be determined from compressibility data.
- Thus the total energy per mole of the lattice is

$$U = E_c + E_R = \frac{A N_0 z^+ z^- e^2}{4\pi\epsilon_0 r} + \frac{N_0 B}{r^n} \quad (1)$$

- Attractive force (E_c) repulsive force (E_R)

This total lattice energy is shown below

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The equilibrium distance between ions is determined by the balance between the attractive and repulsive terms. At equilibrium, $\frac{dU}{dr} = 0$ and the equilibrium distance $r = r_0$.

➤ So, $\left. \frac{dU}{dr} \right|_{r=r_0} = \frac{-N_0 A Z^+ Z^- e^2}{4\pi E_0 r_0^2} - \frac{n N_0 B}{r_0^{n+1}} = 0$

➤ Rearranging this, we get, $B = \frac{-AZ^+Z^-e^2r_0^{n-1}}{4\pi E_0 n}$

Substituting this in equation 1:-

(i) We get $U_{\min} = \frac{AN_0Z^+Z^-e^2}{4\pi E_0 Y_0} - \frac{AN_0Z^+Z^-e^2}{4\pi E_0 Y_0 n}$

$$U_{\min} = \frac{AN_0Z^+Z^-e^2}{4\pi E_0 Y_0} \left(1 - \frac{1}{n}\right)$$

- Calculation of lattice energy on the basis of this equation needs only a knowledge of the geometry of the crystal for ascertaining the value of a and the inter-atomic distance (Y_0); both of which are available from x-ray diffraction studies.
- The “Born exponent”; n depends on the type of the ion involved, larger ions with higher electron densities requiring larger values of n .
- The Born equation leads to the following conclusions:
- The higher the charge on cation and anion, the greater would be the magnitude of lattice energy and there for the greater would be the stability of the crystal.
 - Since the lattice energy is inversely proportional to the interionic distance which is taken as the sum of the radii of the cation and the anion hence the smaller the size of the ions, the smaller would be the inter ionic distance, the higher would be the magnitude of lattice energy and the greater would be the stability of the ionic crystal.
 - The lattice energy and hence stability of an ionic crystal is directly proportional to the Madelung constant (A) which depends upon the coordination no. of each ion and the geometric pattern of the ions in the crystal lattice of the crystal.

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Applications of Lattice energy:

- Can estimate electron affinities, proton affinities, and heat of formation, further applications:
 - (i) In the discussion of the special properties of fluorine in relation to other halogens.
 - (ii) In account of stabilities of metal hydrides, polyamides and peroxides and superoxides.
 - (iii) In the derivation of CFSEs.
 - (iv) In the discussion of the characterization of high oxidation states of metal as fluorides and of their low oxidation states as iodides.

Q. Derive Born Lande equation for lattice energy of an ionic solid.

Ans. The lattice energy of an ionic solid is defined as the amount of energy released when cations and anions in their gaseous states are brought from infinity to their respective lattice sites in a crystal to form one mole of ionic solid.

- The lattice energy can't be measured directly but it can be estimated theoretically on the basis of coulombic interactions present in the crystal. Such a theoretical treatment was initiated by Born and Lande. The derivation follows.
- Consider formation of one mole of ionic solid from gaseous ions as
$$M^{z^+}(g) + X^{z^-}(g) \rightarrow M^{z^+}X^{z^-}(s)$$
- Now the electrostatic energy of ion pair $M^{z^+}X^{z^-}$ is $E = \frac{z^+z^-e^2}{4\pi\epsilon_0r}$ where symbols have their usual meaning.
- In a crystal lattice there will be a large no. of interactions of above type. To take into account of these interactions, a constant called "Madelung constant" is taken. The value for Madelung constant (A) can be calculated for all common crystal systems by summing the contribution of all the ions present in the lattice. The value of Madelung constant depends only on the geometry of the crystal. It is independent of the ionic radius and charge.
- Thus the attractive energy per mole is given by
- $E_c = \frac{AN_0z^+z^-e^2}{4\pi\epsilon_0r}$ Which is (-) ve Since z^+ and z^- have opposite signs.
- Thus unless there is a repulsion energy to balance the attractive coulomb energy there can be no stable lattice.
- Born suggested a repulsion energy term of the form B/r^n , where B is a constant that depends on the structure, and exponent n is a constant called Born exponent, which may be calculated from compressibility data.
- Thus the total energy per mole of the lattice is

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$$U = E_c + E_R = \frac{AN_0Z^+Z^-e^2}{4\pi E_0 r} + \frac{N_0 A}{r^n} \quad \text{---(i)}$$

- The equilibrium distance E_c both the ions is determined by the balance between attractive and repulsive terms.

$$\text{At equilibrium, } \frac{du}{dr} = 0 \text{ \& } \frac{d^2U}{dr^2}$$

$$\text{At equilibrium distance, } r = r_0$$

$$\text{So, } \left. \frac{du}{dr} \right|_{r=r_0} = \frac{-N_0AZ^+Z^-e^2}{4\pi E_0 r_0^2} - \frac{nN_0B}{r_0^{n+1}} = 0$$

∴ rearranging this, we get,

$$B = \frac{-AZ^+Z^-e^2}{4\pi E_0 n} r_0^{n-1}$$

Putting value of B in equⁿ (1) we get

$$U_{\min} = \frac{AN_0Z^+Z^-e^2}{4\pi E_0 r_0} - \frac{AN_0Z^+Z^-e^2}{4\pi E_0 r_0 n}$$

$$U_{\min} = \frac{AN_0Z^+Z^-e^2}{4\pi E_0 r_0} \left(1 - \frac{1}{n} \right) \text{ Born Lande equ}^n$$

- Since Z^+ & Z^- are of opposite signs and $n > 1$ so the lattice energy will be (-) ve & so crystal will be stable.
- Calculation of lattice energy on the basis of this equations needs only a knowledge of geometry of the crystal for ascertaining the value of A and the inter atomic distance (r_0); both of which are available from x-ray diffraction studies.
- The born exponent “n” depends on the type of ion involved. The Born equation leads to the following conclusions.
- (i) The higher charge on cation & anion implies greater magnitude of lattice energy and therefore greater stability of the crystal

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(ii) Smaller the size of ions, smaller would be the interionic distance and higher would be the magnitude of lattice energy which implies more stability.

Note:

- Born exponent n is higher for larger ions which have relatively higher electron density. For ex: He-5, Ne-7, Ar-9, Kr-10, Xe-12.
- When the cation and anion have different Born exponent values, we take the average of the two.

$$\text{For } {}^n\text{NaCl} = \frac{{}^n\text{Na}^+ + {}^n\text{Cl}^-}{2} = \frac{7+9}{2} = 8$$

- If $n \ll 10$, then Madelung energy $E_c \approx 90\%$ of lattice energy. experimental values calculated lattice energy $U (E_c + E_R)$ differs by $\approx 2\%$
- Still greater accuracy can be achieved by taking into account the following factors.
 - Vander Waals forces
 - Zero-point energy
 - Correction for heat capacity

1. NaCl:

- In a crystal of NaCl, each Na^+ is surrounded by six Cl^- at a distance d , not by just one. Twelve other Na^+ are located at a distance $\sqrt{2}d$, eight other Cl^- at $\sqrt{3}d$, six more Na^+ at $2d$, 24 Cl^- at $\sqrt{5}d$, 24 Na^+ at $\sqrt{6}d$ and so on.
- Summing all terms gives the potential energy for whole lattice.

$$\begin{aligned} \text{P.E} &= \frac{-6e^2}{d} + \frac{12e^2}{\sqrt{2}d} - \frac{8e^2}{\sqrt{3}d} + \frac{6e^2}{2d} - \frac{24e^2}{\sqrt{5}d} + \frac{24e^2}{\sqrt{6}d} \\ &= \frac{-e^2}{d} \left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \frac{24}{\sqrt{5}} - \frac{24}{\sqrt{6}} \right) \end{aligned}$$

$$\text{P.E} = -\frac{e^2}{d}(1.747558)$$

- So Madelung constant for NaCl = 1.747558
- For CsCl this value, $A = 1.76267$

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