

Ionic Bonding

(Chemistry-DSC-1002A: Inorganic & Organic Chemistry)

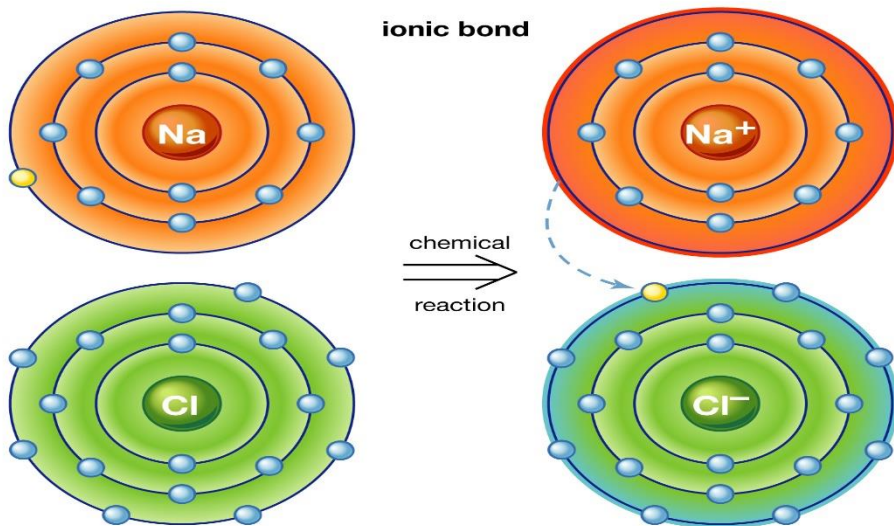
BY

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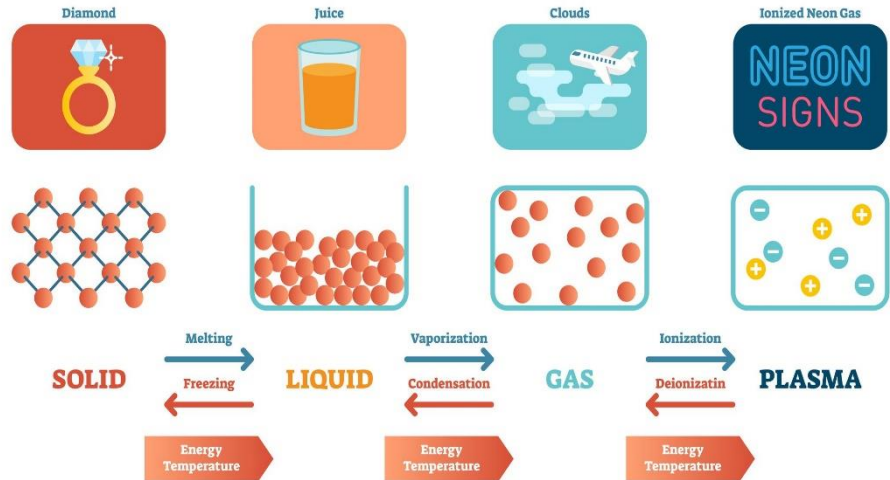
- ❑ Definition and formation of ionic bond. General characteristics of ionic bonding
- ❑ Energetic in Ionic bond formation
- ❑ Born-Haber cycle for NaCl and its applications.
- ❑ Polarizing power and polarizability.
- ❑ Fajan's Rule.
- ❑ Ionic character in covalent compounds.
- ❑ Bond moment, dipole moment and percentage ionic character.

General Introduction

- Matter appears mainly in three forms solid, liquid and gas
- *Other states:* plasma, Bose-Einstein condensates

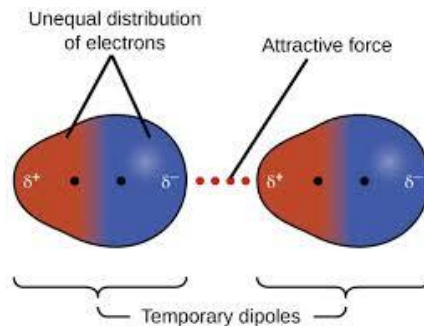
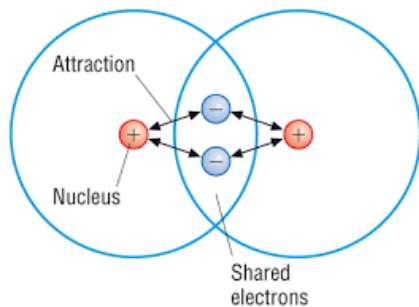
States of Matter

Everything that takes up space and has mass *is* Matter.



- It is formed by the bonds between atoms, ions and molecules.
- To attain stability atoms combine & forms bonds.

- *Chemical Bond: Attractive or binding forces between chemical species such as atoms, ions or molecules.*
- *The forces responsible for the formation of bond are of electric origin & arise due to redistributions of e^- in atoms.*



- *In 1916, Kossel, Lewis & Langmuir succeeded independently in formulating acceptable theory of bonding based on electronic conception of an atom. i.e. Electronic Theory of Valency or Octet Theory.*

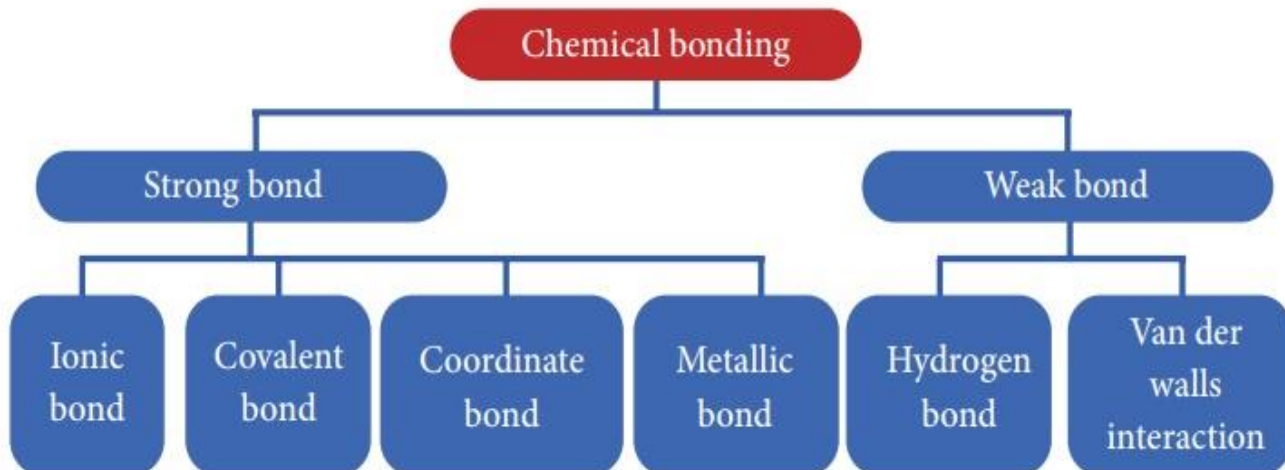
❑ *Octet Theory or Electronic Theory of Valency:*

The tendency or urge of an atom to complete its octet or duplet, either by gaining, losing or sharing of electrons in its valence shell is the real cause of chemical combination.

❑ *To satisfy this urge atoms combine and forms matter.*



Types of Chemical Bonds



Ionic Bond

- ❑ *Introduced by Kossel in 1916*
- ❑ *Also called as Electrovalent bond*
- ❑ *The electrostatic forces of attraction between oppositely charged ions is called as Ionic bond.*
- ❑ *The algebraic sum of +ve and -ve charges in a comp. must be zero.*
- ❑ *e.g. Formation of ionic bond*

According to Kossel, Lewis & Langmuir formation of ionic bond can be described as,

i) Formation of cation:

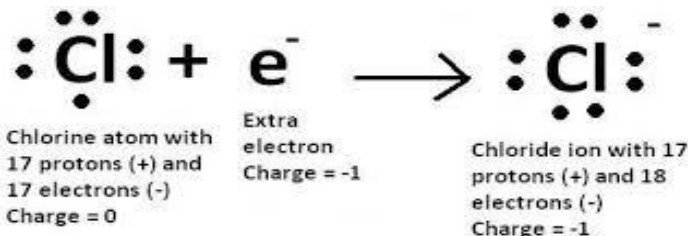
The atom of electropositive elements loses one or more electrons from its valence shell & forms cation with stable E.C. nearest noble element.



First ionisation energy of sodium = _____ kJmol^{-1}

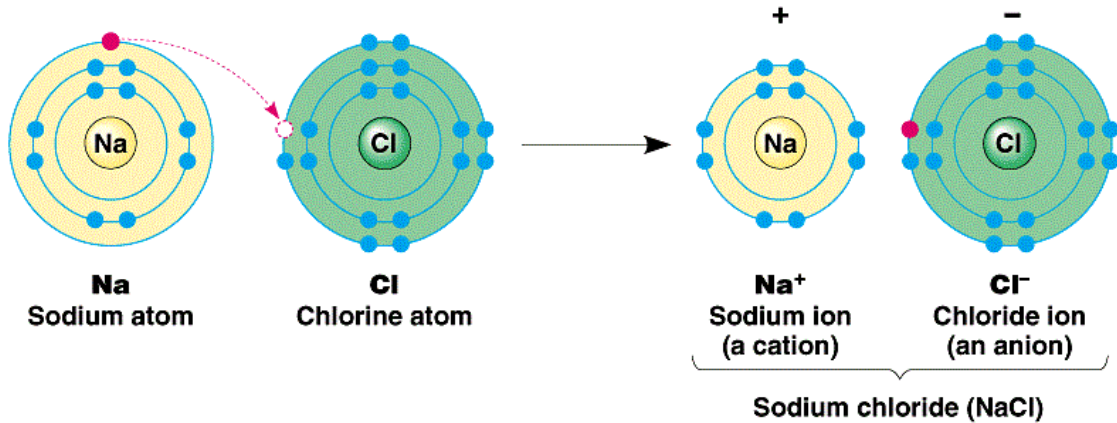
The energy required to loose electron called Ionization energy.

ii) Formation of Anion: Atom of electronegative element gains one or more electrons from electropositive element and forms anion having E. C. of nearest noble gas.

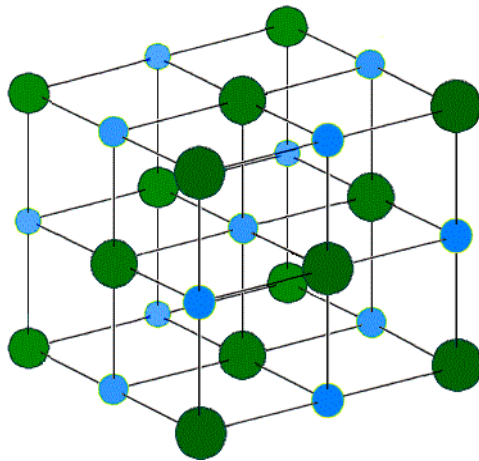


- During this process energy is given out to the system is called as *Electron affinity.*
- The process of formation of Cation and anion is simultaneous & it involves transfer of electrons

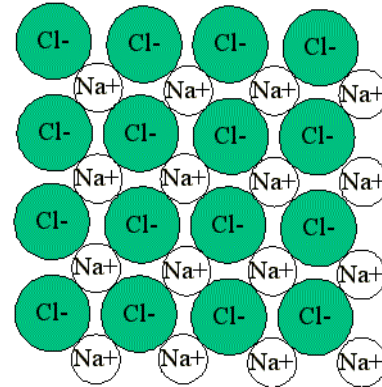
iii) Union of Cation and Anion: Formed cation and anion are held together by strong electrostatic coulombic forces of attraction



- ❑ *As electrostatic field of charged particle is in all direction, the above process will not stop at this stage.*
- ❑ *Ion pairs attracts other ion pairs and forms three dimensional macromolecular structure.*



Slice through a NaCl crystal



□ *Here force of repulsion operates between two like signed ions but as their (like signed ions) interionic distance is relatively larger than oppositely charged ions, the force of attraction is larger than forces of repulsion.*

□ *Forces of attraction increases with addition of each new pair.*

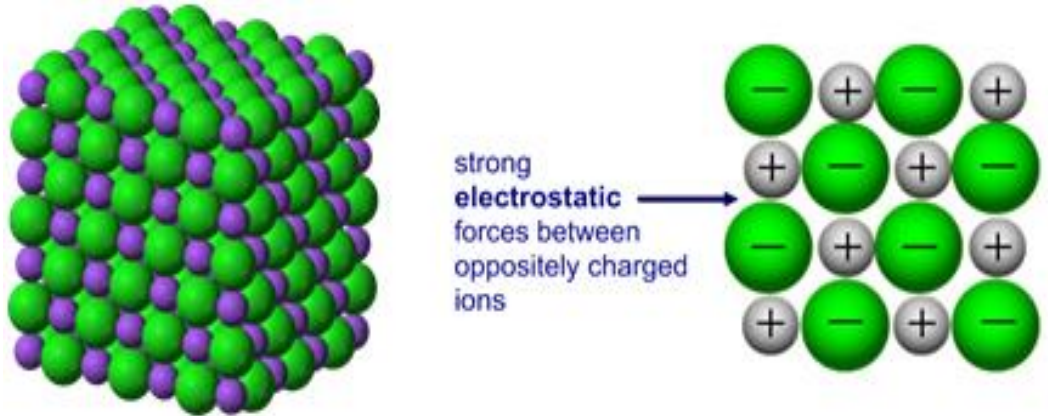
□ *Therefore, P.E. decreases and stability increases due to clustering of ions.*

- ❑ *The limit of size of crystal is set only by its geometry.*
- ❑ *The energy released during this process is called as Lattice Energy.*
- ❑ *Ionic solid is a cluster of ions in which positively charged ions are surrounded by number of negatively charged ions and vice-versa.*
- ❑ *From above discussion it is cleared that formation of ionic compound is related to ease of formation of cation and anion.*

General Characteristics of Ionic Solid

❑ **Structure:** X-ray diffraction shows that constituent units are ions not molecules. The oppositely charged ions are held together by strong electrostatic forces, which are non-directional.

Therefore ionic compounds are hard, brittle due to strong forces of attraction.



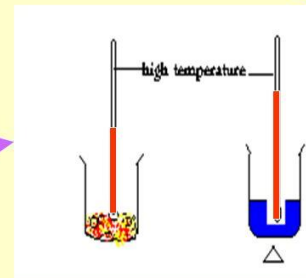
❑ **Ionic comp.** are crystalline, due to orderly arrangement of ions in them.

- ❑ **M.P & B. P. :** High due to strong forces of attraction between oppositely charged ions.

MELTING AND BOILING POINT

Melting point and boiling point in ionic compound are very high

Example: NaCl
Melting point: 801°C
Boiling point: 1413°C



- ❑ **Electrical Conductivity:** Solid ionic compounds do not conduct electricity because their constituents ions are fixed in their positions

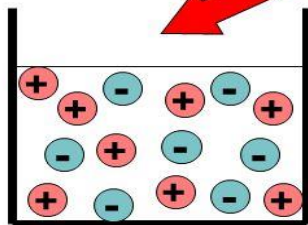
Defective crystals conduct electricity to an insignificant extent.

But when **ionic comp. melted or dissolved** in water, they conduct electricity, because ions becomes free in solution.

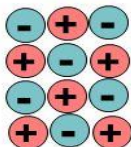
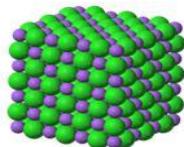
As ionic compounds are made of CHARGED IONS, they can CONDUCT ELECTRICITY but ONLY if the ions can MOVE.

If it is MOLTEN
the ions can
move

MELT

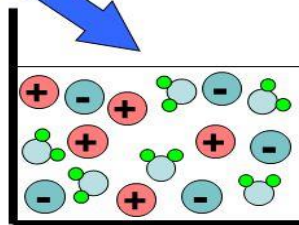


800°C



If it is DISSOLVED
the ions can move

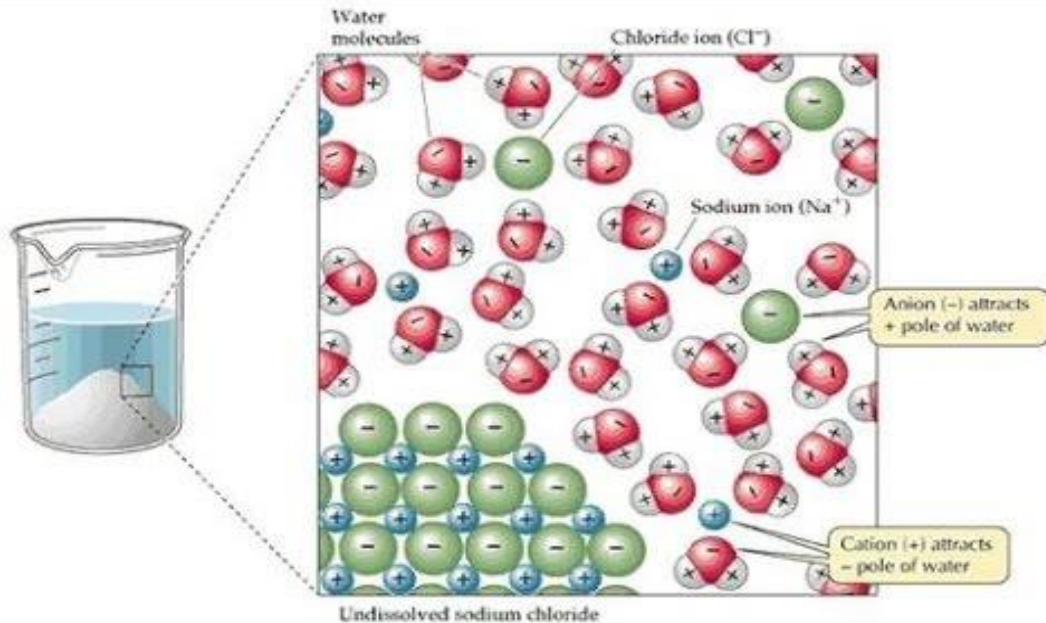
DISSOLVE



20°C



- ❑ **Ionic Reactions:** Reactions are due to its constituent ions & therefore usually they are fast.
- ❑ **Solubility:** Soluble in polar solvents like water.
Insoluble in non-polar solvents like benzene.



Energetics in Ionic Bond Formation

(Factors governing the formation of an Ionic bond)

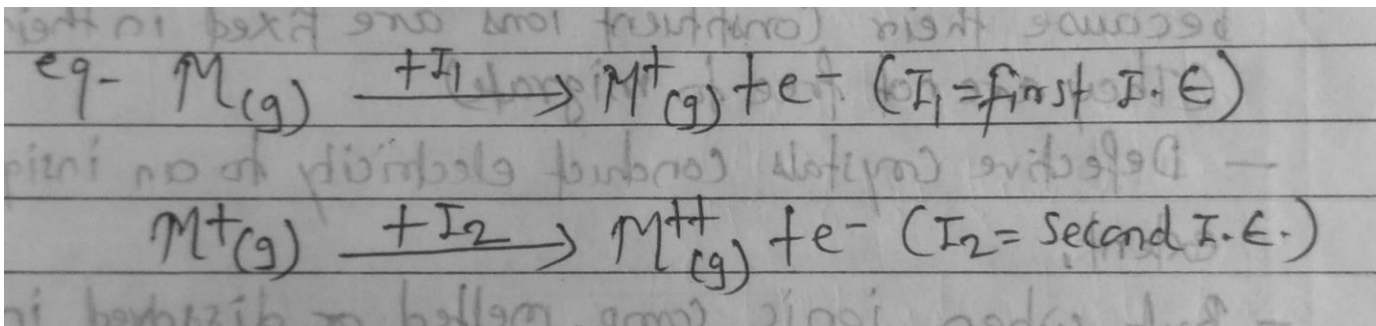
The ionic bond formation depends on

- Ease of formation of cation from electropositive atom or I.E. of atom.*
- Ease of formation of an anion from electronegative atom or **electron affinity** of an atom*
- The ease of combination of appropriately number of oppositely charged ions of resulting ionic solid (**Lattice Energy**)*

❑ **Ionization Energy (I):** *The amt of energy required to remove an e- completely from an isolated gaseous atom is known as ___*

✓ *Also called as Ionization potential or enthalpy.*

✓ *It is always positive*



✓ *I.E. depend on At. Size, effective nuclear charge, screening effect.*

✓ *If I.E. is very low, cation will form easily.*

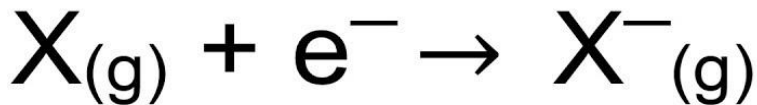
✓ *Alkali metals have low I.E., can readily loose e- from their valence shell.*

2. *Electron affinity (E):*

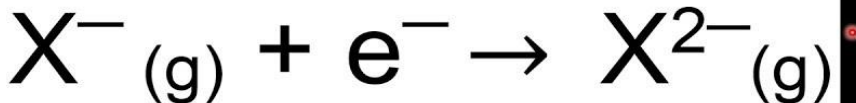
- *It is defined as the amount of energy released when an electron is added to an isolated gaseous atom of an element.*
- *The higher the energy released during this process, the easier will be the formation of an anion.*

Electron affinity

The first electron affinity is the energy released when one mole of electrons is added to one mole of gaseous atoms to form one mole of 1^- ions.



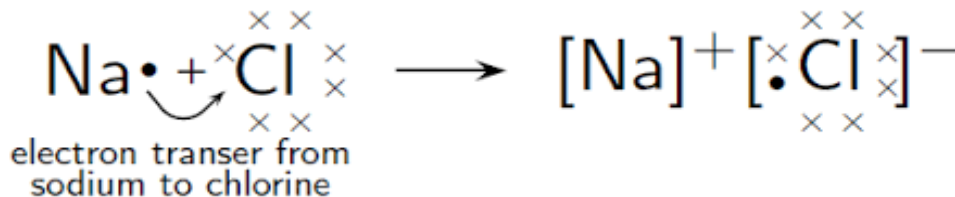
The second electron affinity corresponds to the addition of one mole of electrons to one mole of gaseous 1^- ions.



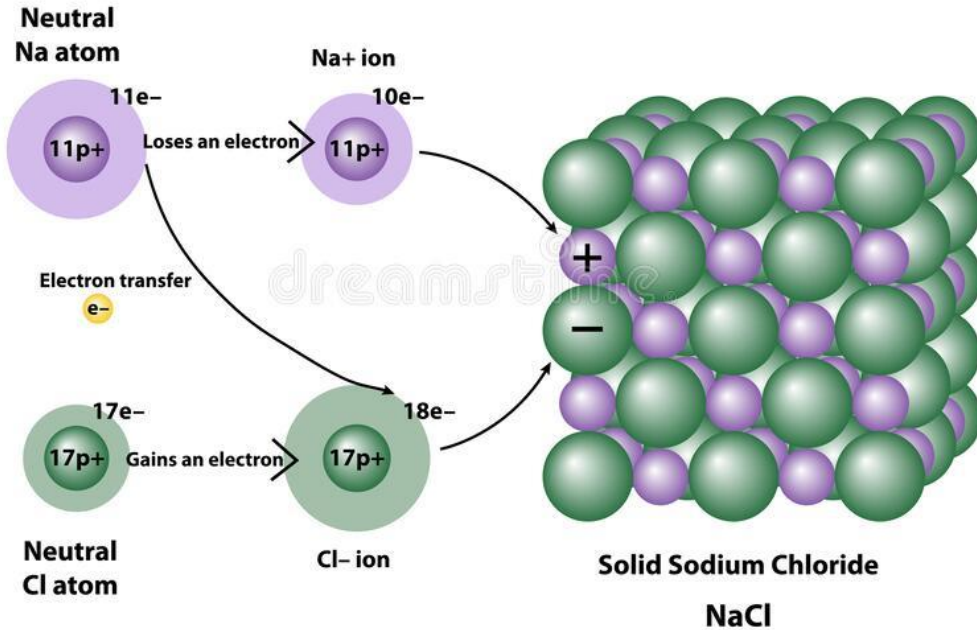
- ✓ *Measured in Kcal/mole or KJ/mole*
- ✓ *Group 17 elements have low electron affinity.*
- ✓ *On other hand elements of group 16 have quite high electron affinity for accepting two e- (positive electron affinity)*
- ✓ *While doing so, the negative ion formed first repels the second newly added electron. Thus energy has to be supplied to overcome such strong repulsion. i.e. formation of doubly charged negative ion is not so easy.*
- ✓ *The high 1st electron affinity of electronegative atom favours the formation of ionic bond.*

3. Lattice energy (U):

- It is defined as the *amount of energy released when appropriate number of oppositely charged ions in their gaseous isolated states are brought together to form one mole of ionic solid.*
- The *higher the lattice energy*, the greater is the tendency of the formation of an ionic bond.
- The *higher the charges on the ions and smaller the distance between them*, the greater is the force of attraction between them.



Ionic Bonding



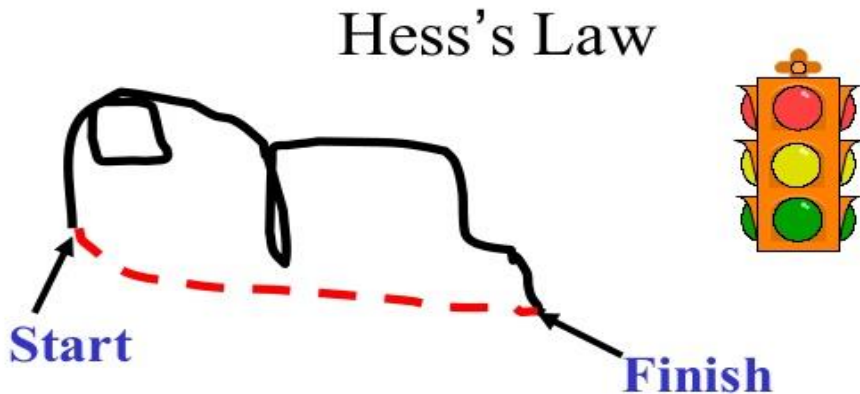
- ✓ **Higher L.E= Greater ease of formation of Ionic bonding**
- ✓ **For high L.E.= electrostatic force of attraction should be high.**

- ✓ *Finally it concludes that,*
- ✓ *Low I. E., High E. A. & very high L.E. of resulting ionic crystal favours the formation of stable Ionic Solid.*

Born-Haber Cycle

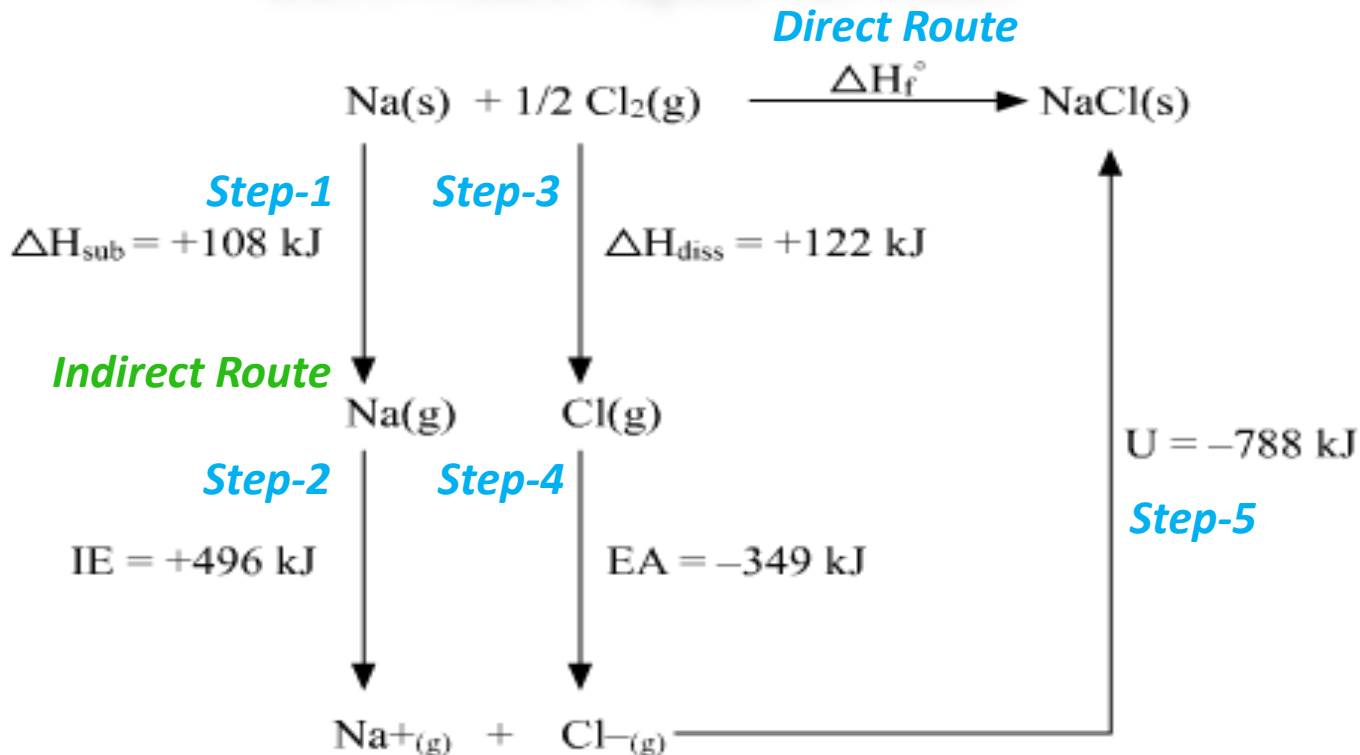
- ❑ *Developed by **Max Born & Fritz Haber** in 1919*
- ❑ *Used to predict the stability of ionic solids*
- ❑ *It is thermochemical method for determination of L.E. of ionic solids.*
- ❑ *In this method, Known thermochemical quantities are related to unknown L.E. by using **Hess's Law**.*

- **Hess's Law:** Change in *heat of reaction at const.* pressure is independent of the *pathway between initial & final states.*



A State Function: Path independent.
Both lines accomplished the same result, they went from start to finish.
Net result = same.

Born-Haber Cycle for NaCl



$$\Delta H_f^\circ = \Delta H_{\text{sub}} + \text{IE} + \Delta H_{\text{diss}} + \text{EA} + U$$

$$\Delta H_f^\circ = 108 + 496 + 122 - 349 - 788 = -411 \text{ kJ/mol}$$

Importance of Born-Haber Cycle

- ✓ To calculate Lattice energy of any ionic solid when all other values are known.
- ✓ To calculate electron affinity of electronegative atom.
- ✓ To study hypothetical ionic solid. (Positive value of heat of formation & L.E. indicate impossibility of existence of ionic compound.
- ✓ It also shows that metals do not form compounds with their abnormal valencies.
- ✓ E.g. U & H of CaF is -62 & -190 Kcal/mol (favourable for formation of ionic compound) but CaF immediately converted in CaF_2 .

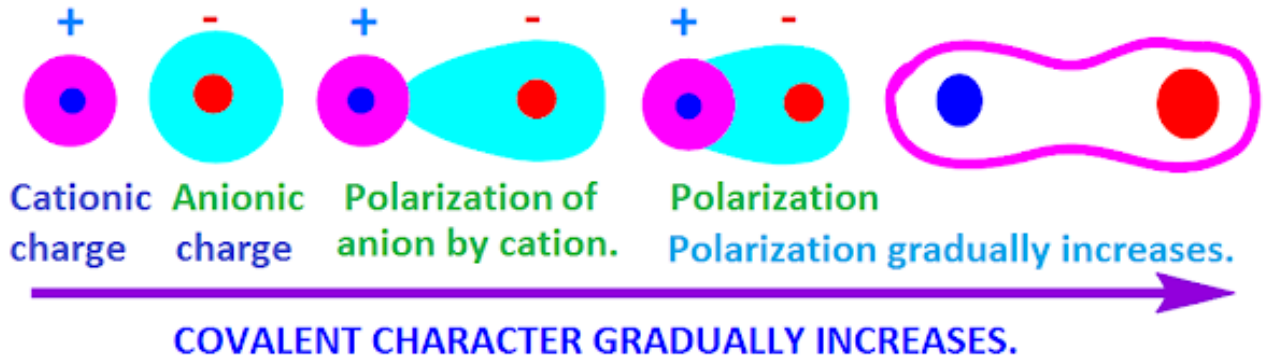
Fajan's Rule & its applications for Polarizing power & Polarizability

- *Generally ionic solids have high M.P., B. P., equivalence conductance & Colorless appearance.*
- *But some ionic solids exhibit low M. P., B. P. & equivalence conductance & **Colored appearance.***
- *To account these facts, Fajan discussed the variation in the degree of covalent character in ionic compounds.*

Statement

When two oppositely charged ions are brought together at eqm distance, cation attracts the electron cloud of anion & repels its positively charged nucleus. This results in *distortion or polarization* of anion.

Fajan's rule-Polarization of anion by cation.



- *The power of cation to polarize anion is known as **Polarizing power of cation***
- *The tendency of an anion to get polarize by cation is called as **Polarizability of Anion.***
- **Polarization or Distortion:** *The phenomenon in which regular shape of the anion gets distorted by cation at eqm distance is known as **Polarization.***

i.e. complete or partial separation of positive & negative charges.

- *Polarization of **cation by anion** is also possible but extent is very less due to **small size of cation.***

Effect of Polarization

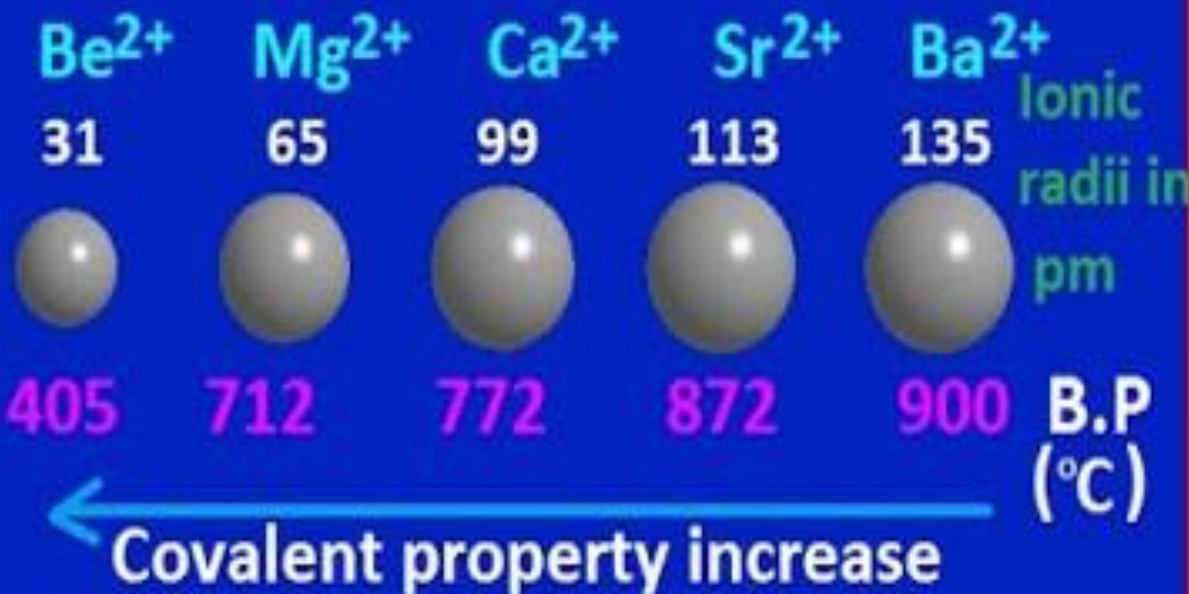
- Due to polarization there is increase in electron density between two ions & acquires some covalent character.***
- It causes lowering in M.P., B. P. than expected.***
- Increase in degree of polarization, increases covalent character in ionic bond.***
- The degree of polarization depends on polarising power of cation & polarizability of anion.***

Fajan's Rule

In 1924 Kasimir Fajan suggested rules regarding polarization are as...

i) Covalent character of ionic comp. increases with decreasing size of the cation or increasing charge on cation.

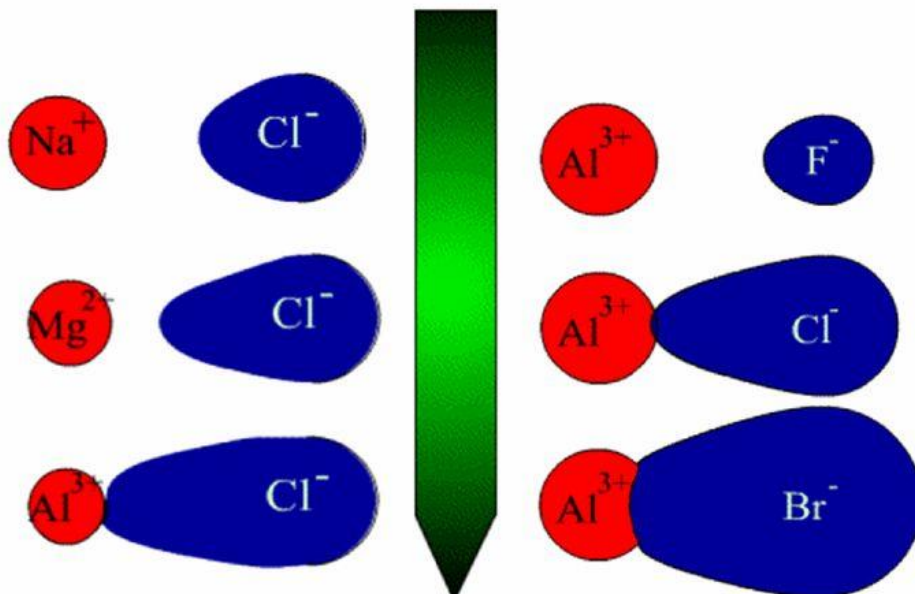
- e.g. SIZE: $\text{CaCl}_2 < \text{BeCl}_2$: Radius of Be^{2+} is less than Ca^{2+} ,
- Therefore BeCl_2 comp. have more covalent character.
- Hence M. P., B. P. & equivalent conductance of BeCl_2 is lower than CaCl_2
- Charge: High charge cation polarize e^- cloud around anion.
- $\text{NaCl (+1)} < \text{MgCl}_2 (+2) < \text{AlCl}_3 (+3)$



Charge : $Al^{3+} > Mg^{2+} > Na^{+}$

$\frac{\text{Charge}}{\text{Size}}$: $Al^{3+} > Mg^{2+} > Na^{+}$

Polarizing power : $Al^{3+} > Mg^{2+} > Na^{+}$



ii) Covalent character increases with increase in **size or charge of anion**

Charge on Anion: $HF < H_2O < NH_3 < CH_4$

-1 -2 -3 -4

Size of Anion

Polarization of anion increase 

ions: F^-

radii: 133 pm



Silver

salt: AgF

Cl^-

181 pm



$AgCl$

Br^-

196 pm




$AgBr$

I^-

220 pm



AgI

 Solubility in polar solvent increase



iii) Covalent character is greater for cations with a noble gas configuration (18e-) than for noble gas (8e-) type configuration.

- *CuCl, AgCl => More covalent => due to 'd' e- (18e-) cloud*
- *NaCl & KCl => Less Covalent => due to 8e- configuration*
- *NaCl (8e-) < CaCl₂ (18e-)*

Applications of Fajan's Rule

- ❑ *AgF soluble in water but other silver halides are insoluble.*
- ❑ *KCl is insoluble while KI is soluble in alcohol.*
- ❑ *Alkali metal chloride are insoluble in alcohol while LiCl is soluble.*
- ❑ *FeCl₃ soluble in ether but AlCl₃ not.*
- ❑ *ZnCl₂ (18e-) more volatile than MgCl₂ (8e-) & more soluble in organic solvents.*
- ❑ *Covalent character increases in the following compound*
- ❑ *NaCl < MgCl₂ < AlCl₃*
- ❑ *Decomposition tempt of metallic carbonates: Greater polarizing power lower decomposition tempt. **BeCO₃** < **CaCO₃** < **SrCO₃** < **BaCO₃***

Ionic Character in Covalent Compounds

- ❑ Comp having covalent bond called **Covalent compound**
- ❑ Covalent bond indicated by dash or hyphen. i.e. **A-B**
- ❑ Let electronegativity of A is X_A & B is X_B
- ❑ On the basis of electronegativity diff., we can predict whether **A-B** bond will be polar-Covalent or Non-polar-Covalent or ionic bond.

- ❑ If $(X_A - X_B)$ is = 0 => Covalent nonpolar bond (e.g. H-H, F-F, etc.)
- ❑ If $(X_A - X_B)$ is very small diff. => Polar Covalent bond (**small ionic character**) (i.e. $A^{\delta+} - B^{\delta-}$)
- ❑ If $(X_A - X_B)$ is very large diff. => Very large diff. between electronegativities => **Pure ionic compound**

Dipole Moment (μ):

- *Mathematical product of the magnitude of the electrostatic of the electrostatic charge & distance between ends of the dipoles.*

$$\mu = q * r$$

- *Depends upon electronegativity diff. of bonded atoms*
- ***Greater electronegativity diff. -> Greater dipole moment -> Greater magnitude of ionic character.***



::::Thank You::::

::::Keep Learning::::