



# CHEMISTRY

Target : JEE (Main)

CHEMICAL BONDING



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### JEE (Main) Syllabus

Chemical Bonding and Molecular Structure

Valence electrons, ionic bond, covalent bond, bond parameters, Lewis structure, polar character of covalent bond, valence bond theory, resonance, geometry of molecules, VSEPR theory, concept of hybridization involving s, p and d orbitals and shapes of some simple molecules, molecular orbital theory of homonuclear diatomic molecules (qualitative idea only). Hydrogen bond.

### JEE (Advanced) Syllabus

Orbital overlap and covalent bond; Hybridisation involving s, p and d orbitals only; Orbital energy diagrams for homonuclear diatomic species; Hydrogen bond; Polarity in molecules, dipole moment (qualitative aspects only); VSEPR model and shapes of molecules (linear, angular, triangular, square planar, pyramidal, square pyramidal, trigonal bipyramidal, tetrahedral and octahedral).

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# Chemical Bonding

## INTRODUCTION :

It is a well known fact that none of the elements exist as independent atoms, except for noble gases, Most of the elements exist as molecules which are in a cluster. The questions that arise are.

- Why do atoms combine and form bonds ?
- How do atoms combine to form molecules ?
- Why is a molecule more stable than the individual atom ?
- Such doubts will be discussed in this chapter.

## DEFINITION :

- (i) An attractive force that acts between two or more particles (atoms, ions or molecules) to hold them together, is known as a chemical bond.
- (ii) It is a union of two or more atoms to acquire stable inert gas configuration  $s^2p^6$ .

To explain nature of chemical bond Different theories are given at first KOSSEL & LEWIS proposed the theory.

**Kossel & Lewis approach chemical bonding :** In early days , the ability if various elements to combine with one another was expressed in terms of their valency. The concept of valency was not based on any logical understanding. The development in the field of atomic structure provide foundations for various theories of valency. The initial contributions in this field came from. W. Kossel and G. N. Lewis in 1916. They were the first to provide some logical explanation of valency which based on the inertness of noble gases. This view, later on, came to be known as octate rule.

## OCTET RULE : (Tendency to acquire noble gas configuration)

- (i) It has been observed that atoms of noble gases have little or no tendency to combine with each other or with atoms of other elements.
- (ii) It means that these atoms must have a stable electronic configuration.
- (iii) These elements (noble gases) have 8 electrons ( $ns^2 np^6$ ) except helium which has 2 electrons ( $1s^2$ ) in their outer most shell.

Element	Ne	Ar	Kr	Xe	Rn
Outer most shell configuration	$2s^2 2p^6$	$3s^2 3p^6$	$4s^2 4p^6$	$5s^2 5p^6$	$6s^2 6p^6$

- (iv) It is therefore concluded that  $s^2p^6$  configuration in the outer energy level constitutes a structure of maximum stability or minimum energy
- (v) "Tendency of atoms to have eight electrons in their outermost shell is known as Lewis octet rule". To achieve inert gas configuration atoms lose, gain or share electrons.

## Lewis Dot Structures :

The Lewis dot structures can be written for other molecules also, in which the combining atoms may be identical or different.

To write the Lewis dot structure following steps are to be followed :

- (i) The total number of electrons are obtained by adding the valence electrons of combining atoms.
- (ii) For Anions, we need to add one electron for each negative charge.
- (iii) For cations, we need to subtract one electron for each positive charge.
- (iv) After then the central atom is decided.

To decide, Central atom, following steps are followed :

- (i) In general the **least electronegative atom** occupies the central position in the molecule/ion. For example in the  $NF_3$  and  $CO_3^{2-}$ , nitrogen and carbon are the central atoms whereas fluorine and oxygen occupy the terminal positions.
- (ii) Generally the atom which is/are less in number acts as central atom.
- (iii) Generally central atom is the atom which can form maximum number of bonds( which is generally equal to the number of electrons present in the valence shell of the atom).
- (iv) Atom of highest atomic number or largest atom generally acts as central atom.

Hence Fluorine never act as central atom.  
 After accounting for the shared pairs of electrons for single bonds, the remaining electrons utilized for multiple bonding or remain as the lone pairs. The basic requirement being that each bonded atom gets an octet of electrons.  
 Lewis representations of a few molecules/ions are given in the following Table

Table-1

Molecule/ion	H <sub>2</sub>	O <sub>2</sub>	O <sub>3</sub>	NF <sub>3</sub>	CO <sub>3</sub> <sup>2-</sup>	HNO <sub>3</sub>	CH <sub>4</sub>	HCHO
Lewis Representation	H - H	:O=O:						

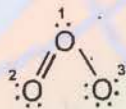
Each H-atom attains the configuration of helium (a duplet of electrons)

### Formal Charge :

The formal charge of an atom in a molecule or ion is defined as the difference between the number of valence electrons of that atom in an isolated or free state and the number of electrons assigned to that atom in the Lewis structure.

$$\text{Formal charge (F.C.) On an atom in a Lewis structure} = \left[ \text{Total number of valence electron in the free atom} \right] - \left[ \text{Total number of non bonding (lone pair) electrons} \right] - \left( \frac{1}{2} \right) \left[ \text{Total number of bonding (shared) electrons} \right]$$

Let us consider the ozone molecule (O<sub>3</sub>). The Lewis structure of O<sub>3</sub>, may be drawn as :



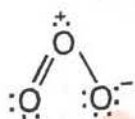
The atoms have been numbered as 1, 2 and 3. The formal charge on :

The central O atom marked 1 =  $6 - 2 - \frac{1}{2}(6) = +1$

The terminal O atom marked 2 =  $6 - 4 - \frac{1}{2}(4) = 0$

The terminal O atom marked 3 =  $6 - 6 - \frac{1}{2}(2) = -1$

Hence, we represent O<sub>3</sub> along with the formal charges as follows :

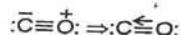


It should be kept in mind that formal charges do not indicate real charge separation within the molecule. Indicating the charges on the atoms in the Lewis structure only helps in keeping track of the valence electrons in the molecule. **Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given species.** Generally the lowest energy structure is the one with the smallest formal charges on the atoms.



Note: (i) The formal charge is a factor based on a pure covalent view of bonding in which electron pairs are shared equally by neighbouring atoms.

(ii) Pair of +1 and -1 formal charge on adjacent atoms is considered a coordinate bond.



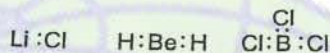
(iii) Lewis dot structure with minimum formal charges is most stable.

**Limitations of the Octet Rule :**

The octet rule, though useful, is not universal. It is quite useful for understanding the structures of most of the organic compounds and it applies mainly to the second period elements of the periodic table. There are three types of exceptions to the octet rule.

**1. The incomplete octet of the central atom**

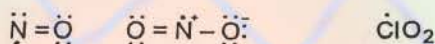
In some compounds, the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons. Examples are LiCl, BeH<sub>2</sub> and BCl<sub>3</sub>.



Li, Be and B have 1, 2 and 3 valence electrons only. Some other such compounds are AlCl<sub>3</sub> and BF<sub>3</sub>.

**2. Odd-electron molecules**

In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide, NO<sub>2</sub>, the octet rule is not satisfied for all the atoms



**3. The expanded octet/ super octet / hypervalent compound**

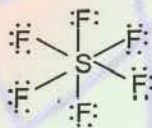
Elements in and beyond the third period of the periodic table have, apart from 3s and 3p orbitals, 3d orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Obviously the octet rule does not apply in such cases.

Some of the examples of such compounds are: PF<sub>5</sub>, SF<sub>6</sub>, H<sub>2</sub>SO<sub>4</sub> and a number of coordination compounds.



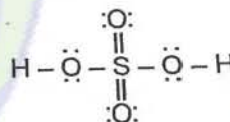
PF<sub>5</sub>

10 electrons around the P atom



SF<sub>6</sub>

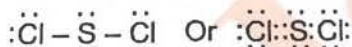
12 electrons around the S atom



H<sub>2</sub>SO<sub>4</sub>

12 electrons around the S atom

Interestingly, sulphur also forms many compounds in which the octet rule is obeyed. In sulphur dichloride, the S atom has an octet of electrons around it.



**4. Other drawbacks of the octet theory**

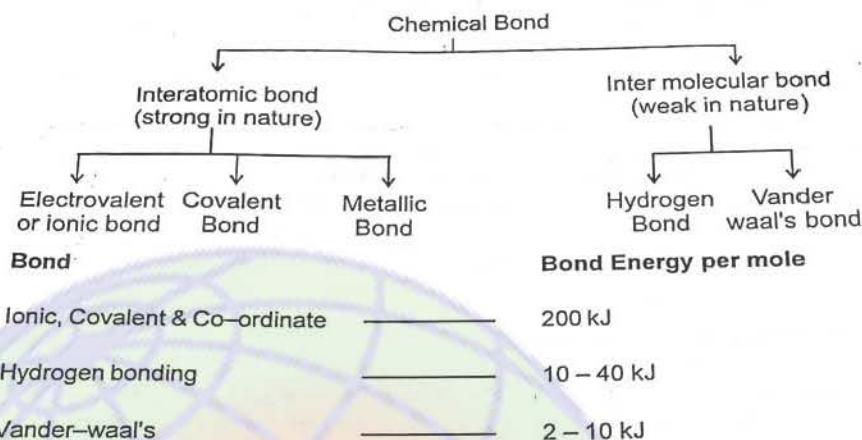
It is clear that octet rule is based upon the chemical inertness of noble gases. However, some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like XeF<sub>2</sub>, KrF<sub>2</sub>, XeOF<sub>2</sub> etc.,

- This theory does not account for the shape of molecules.
- It does not explain the relative stability of the molecules being totally silent about the energy of a molecule.

Chemical Bonding

**CLASSIFICATION OF CHEMICAL BONDS :**

On the basis of electronic valency theory and structure, chemical bonds can be classified as follows.



**ELECTROVALENT OR IONIC BOND :**

The chemical bond formed between two or more atoms as a result of complete transfer of one or more electrons from one atom to another is called ionic or electrovalent bond.

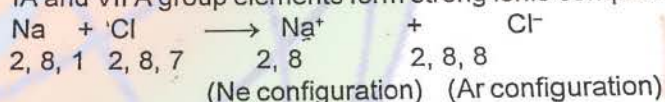
Electrovalent bond is not possible between similar atoms. This type of bonding requires two atoms of different nature. One atom should have the tendency to loose electrons i.e. electropositive in nature and the other atom should have the tendency to accept electrons i.e. electronegative in nature.

Electropositive atom loses electrons (group IA to IIIA)

Electronegative atom gains electron (group IVA to VII A)

**Example :**

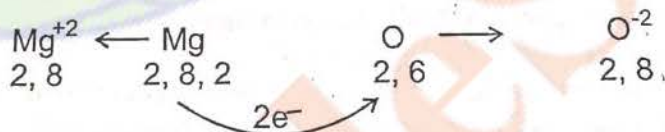
IA and VII A group elements form strong ionic compound.



More the distance between two elements in the periodic table more will be the ionic character of the bond. Total number of electrons lost or gained is called electrovalency.

**Example :**

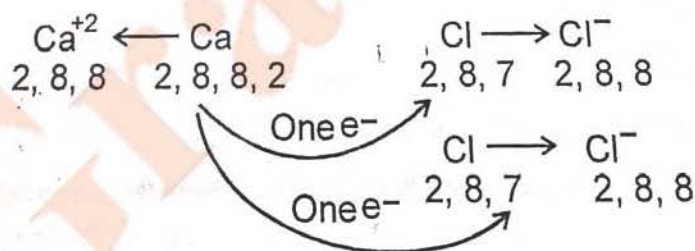
(1)



electrovalency of Mg = 2

electrovalency of O = 2

(2)

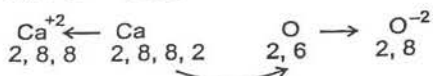


electrovalency of Ca = 2

electrovalency of Cl = 1

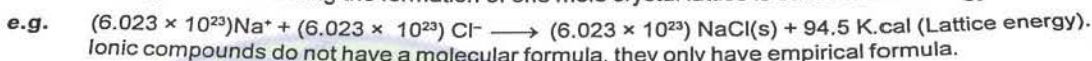
Chemical Bonding

(3)



electrovalency of Ca = 2  
electrovalency of O = 2

Electrostatic force of attraction between cation and anion is called ionic bond or electrovalent bond.  
Force of attraction is equal in all direction so ionic bond is non-directional.  
A definite three dimensional structure called crystal lattice is formed.  
Energy released during the formation of one mole crystal lattice is called lattice energy.



e.g. NaCl is the empirical formula of sodium chloride.

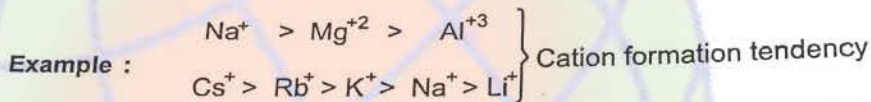
**Factors favouring formation of ionic bonds :**

Formation of ionic bond depends upon three factors :

(A) **Ionisation energy (IE)** : Amount of energy required to remove an electron from the outermost orbit of an isolated gaseous atom to form positive ion or cation is called ionization energy [energy is absorbed so it is an endothermic process]



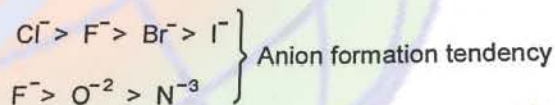
Less ionisation energy  $\Rightarrow$  Greater tendency to form cation.



(B) **Electron affinity** : Amount of energy released when an electron is added to an isolated gaseous atom to form negative ion or anion is called electron affinity [energy is released so it is an exothermic process]



High electron affinity  $\Rightarrow$  Greater tendency to form anions

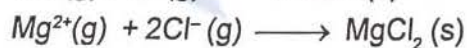


**LATTICE ENTHALPY :**

The Lattice Enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions. For example, the lattice enthalpy of NaCl is 788 kJ mol<sup>-1</sup>. This means that 788 kJ of energy is required to separate one mole of solid NaCl into one mole of Na<sup>+</sup>(g) and one mole of Cl<sup>-</sup>(g) to an infinite distance.

This process involves both the attractive forces between ions of opposite charges and the repulsive forces between ions of like charge. The solid crystal being three-dimensional; it is not possible to calculate lattice enthalpy directly from the interaction of forces of attraction and repulsion only.

Factors associated with the crystal geometry have to be included.



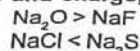
**Factors affecting L.E.**

(i) Lattice energy (L.E.)  $\propto \frac{1}{r}$   $r = r_+ + r_-$   
= interionic distance

(ii) L.E.  $\propto Z_+, Z_-$   
 $Z_+ \Rightarrow$  charge on cation in terms electronic charge  
 $Z_- \Rightarrow$  charge on anion in terms electronic charge

- (iii) Size of cation ↑ C.N. ↑ L.E. ↑  
 (a) NaCl > KCl (size)  
 (b) NaCl < MgO (size, charge)  
 (c) NaCl < MgCl<sub>2</sub> (size)

In size and charge, charge will dominate



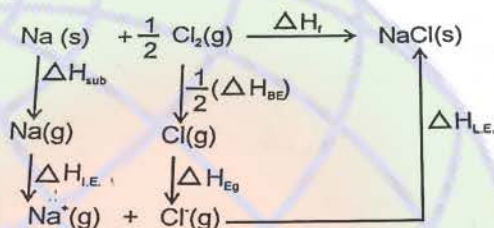
- (d) Al<sub>2</sub>O<sub>3</sub> Na<sub>2</sub>O MgO  
 Al<sub>2</sub>O<sub>3</sub> > MgO > Na<sub>2</sub>O

Calculation of L.E. :

Indirect methods : Born-Haber Cycle ( Hess's law)

Hess's Law ⇒ the net enthalpy change of a chemical reaction or of any process always remain same whether the reaction takes place in 1 step or many step

\* Born Haber Cycle for NaCl (s)



$\Delta H_f$  ⇒ enthalpy of formation of any compound is defined as the enthalpy change when 1 mol of that compound is formed from the elements in their standard states

$$\Delta H_f = \Delta H_{\text{sub}} + \Delta H_{\text{IE}_1} + \frac{1}{2} \Delta H_{\text{BE}} + \Delta H_{\text{eg}} + \Delta H_{\text{LE}}$$

+ve/-ve  
 Generally      ↓                      ↓                      ↓                      ↓  
                     +ve                      +ve                      +ve                      +ve/-ve

### Solved Examples

Ex-1 Calculate the lattice energy of solid KF with the help of following data :

$\Delta H_f^\circ(\text{KF}) = -562.6 \text{ kJ mol}^{-1}$

$\Delta H_{\text{sub}}(\text{K}) = 89.6 \text{ kJ mol}^{-1}$

$\Delta H_{\text{IE}_1}(\text{K}) = 419.0 \text{ kJ mol}^{-1}$

$\Delta H_{\text{diss}}(\text{F}_2) = 158.2 \text{ kJ mol}^{-1}$

$\Delta H_{\text{EA}}(\text{F}) = a - 332.6 \text{ kJ mol}^{-1}$

Sol.  $\text{K(s)} + \frac{1}{2} \text{F}_2(\text{g}) \longrightarrow \text{KF(s)} ; -562.6 \text{ kJ mol}^{-1}$

$\text{K(s)} \longrightarrow \text{K(g)} ; 89.6 \text{ kJ mol}^{-1}$

$\text{K(g)} \longrightarrow \text{K}^+(\text{g}) + \text{e}^- ; 419.0 \text{ kJ mol}^{-1}$

$\frac{1}{2} \text{F}_2(\text{g}) \longrightarrow \text{F(g)} ; \frac{1}{2} 158.2 = 79.1 \text{ kJ mol}^{-1}$

$\text{F(g)} + \text{e}^- \longrightarrow \text{F}^-(\text{g}) ; -332.6 \text{ kJ mol}^{-1}$

Let  $\Delta H_{\text{lattice}}(\text{KF})$  be U, then according to Hess's law of constant heat summation.

$-562.6 = 89.6 + 419.0 + 79.1 - 332.6 - U$

So,  $U = 817.7 \text{ kJ mol}^{-1}$

Ans. Lattice energy of KF = 817.7 kJ mol<sup>-1</sup>

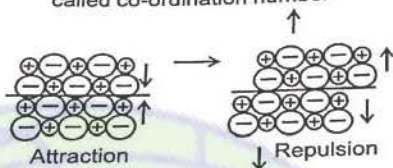


Chemical Bonding

Characteristics of ionic compounds :

(i) Physical state

- (a) Electrovalent compounds are generally crystalline, hard & brittle in nature.
- (b) These compounds are generally made from ions which are arranged in a regular way as a lattice structure.
- (c) Thus electrovalent compounds exist as three dimensional solid aggregates.
- (d) Normally each ion is surrounded by a number of oppositely charged ions and this number is called co-ordination number



{Same charged ions comes near. So they repell each other}

(ii) Boiling point and melting point :

High boiling point and melting points are due to strong electrostatic force of attraction.

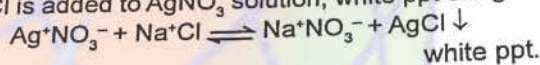
(iii) Electrical conductivity :

It depends on ionic mobility. In solid state there are no free ions so they are bad conductors of electricity  
In fused state or aqueous solution free ions are present so they are good conductors of electricity  
(Conductivity order) Solid state < Fused state < Aqueous solution

(iv) Ionic reactions :

- ★ Ionic compounds show ionic reactions & covalent compounds show molecular reactions.  
Ionic reactions are fast reactions.

Example : When NaCl is added to AgNO<sub>3</sub> solution, white ppt of AgCl is formed at once.

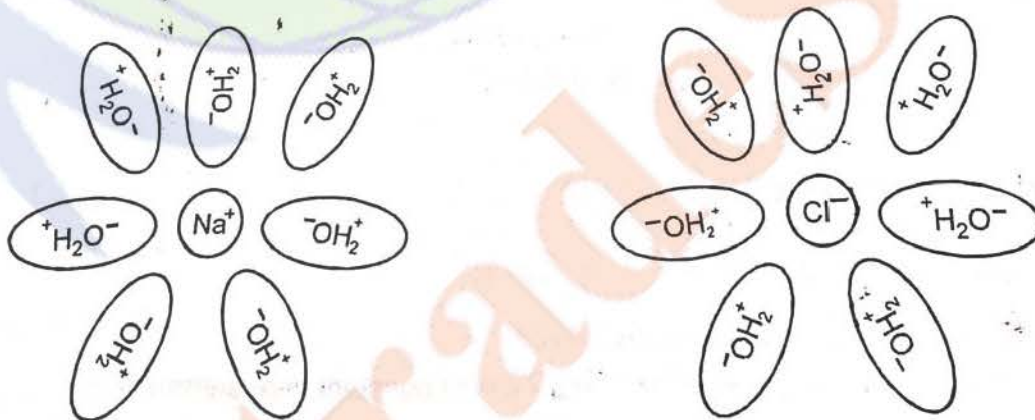


(v) Solubility – Ionic compounds are soluble in polar solvent like H<sub>2</sub>O, HF etc.

To explain solubility of ionic compound consider an example of NaCl in water.

H<sub>2</sub>O is polar solvent it can represent as

- ★ The Na<sup>+</sup> ions gets associated with partially negatively charged 'O' of water
- ★ And Cl<sup>-</sup> ions gets associated with partially positively charged 'H' of water.



Oxygen atom of H<sub>2</sub>O gives its electron to Na<sup>⊕</sup>

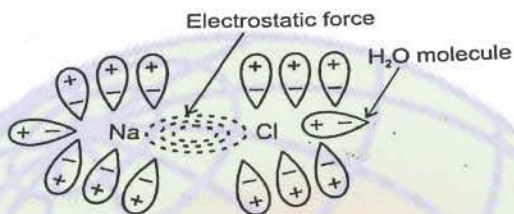
H atom of H<sub>2</sub>O gain electron from Cl<sup>⊖</sup>

Chemical Bonding

Thus charge on  $\text{Na}^+$  and  $\text{Cl}^-$  decreases and electrostatic force also decreases which leads to free ion.

- \* Here, attraction force between  $\text{H}_2\text{O}$  and  $\text{Na}^+$  or  $\text{Cl}^-$  (Hydration energy)  $>$  Electrostatic force between ions in lattice. (Lattice energy)
- \* Energy released due to interaction between polar solvent molecule and ions of solute is called solvation energy. If water used as solvent it is called hydration energy.
- \* Condition of the solubility of ionic compound in water is (Hydration energy  $>$  Lattice energy)

Solvation or Hydration :



Whenever any compound generally ionic or polar covalent is dissolved in an polar solvent or in water then, different ions of the compound will get separated and will get surrounded by polar solvent molecules. This process is known as solvation or hydration. Energy released in this process is known as solvation energy or hydration energy

The ionic compound will be soluble only if solvation energy (H.E.) is more than the lattice energy

Factors affecting solvation energy or hydration energy.

$$\text{S.E.} \propto Z_+ Z_-$$

$$\propto \left( \frac{1}{r_+} + \frac{1}{r_-} \right)$$

$$\propto \left( 1 - \frac{1}{\epsilon_r} \right) \text{ (nature of solvent) where } \epsilon_r \text{ is dielectric constant.}$$

Greater the polarity, greater will be  $\epsilon_r$

$$\epsilon_r \uparrow \Rightarrow 1/\epsilon_r \downarrow, 1 - 1/\epsilon_r \uparrow \Rightarrow \text{S.E.} \uparrow$$

	$\text{H}_2\text{O}$	$\text{CH}_3\text{OH}$	$\text{C}_2\text{H}_5\text{OH}$	$\text{C}_6\text{H}_6$
$\epsilon_r$	81	34	27	34

Applications of Hydration energy :

- (a) **Size of the hydrated ions:** Greater the hydration of the smaller ion, greater will be its hydrated radii  
 $\text{Li}^+(\text{aq}) > \text{Na}^+(\text{aq})$
- (b) **Mobility of the ion:** more is the hydration smaller will be the mobility of the ions  
 $\text{Li}^+(\text{aq}) < \text{Na}^+(\text{aq}) < \text{K}^+(\text{aq}) < \text{Rb}^+(\text{aq}) < \text{Cs}^+(\text{aq})$ .
- (c) **Electrical conductance :** is related to mobility so follows the same order

Important facts about solubility of ionic compounds in polar solvent can be predicted as

Now we have  $\rightarrow \text{L.E.} \propto \frac{1}{r_+ + r_-}$  and  $\text{S.E.} \propto \left( \frac{1}{r_+} + \frac{1}{r_-} \right)$



**COVALENT CHARACTER IN IONIC COMPOUNDS (FAJAN'S RULE) :**

When anion and cation approach each other, the valence shell of anion is pulled towards cation nucleus and thus shape of anion is deformed. This phenomenon of deformation of anion by a cation is known as polarisation and the ability of cation to polarize a near by anion is called as polarizing power of cation.



Fajan's pointed out that greater is the polarization of anion in a molecule, more is covalent character in it. *More distortion of anion, more will be polarisation then covalent character increases.*

Fajan's gives some rules which govern the covalent character in the ionic compounds, which are as follows:

- (i) **Size of cation :** Smaller is the cation more is its polarizing power and thus more will be the polarisation of anion. Hence more will be covalent character in compound.

**Size of cation  $\propto$  1 / polarisation.**

e.g.  $\text{BeCl}_2$                        $\text{MgCl}_2$                        $\text{CaCl}_2$                        $\text{SrCl}_2$                        $\text{BaCl}_2$

Size of cation increases,      Polarisation decreases,      Covalent character decreases

- (ii) **Size of anion :** Larger is the anion, greater is its polarisability and, therefore, more will be the polarisation. Thus more will be covalent character in compound.

**Size of anion  $\propto$  polarisation**

e.g.,       $\text{LiF}$        $\text{LiCl}$        $\text{LiBr}$        $\text{LiI}$

- Size of anion increases
- Polarisation increases
- Covalent character increases

- (iii) **Charge on cation :** Higher is the oxidation state of cation, more will be the deformation of anion and thus, more will be covalent character in compound.

**Charge on cation  $\propto$  polarisation.**

e.g.,       $\text{NaCl}$        $\text{MgCl}_2$        $\text{AlCl}_3$   
              $\text{Na}^+$        $\text{Mg}^{2+}$        $\text{Al}^{3+}$

- Charge of cation increases
- Polarisation increases
- Covalent character increases

- (iv) **Charge on anion :** Higher is the charge on anion more will be the polarisation of anion and thus more will be covalent character in the compound.

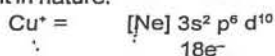
**Charge on anion  $\propto$  polarisation.**

e.g.,       $\text{AlF}_3$        $\text{Al}_2\text{O}_3$        $\text{AlN}$   
              $\text{F}^-$  ,       $\text{O}^{2-}$  ,       $\text{N}^{3-}$

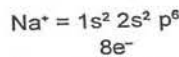
- Charge on anion increases
- Polarisation increases
- Covalent character increases

Chemical Bonding

- (v) **Pseudo inert gas configuration of cation** : Cation having pseudo inert gas configuration has more polarizing power than the cation that has inert gas configuration. Thus NaCl having inert gas configuration will be more ionic whereas CuCl having pseudo inert gas configuration will be more covalent in nature.



Pseudo inert gas configuration  
(poor shielding of d-electrons)



Inert gas configuration  
(more shielding of s and p electrons)

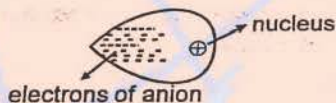
**Application & Exceptions of Fajan's Rules :**

- (i)  $\text{Ag}_2\text{S}$  is less soluble than  $\text{Ag}_2\text{O}$  in  $\text{H}_2\text{O}$  because  $\text{Ag}_2\text{S}$  is more covalent due to bigger  $\text{S}^{2-}$  ion.
- (ii)  $\text{Fe}(\text{OH})_3$  is less soluble than  $\text{Fe}(\text{OH})_2$  in water because  $\text{Fe}^{3+}$  is smaller than  $\text{Fe}^{2+}$  and thus charge is more. Therefore,  $\text{Fe}(\text{OH})_3$  is more covalent than  $\text{Fe}(\text{OH})_2$ .
- (iii) The colour of some compounds can be explained on the basis of polarisation of their bigger negative ions.

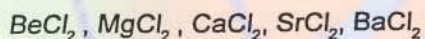
**For example :**

$\text{AgCl}$  is white  $\text{AgBr}$ ,  $\text{AgI}$ ,  $\text{Ag}_2\text{CO}_3$  are yellow. Similarly,  $\text{SnCl}_2$  is white but  $\text{SnI}_2$  is black.  $\text{PbCl}_2$  is white but  $\text{PbI}_2$  is yellow.

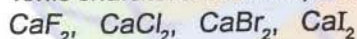
The bigger anions are more polarised and hence their electrons get excited by partial absorption of visible light.



**(iv) Variation of melting point [melting point of covalent compound < melting point of ionic compound]**



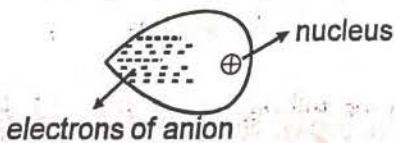
→  
Ionic character increases, melting point increases ; since size of cation increases & size of anions is constant.



→  
Covalent character increase, melting point decrease ; since size of cations increase & size of anions is constant.

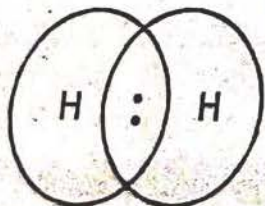
- Ex.**  $\text{AgCl}$  is colourless whereas  $\text{AgI}$  is yellow, because of :
- (A)  $\text{Ag}^+$  have 18 electron shell to screen the nuclear charge.
  - (B)  $\text{Ag}^+$  shows pseudo inert gas configuration.
  - (C) distortion of  $\text{I}^-$  is more pronounced than  $\text{Cl}^-$  ion.
  - (D) existence of d - d transition.

**Sol.** (C) the bigger anions are more polarised and hence their electrons get excited by partial absorption of visible light.

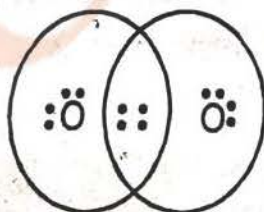


**COVALENT BOND :**

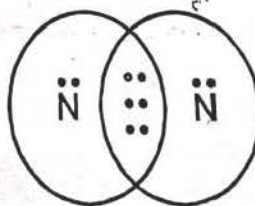
A covalent bond may be defined as the bond formed by mutual sharing of electrons between the participating atoms (which are short of electrons) of comparable electronegativity.



$\text{H}_2$  molecule



$\text{O}_2$



$\text{N}_2$



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