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B. Ionic Bonding

Ionic Bond

Def - The bond formed by transfer of electron from one atom to another atom is called as ionic bond.

- The atom from which the electrons are transfered carries +ve charge and atom which gains electrons carries -ve charge.
- The atom which carries +ve charge is called as electropositive atom while the atom which carries -ve charge is called as electronegative atom. Therefore another defination of ionic bond is
- The bond formed between electropositive atom and electronegative atom is called as ionic bond.

eg formation of sodium chloride molecule.

$$\underset{(2,8,1)}{Na} + \underset{(2,8,7)}{Cl} \longrightarrow \underset{(2,8)}{[Na^+]}\underset{(2,8,8)}{[Cl^-]} \text{ OR } Na^+ - Cl^- \rightarrow NaCl$$

- Thus, there exists an electrostatic force of attraction between positive charge sodium ion and negative charge chloride ion in NaCl molecule.
- The formation of an ionic bond is favoured when metal has low ionisation energy and other element has high electron affinity forms a ionic compound with high lattice energy.

Types of cations

The formation of an ionic compound is obtained by attaining inert gas configuration by an anion while the cation is achived by any one of the following configuration.

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(ii) Ion with inert gas configuration:
The ions having inert gas configuration (ns^2np^6) in their outermost shell. (except - n=1)

He ($1s^2$) ⟶ Li^+
Ne ($2s^22p^6$) ⟶ Na^+, Mg^{2+}, Al^{3+}
Ar ($3s^23p^6$) ⟶ K^+, Ca^{2+}, Sc^{3+}, Ti^{4+}
Kr ($4s^24p^6$) ⟶ Rb^+, Sr^{2+}, Y^{3+}, Zr^{4+}
Xe ($5s^25p^6$) ⟶ Cs^+, Ba^{2+}, La^{3+}, Ce^{4+}
Rn ($6s^2 6p^6$) ⟶ Fr^+, Ra^{2+}, Ac^{3+}, Th^{4+}

(iii) Ions with pseudo ~~inter~~ inner gas configuration ($ns^2np^6nd^{10}$)
$4s^2, 4p^6, 4d^{10}$ ⟶ Ag^+, Cd^{2+}, In^{3+}, Sn^{4+}
$5s^2$ $5p^6$ $5d^{10}$ ⟶ Au^+, Hg^{2+}, Ti^{3+}, Pb^{4+}

(iv) The inert s^2 pair configuration
$(n-1)s^2p^6d^{10}ns^2$
when the elements having valence shell configuration ns^2np^x ($x = 1, 2, 3$), lose their p electron only, then cation with ns^2 configuration are formed.
for $4s^2$ ⟶ Ga^+, Ge^{2+}, As^{3+}
for $5s^2$ ⟶ In^+, Sn^{2+}, Sb^{3+}
for $6s^2$ ⟶ ~~Tl~~ Pb^{2+}, Bi^{3+}

(v) The d & f ions:
The transition metal ions are formed by the loss of d-electrons
eg Ti^{2+}, V^{2+}, Cr^{2+}

(vi) Ion with Irregular configuration:
These ions can not be ~~cannot~~ classifed into any particular class.
eg Ga^{4+} (Ga^{2+} – Ga^{2+})

Energetics of Ionic Bond formation:

The energies involved in the formation of ionic bond are

(a) Ionisation energy
(b) Electron affinity and
(c) Lattice energy.

(a) Ionisation Energy:

- It is related to formation of cation

Def - The minimum amount of energy required to remove the electron from last orbit from isolated gaseous atom of an element to form cation is called as ionisation energy.

$$M_{(g)} \longrightarrow M^{+}_{(g)} + e^{-} \qquad \Delta H = +I$$

where I is energy

→ +ve sign indicate that energy is supplied.

→ It is measured in eV or Kcal/mole

→ and energy requried in this process is called as first ionisation energy.

→ The energy requried to remove one electron from +ve charged ion to form dipositive ion is called as second ionisation energy and so on...

→ The magnitude of ionisation energy measure cation formation

- If ionisation energy is low, then cation is readily formed eg Alkali and Alkaline earth metals

(b) Electron affinity

- It is related to formation of anion.
- The amount of energy released when an electron is added to the isolated gaseous atom to form an anion is called as electron affinity.

$$X_{(g)} + e^{-} \longrightarrow X^{-}_{(g)} \; ; \; \Delta H = -E$$

where E is energy

-ve sign indicate that energy is released.

→ It is measured in eV or kcal/mole.
→ simillar to ionisation potential, there is also first, second, third… electron affinity.
→ The magnitude of electron affinity measures anion formation.

(c) Lattice Energy:

- It is related to formation of ionic compound from its ions.
- Lattice energy of an ionic crystal is defined in two ways.

(i) The energy relased when exact number of gaseous cation $M^+_{(g)}$ and gaseous anion $X^-_{(g)}$ come close tougather from infinity to form one mole of ionic solid crystal $M^+X^-_{(s)}$ is called as Lattice energy.

$$M^+_{(g)} + X^-_{(g)} \longrightarrow M^+X^- + \text{Energy Released.}$$

(ii) The energy requried for removing ions of one mole of ionic solid from their equilibrium positions to infinity is called as lattice energy.

$$M^+X^-_{(s)} + \text{Energy supplied} \longrightarrow M^+_{(g)} + X^-_{(g)}$$

- It is represented by U
- It measure stability of ionic solid.
- If value of lattice energy is high, ~~that means~~ then ionic crystal is stable and more energy is requried to seperate ions from its ionic crystal.

Factors affecting the formation of Ionic Bond

The formation of ionic compound favoured if

Sequence Low High High

(i) The ionisation energy of element M is low
(ii) Electron affinity of X is high.
(iii) Lattice energy of compound MX is high

electrostatic forces

Calculation of Lattice Energy

Lattice energy may be calculated theoretically by using Madelung constant. or it may be determined experimentally by using Born-Haber cycle.

① Theoretical calculation of Lattice energy by using Madelung constant.

Lattice energy can be theoretically calculated using Born-Lande equation

$$U = \frac{e^2 z^+ z^- - N_A \left(1 - \frac{1}{n}\right)}{r}$$

Where, $e \rightarrow$ charge on electron

$z^+ z^- \rightarrow$ charge on cation and anion resp.

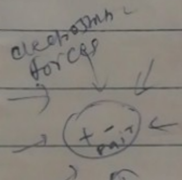
$N_A \rightarrow$ Avogadro's No. (6.023×10^{23})

$r \rightarrow$ Dist. between nuclei of cation and anion in centimeters.

$n \rightarrow$ Born Exponent.

$U \rightarrow$ Lattice energy of the ionic compound.

Madelung constant



- It is a correction factor.
- It considered the electrostatic forces exerted by neighbouring ions on ion pair.
- It depends upon the arrangment of +ive and -ive ions in the crystal ie geometry of crystal.
- It does not depend upon nature of ions present in the crystal.

eg.

crystal type	Madelung const
sodium chloride (NaCl)	1.747558
Caesium chloride (CsCl)	1.762670
fluoride (CaF_2)	5.03878
Rutile (TiO_2)	4.816.

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Born exponent (n)

- It is repultion exponent.
- It measure repulsive forces between the electron clouds of oppositely charged ions.

Experimental Determination of Lattice energy using Born-Haber cycle

- The lattice energy of an ionic solid is determined by using Born-Haber cycle.
- It is thermochemical cycle.

Calculation of Lattice Energy of sodium chloride by using Born-Haber cycle.

Method - I :

It is the direct combination of solid sodium and gaseous chlorine to give solid sodium chloride.

$$Na_{(s)} + \frac{1}{2} Cl_{2(g)} \longrightarrow Na^{+}Cl^{-}_{(s)} \qquad \Delta H_f = -414.2 \text{ kJ mol}^{-1}$$

-ve sign indicate that, Heat is given out and this energy is called as heat of formation of sodium chloride in (ΔH_f).

Method - 2

It involves five different steps.

Step - I -

Sublimation of sodium :

- In this process, one mole of solid sodium ($Na_{(s)}$) changes to gaseous sodium $Na_{(g)}$.
- The energy is required for this process is S_{Na} (Heat of sublimation of sodium) = 108.7 kJ mol^{-1}

$$Na_{(s)} \longrightarrow Na_{(g)} \; ; \; S_{Na} = 108.7 \text{ kJ/mol}^{-1}$$

Step-II - Dissociation of chlorine.

- In this process, half mole of chlorine is dissociated into 1 mole of chlorine atom.
- The energy is required for this process is $\frac{1}{2}D_{Cl_2}$ (Where D_{Cl_2} is the heat of dissociation of one mole of chlorine) = 112.95 kJ.

$$\frac{1}{2}Cl_{2(g)} \longrightarrow Cl_{(g)}, \quad \frac{1}{2}D_{Cl_2} = 112.95 \text{ kJmol}^{-1}$$

Step-III

Formation of sodium ions:

- In this process, 1 mole of gaseous sodium atoms are converted into sodium ions by loss of e^-.
- The energy is required for this process is I_{Na} (Ionisation energy of sodium) = 489.5 kJmol^{-1}

$$Na_{(g)} \longrightarrow Na^+_{(g)} + e^- \quad I_{Na} = 489.5 \text{ kJmol}^{-1}$$

Step-IV

Formation of chloride ions:

- In this process, 1 mole of chlorine atoms which is formed in step 2, take up electrons given by sodium and converted into negatively charge chloride ions.
- In this process energy is released which is called as electron affinity is 351.4 kJmol^{-1}

$$Cl_{(g)} + e^- \longrightarrow Cl^-_{(g)} \quad E_{Cl} = -351 \text{ kJmol}^{-1}$$

Step-V

Formation of Ionic crystal NaCl

- In this process, gaseous sodium ions and chloride ions formed in step (3) and (4) combine tougheter to give crystals of sodium chloride
- In this process, energy is given out, called as Lattice energy of NaCl.
- It is denoted by U_{NaCl}
- Its value is determined from other values

$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow Na^+Cl^-$ $\quad U_{NaCl} = ?$

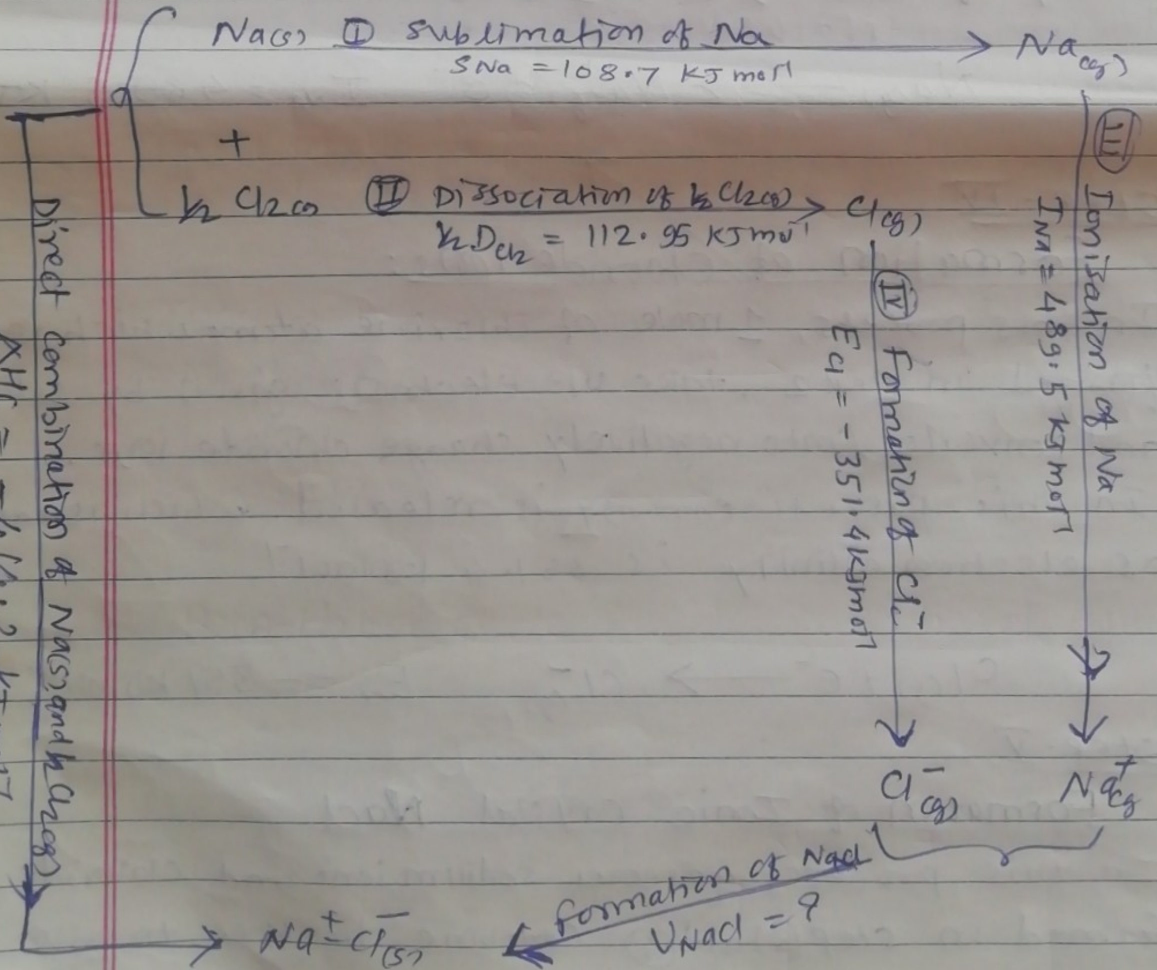
According to Hess's law,
The energy change in method ① must be equal to total energy changes of all steps in method ② ie,

$$\Delta H_f = S_{Na} + \frac{1}{2} D_{Cl_2} + I_{Na} + E_{Cl} + U_{NaCl}$$

$$-414.2 = +108.7 + \left(\frac{1}{2} \times 225.9\right) + 489.5 - 351.4 + U_{NaCl}$$

$$\therefore U_{NaCl} = -414.2 - 108.7 - 112.95 - 489.5 + 351.4$$
$$= -773.95 \text{ kJ mol}^{-1}$$

It is represented as



Numericals

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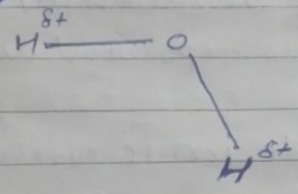
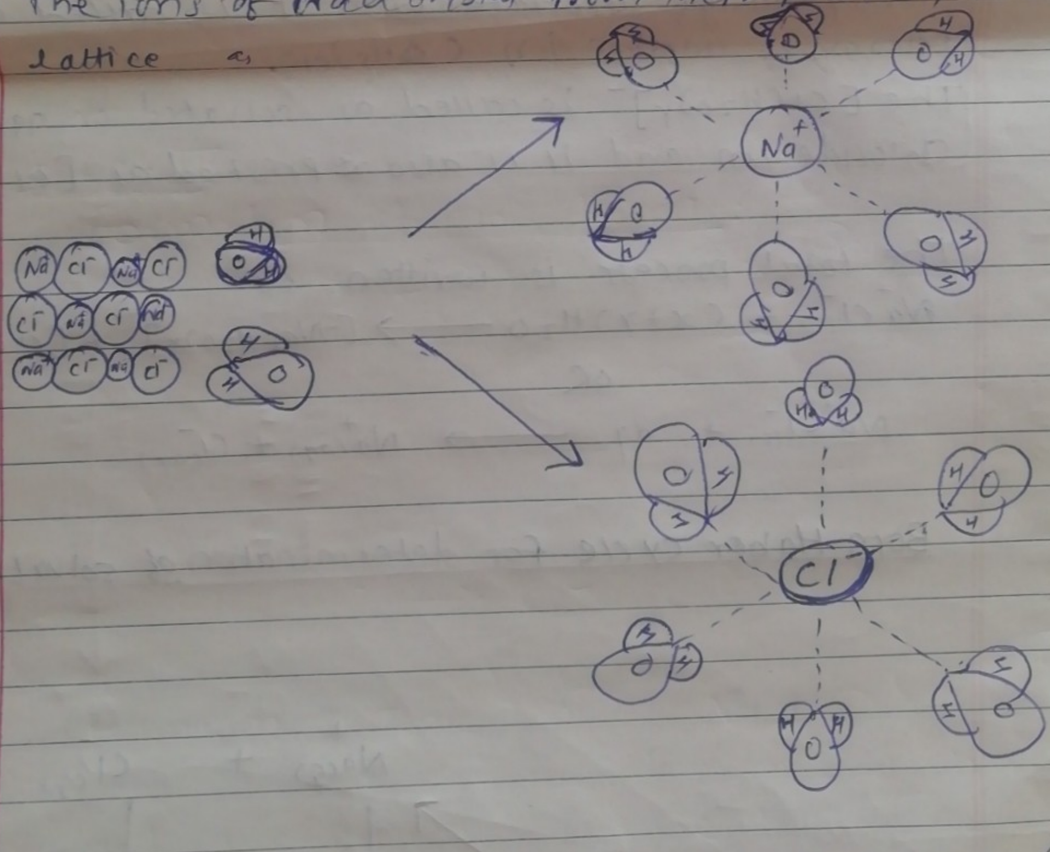
Solvation of Ion and solvation Energy

When solute is added into the solvent then intraction takes Place. This process is called as solvation. and and energy changes with this process is called as solvation energy.

eg when NaCl (ionic solute) is added into water. er is polar solvent



When NaCl is added into water then negative end of water molecule attract +ve ions and +ve ends attract -ve ions of NaCl crystal. These attractive forces weaken the attraction in the Na-Cl crystal and pull some of the ions of NaCl crystal from their possition in crystal lattice as



once the Na^+ and Cl^- ions are broken away from crystal lattice then Following two processes are taking place simultaneously.

(1) Each sodium ion is surrounded by definite but unknown number of water molecules say x with

their -ve ends (oxygen end).

$$Na^+ + x \cdot H_2O \longrightarrow [Na(H_2O)_x]^+$$

This process is called as solvation of sodium ion and ~~and~~ energy change associated with it is called as solvation energy of sodium ion $(\Delta H_s)_{Na^+}$.
The $[Na(H_2O)_x]^+$ is called as solvated or aquated sodium ion and it is also represted as $[Na(aq)]^+$.

(ii) Each chloride ion is surrounded by definite but unknown number of water molecules say 'Y' with their +ve ends (Hydrogen end).

$$Cl^- + Y \cdot H_2O \longrightarrow [Cl(H_2O)_Y]^-$$

this process is called as solvation of chloride ions and energy change associated with it is called as solvation energy of chloride ion $(\Delta H_s)_{Cl^-}$.
The $[Cl(H_2O)_Y]^-$ is called as solvated or aquated chloride ion and it is also represted as $[Cl(aq)]^-$.

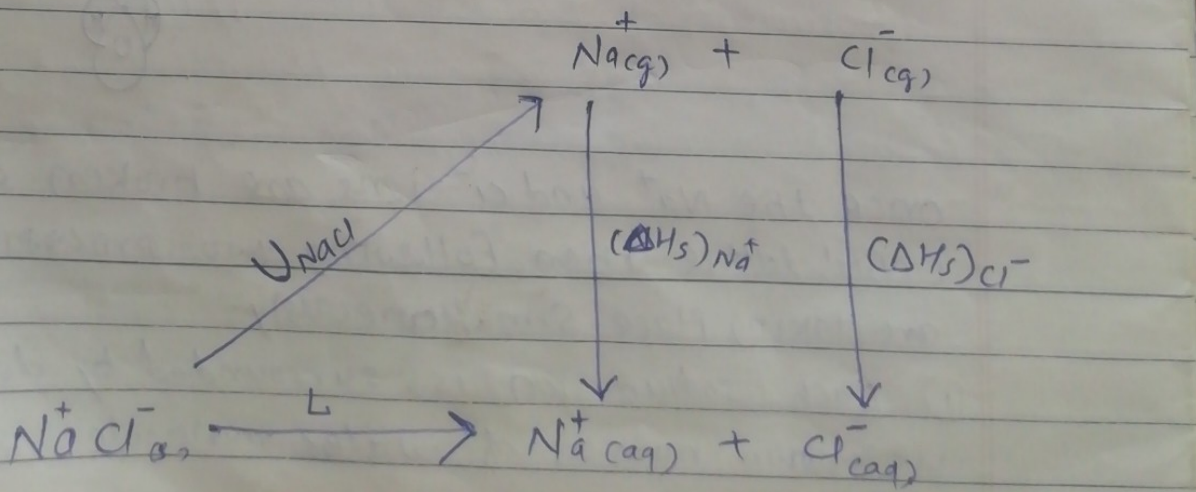
The total process is written as

$$Na^+Cl^-_{(s)} + (x+Y)H_2O \longrightarrow [Na(H_2O)x]^+ + [Cl(H_2O)_Y]^-$$

OR

$$Na^+Cl^-_{(s)} + aq \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}.$$

<u>Born-Haber cycle for determination of solvation Energy</u>



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Calculation of solvation Energy

The energy changes during solvation of Na^+ and Cl^- ions is calculated by using Bohr-Haber cycle.

$$L_1 = U_{NaCl} + (\Delta H_s)_{Na^+} + (\Delta H_s)_{Cl^-}$$

where L_1 = Heat of solution of NaCl at infinite dilution (i.e total amount of heat evolved or absorbed when one mole of sodium chloride dissolved in large excess of water that futher addition of water does not ~~change~~ produce any heat change.)

U → Lattice energy of NaCl.

$(\Delta H_s)_{Na^+}$ and $(\Delta H_s)_{Cl^-}$ are the solvation energies of Na^+ & Cl^- ions

Factors affecting solvation and solvation energy

(1) solvation energy and lattice energy :-

If solvation energy is greater than lattice energy, the dissolution [solubility] of ionic compound in polar solvent increases

(2) Dielectric constant and solvation energy :-

If dielectric const- increases then solvation energy increases and the dissolution of ionic compound in polar solvent increases.

(3) Ionic size.

with the increase in ionic size, solubility increases

(4) Ionic charge.

with the increase in ionic charge, solubility decrease

=x=

End.