

# CHEMICAL BONDING

## INTRODUCTION

- (a) It is well known fact that except for inert gases, no other element exists as independent atoms under ordinary condition.
- (b) Most of the elements exist as molecules which are cluster of atoms. How do atoms combine to form molecules and why do atoms form bonds? Such doubts will be discussed in this chapter.
- (c) A molecule will only be formed if it is more stable and has a lower energy, than the individual atoms.

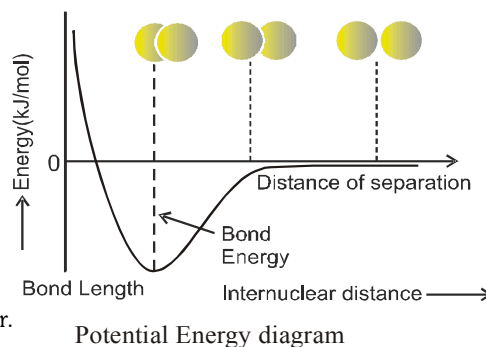
### Chemical Bond :

- (a) A force that acts between two or more atoms to hold them together as a stable molecule.
- (b) It is union of two or more atoms involving redistribution of  $e^-$  among them.
- (c) This process accompanied by decrease in energy.
- (d) Decrease in energy  $\propto$  Strength of the bond.
- (e) Therefore molecules are more stable than atoms.

## CAUSE OF CHEMICAL COMBINATION

### 1. Tendency to acquire minimum energy :

- (a) When two atoms approaches to each other-  
Nucleus of one atom attracts the electron of another atom.
- (b) Two nuclei and electron of both the atoms repels each other.
- (c) If net result is attraction, the total energy of the system (molecule) decreases and a chemical bond forms.
- (d) So Attraction  $\propto 1/\text{energy} \propto$  Stability.
- (e) Bond formation is an exothermic process



### 2. Octet rule

Octet rule was given by Lewis & Kossel

Atoms Combines to complete an octet of electrons in their outer most orbit. Complete orbital represents to get most stable state. Hence all atoms have a tendency to acquire octet ( $s^2p^6$ ) configuration in their outermost orbit.

The octet may be complete in following manner:

Complete transfer of electrons from one atom to another.

**Ex.** NaCl,  $\text{CaCl}_2$  & MgO etc. (Ionic Bond)

Sharing of electrons between atoms.

- (a) Sharing of equal number of electron between two atoms.

**Ex.**  $\text{Cl}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$  etc., (Covalent bond)

- (b) Sharing of electron pair given by only one atom

**Ex.**  $[\text{NH}_3 \rightarrow \text{H}^+]$  &  $\text{NH}_3 \rightarrow \text{BF}_3$  (Co-ordinate Bond)

## EXCEPTIONS OF OCTET RULE

### 1. Transition metal ions

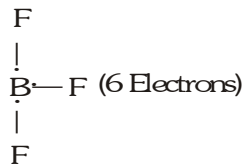
$\text{Cr}^{3+}$	$\text{Mn}^{2+}$	$\text{Fe}^{2+}$
$[\text{Ar}]3d^3$	$[\text{Ar}]3d^5$	$[\text{Ar}]3d^6$
[2, 8, 11]	[2, 8, 13]	[2, 8, 14]

### 2. Pseudo inert gas configuration $[s^2p^6d^{10}]$

$\text{Zn}^{2+}$	$\text{Cd}^{2+}$
$[\text{Ar}]3d^{10}$	$[\text{Kr}]4d^{10}$

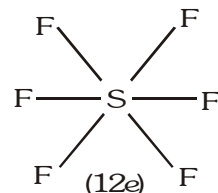
### 3. Contraction of octet (incomplete octet)

$\text{BeF}_2$	$\text{BF}_3$	$\text{AlCl}_3$	$\text{BCl}_3$
(4e)	(6e)	(6e)	(6e)



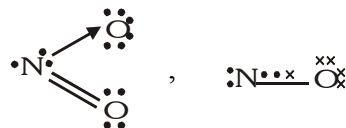
### 4. Expansion of Octet (due to empty d-orbitals)

$\text{PCl}_5$	$\text{SF}_6$	$\text{ClF}_3$	$\text{ICl}_5$	$\text{IF}_7$
↓	↓	↓	↓	↓
(10e)	(12e)	(10e)	(12e)	(14e)



### 5. Odd electron species

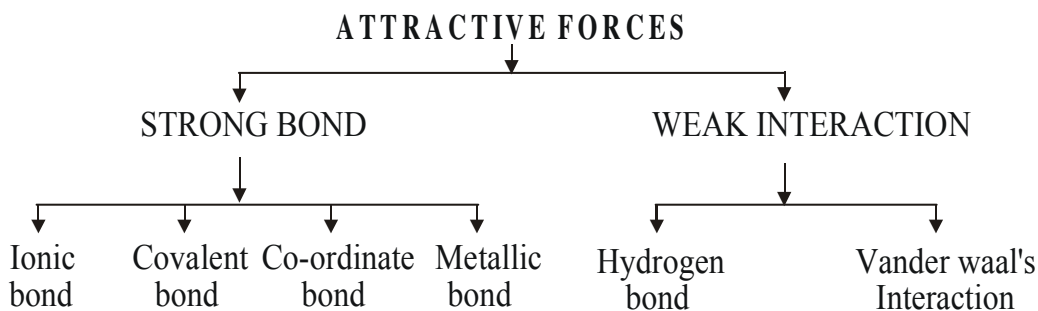
Ex. NO, NO<sub>2</sub>, ClO<sub>2</sub> etc.



### 6. Compounds of Noble gases

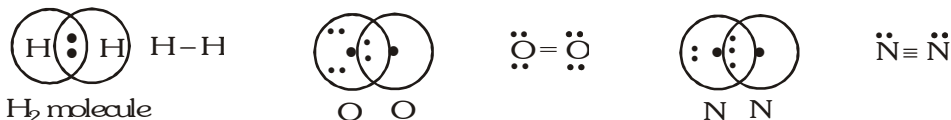
Noble gases which have already completed their octets (or duplet in case of He.) should not form compounds. However, their compounds like XeF<sub>2</sub>, XeF<sub>6</sub> & KrF<sub>2</sub> etc., have been actually prepared.

## CLASSIFICATION OF BONDS



## COVALENT BOND

- (a) A covalent bond is formed by the mutual sharing of electrons between two atoms of electronegativity elements to complete their octet. (Except H which completes its duplet)

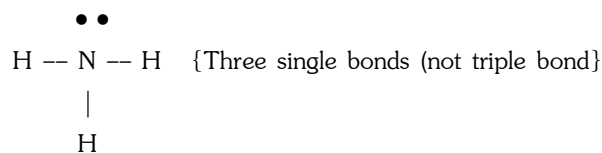


- (b) The shared pair of electrons should have opposite spins, and are localised between two atoms concerned.

(c) Shairing of electrons may occurs in three ways –

No. of electrons shared between two atoms	Bonded Electron pair	Bond.
2	1	Single bond (–)
4	2	Double bond (=)
6	3	Triple bond (≡)

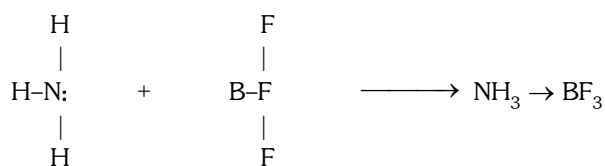
Ex.



$\text{N} \equiv \text{N}$  Triple bond. (not three single bond)  $\text{O} = \text{O}$  (Double bond)  $\text{H} - \text{O} - \text{H}$  (Two single bonds.)

### CO-ORDINATE BOND

- It is a covalent bond in which the shared electron pair come from one atom is called coordinate bond.
- Necessary conditions for the formation of co-ordinate bond are -
  - Octet of donor atom should be complete and should have atleast one lone pair of electron.
  - Acceptor atom should have a defficiency of at least one pair of electron.
- Atom which provide electron pair for shairing is called donor.
- Other atom which accepts electron pair is called acceptor. That is why it is called donor-acceptor or dative bond.

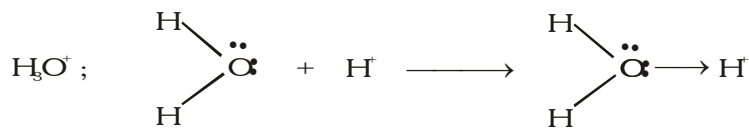
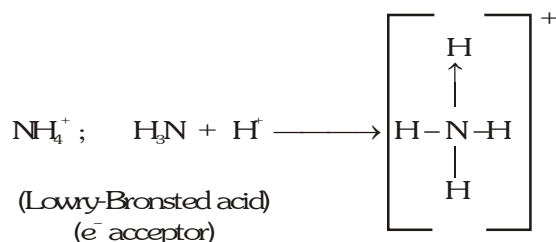


$\text{BF}_3$  is electron defficient compound.

Metal co-ordinate compounds -



Ex.



◆ **Note :** Compounds in which Ionic, covalent and co-ordinate bonds are present, are as follows -  
 $\text{NH}_4\text{Cl}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{K}_4[\text{Fe}(\text{CN})_6]$ ,  $\text{KNC}$ ,  $\text{KNO}_3$ , etc.

## WAVE MECHANICAL CONCEPT OF CO-VALENT BONDING –

- (a) One orbital can accommodate at the most 2 electrons with opposite spins
- (b) Half filled orbital or unpaired electron orbital accepts one electron from another atom, to complete its orbital.
- (c) Tendency to complete orbital or to pair the electron is an condition of covalent bond.

Completion of octet is not the essential condition of covalent bond.

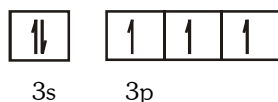
- (d) If the outermost orbit has empty orbitals then covalent bonds are formed in excited state.

### **Variable valency in covalent bonds :**

- (i) Variable valencies are shown by those elements which have empty orbitals in outermost shell.
- (ii) Lone pair electrons get excited in the subshell of the same shell to form the maximum number of unpaired electrons. Maximum covalency is shown in excited state.
- (iii) The energy required for excitation of electrons is called promotion energy.
- (iv) Promotion rule – Excitation of electrons in the same orbit.

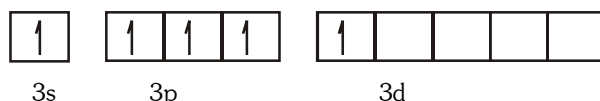
### **Ex.**

- (I) Phosphorus → Ground state



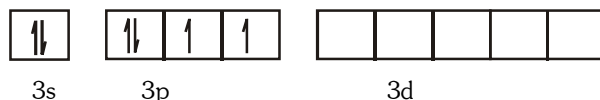
Covalency 3 ( $\text{PCl}_3$ )

Phosphorus → Excited state



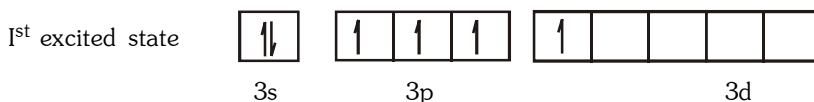
Covalency – 5 ( $\text{PCl}_5$ )

- (II) Sulphur → Ground state.

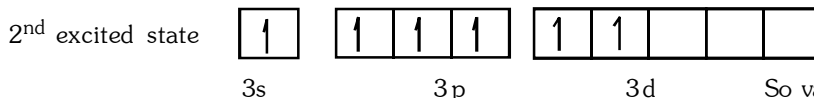


Covalency - 2 ( $\text{SF}_2$ )

Sulphur → Excited state



Covalency - 4 ( $\text{SF}_4$ )



Covalency - 6 ( $\text{SF}_6$ )

So variable covalency of S is 2, 4, & 6.

- (III) Iodine has three lone pair of electrons



So it shows three excited states – Maximum number of unpaired electrons = 7

Variable Valencies are 1, 3, 5, 7

To explain the formation of covalent bond two theories based on quantum mechanics have been proposed.

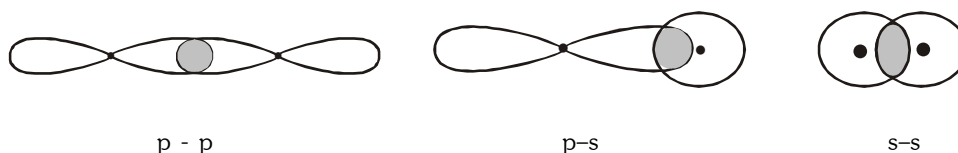
- Valence bond theory (VBT)
- Molecular orbital theory (MOT)

### • **VALENCE BOND THEORY (VBT)**

- (A) Overlapping theory                      (B) Hybridisation theory

## (A) OVERLAPPING THEORY :

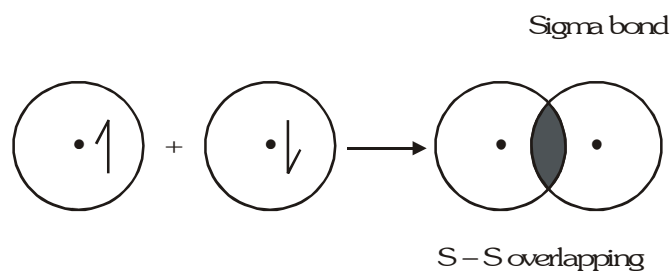
- (1) It was presented by Heitler & London to explain how a covalent bond is formed.
- (2) The main points of theory are –
  - (a) To form a covalent bond overlapping occurs between half filled valence shell orbitals of the two atoms.
  - (b) Resulting bond acquires a pair of electrons with opposite spins to get stability.
  - (c) Orbitals come closer to each other from the direction in which there is maximum overlapping
  - (d) So covalent bond has directional character.
  - (e) Extent of overlapping  $\propto$  strength of chemical bond.
  - (f) Extent of overlapping depends on two factors.
    - (i) Nature of orbitals – p, d and f are directional orbitals  $\rightarrow$  more overlapping  
s-orbital  $\rightarrow$  non directional – less overlapping
    - (ii) Nature of overlapping –  
Co-axial overlapping - extent of overlapping more.  
Collateral overlapping - extent of overlapping less  
Order of strength of Co - axial overlapping –  $p - p > s - p > s - s$

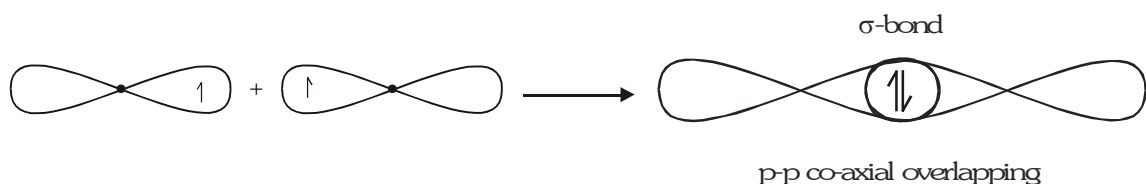


- (g) As the value of  $n$  increases, bond strength decreases.
$$1s - 2p > 2s - 2p > 3s - 3p$$
- (h) If  $n$  is same 
$$2p - 2p > 2s - 2p > 2s - 2s$$
- (i) Electron which is already paired in valency shell can enter into bond formation, if they can be unpaired first and shifted to vacant orbitals of slightly higher energy of the same energy shell.
- (j) This point can explain the trivalency of boron, tetravalency of carbon, pentavalency of phosphorus etc.
- (k) Three types of bonds are formed on account of overlapping.
  - (1) Sigma ( $\sigma$ ) bond
  - (2) Pi ( $\pi$ ) bond
  - (3) delta ( $\delta$ ) bond

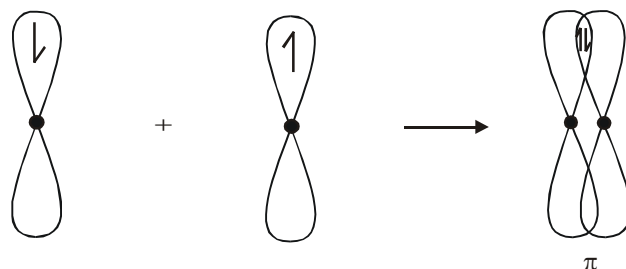
### 1. Sigma ( $\sigma$ ) bond :

When orbitals overlap along their inter nuclear axis,  $\sigma$ -bond is formed **Ex.** The bond formed by overlapping of  $s - s$ ,  $s - p$ ,  $p - p$  (axial),  $sp^3 - s$ ,  $sp^2 - s$ ,  $sp^3 - sp^3$ ,  $sp^3 - sp^2$  &  $sp - sp$  atomic orbitals.



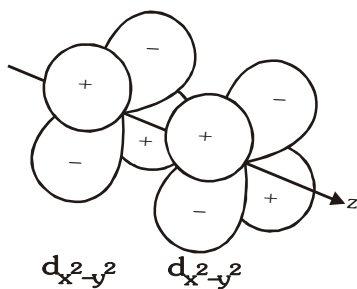


2. **Pi ( $\pi$ ) bond** : When two p-orbitals along the lateral axis (side way),  $\pi$ -bond is formed.



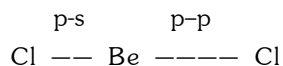
Difference between sigma and pi-bond	
Sigma-bond	Pi-bond
<ol style="list-style-type: none"> <li>1. A <math>\sigma</math>-bond is formed by the axial overlapping of atomic orbitals.</li> <li>2. <math>\sigma</math>-bond formation involves overlapping of s-s, s-p and p-p orbitals.</li> <li>3. <math>\sigma</math>-bond is stronger because of larger extent of overlapping</li> <li>4. The molecular orbital is symmetrical about internuclear axis and electron cloud is present on this axis</li> <li>5. Free rotation exists around a <math>\sigma</math>-bond.</li> <li>6. A sigma bond may exist either alone or or along with <math>\pi</math>-bonds.</li> <li>7. Hybridised orbitals or unhybridised orbitals are involved in <math>\sigma</math>-bond.</li> </ol>	<p>A <math>\pi</math>-bond is formed by the side ways overlapping of orbitals. It involves overlapping of p-p orbitals.</p> <p><math>\pi</math>-bond is relatively weaker because of smaller extent of overlapping.</p> <p>The molecular orbital is discontinuous and consists two electron clouds below and above the internuclear axis</p> <p>Free rotation does not exist around <math>\pi</math>-bonds.</p> <p>A <math>\pi</math>-bond is always present along with a sigma-bond</p> <p>Hybridised orbitals are never involved in <math>\pi</math>-bond.</p>

3. **Delta( $\delta$ )-bond**: It is special type of lateral overlapping in which all four lobes of d-orbital are overlap laterally with other similar d-orbital produce delta( $\delta$ )-bond.



## (B) HYBRIDISATION THEORY

- (a) It is introduced by Pauling and Slater, to explain equivalent nature of covalent bonds in a molecule.  
Consider an example of Be compound :-  
If it is formed without hybridisation then -



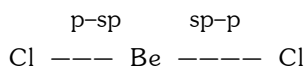
both the Be-Cl bonds should have different parameters and p-p bond strength > s-p bond strength.

Practically bond strength and distance of both the Be-Cl bonds are same.

This problem may be overcome if hybridisation of s and p-orbital occurs.

- (b) **Definition :** Mixing of different shapes and approximate equal energy atomic orbitals, and redistribution of energy to form new orbitals, of same shape & same energy. These new orbitals are called hybrid orbitals. and the phenomenon is called hybridisation.

Now after considering s-p hybridisation in  $\text{BeCl}_2$



bond strength of both the bonds will be equal.

### Characteristic of Hybridisation :

- (a) Hybridisation is a mixing of orbitals and not electrons. Therefore in hybridisation full filled, half filled and empty orbitals may take part.
- (b) Number of the hybrid orbitals formed is always be equivalent to number of atomic orbital which have taken part in the process of hybridisation.
- (c) Each hybrid orbital having two lobes, one is larger and other is smaller. Bond will be formed from large lobe.
- (d) The number of hybrid orbitals on central atom of a molecule or ion = number of  $\sigma$  bonds + lone pair of electron.
- (e) One element can represent many hybridisation state depending on experimental conditions

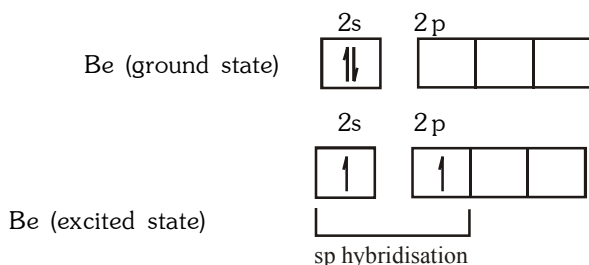
**Ex.** C showing  $sp$ ,  $sp^2$  and  $sp^3$  hybridisation in its compounds.

- (f) Hybrid orbitals are differentiated as  $sp$ ,  $sp^2$ ,  $sp^3$  etc.
- (g) The directional properties in hybrid orbital is more than atomic orbitals. Therefore hybrid orbitals form stronger sigma bond. The directional property of different hybrid orbitals will be in following order.  
 $sp < sp^2 < sp^3 < sp^3d < sp^3d^2 < sp^3d^3$
- (h) Hybridized orbitals show axial overlapping & form  $\sigma$  bond

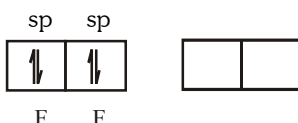
### TYPES OF HYBRIDISATION :

#### 1. $sp$ hybridisation :

- (a) In this hybridisation one s- & one p- orbital of an atom are mixed to give two new hybrid orbitals which are equivalent in shape & energy known as  $sp$  hybrid orbitals.
- (b) These two  $sp$  hybrid orbitals are arranged in a straight line & at bond angle  $180^\circ$ .
- (c) s-character 50%

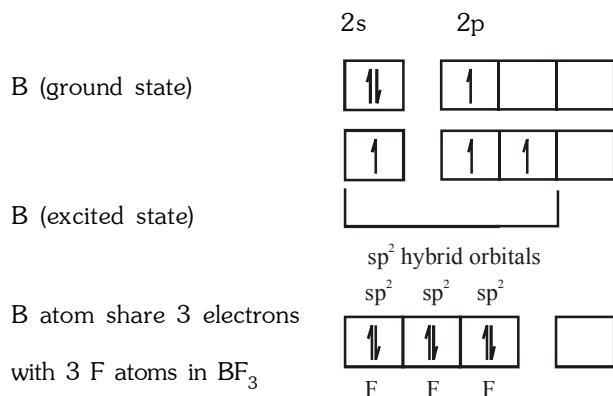


Be atom share two electrons  
with F in  $\text{BeF}_2$ ,



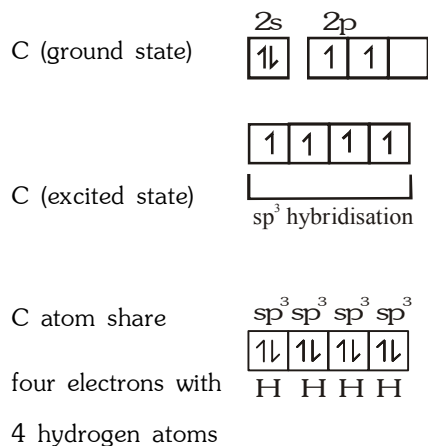
## 2. $sp^2$ Hybridisation :

- In this hybridisation one s & two p orbitals are mixed to give three new  $sp^2$  hybrid orbitals which all are in same shape & equivalent energies.
- These three  $sp^2$  hybrid orbitals are at angle of  $120^\circ$  & giving trigonal planar shape.
- s-character 33.33% in each orbital.



## 3. $sp^3$ Hybridisation :

- In this hybridisation one s orbital & three p orbitals of an atom of a molecule or ion, are mixed to give four new hybrid orbitals called as  $sp^3$  hybrid orbitals.
- The angle between these four hybrid orbitals will be  $109^\circ 28'$

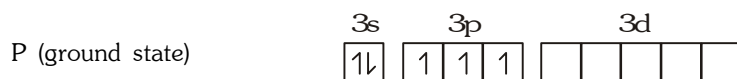


- The shape obtained from these hybrid orbitals would be tetrahedron.

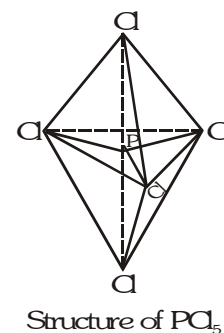
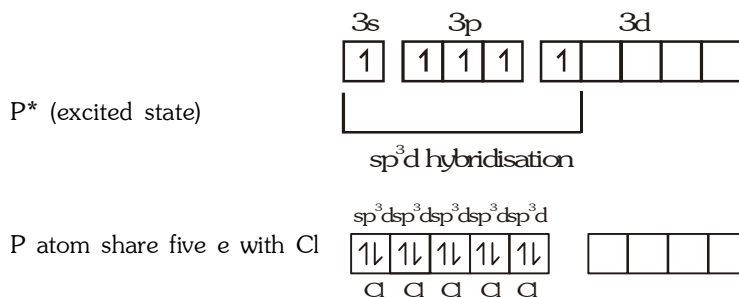
## 4. $sp^3d$ Hybridisation :

- In this hybridisation one s orbital, three p orbitals and one d orbital are mixed to give five new hybrid orbitals which are equivalent in shape and energy called as  $sp^3d$  hybrid orbitals.
- Out of these five hybrid orbitals, three hybrid orbitals are at  $120^\circ$  angle and two hybrid orbitals are perpendicular to the plane of three hybrid orbitals that is trigonal planar, the shape of molecule becomes is trigonal bipyramidal.

For example,  $PCl_5$  showing  $sp^3d$  hybridisation







- (c) In this hybridisation  $dz^2$  orbital is hybridised with s and p orbitals.

In this way five  $sp^3d$  hybrid orbitals form five sigma bond with five Cl atoms and give a molecule of  $PCl_5$ , shape of this molecule is trigonal bipyramidal.

Axial two P-Cl bonds are longer than equatorial three P-Cl bond due to repulsion

between 3 equatorial b.p. of  $e^-$  and 2 axial b.p. of  $e^-$

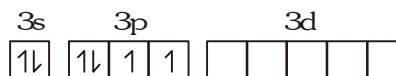
## 5. $sp^3d^2$ Hybridisation :

- (a) In this hybridisation, one s-orbital, three p-orbitals & two d-orbitals are mixed to give six new hybrid orbitals known as  $sp^3d^2$  hybrid orbitals.
- (b) The shape of molecule obtained from above six hybrid orbitals will be symmetrical octahedral.
- (c) The angle between all hybrid orbitals will be  $90^\circ$ .

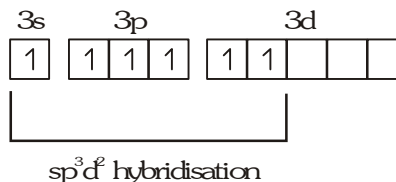
**Ex.**  $SF_6$ ,  $AlF_6^{-3}$ ,  $PF_6^-$ ,  $ICl_5$ ,  $XeF_4$ ,  $XeOF_4$ ,  $ICl_4^-$ ,

- (d) Two 'd' orbital participates in the hybridisation are  $dx^2-y^2$  and  $dz^2$ .

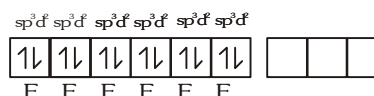
**$SF_6$**  S (ground state)



S ( $II^{nd}$  excited state)

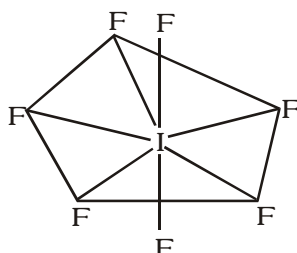


S (after hybridisation) share  $6e^-$  with 6 F atoms





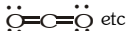
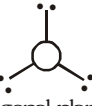
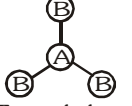
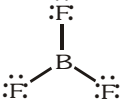
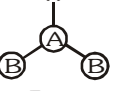
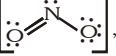

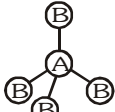
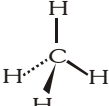
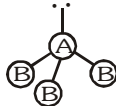
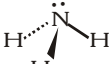


## 6. $sp^3d^3$ Hybridisation :


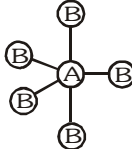
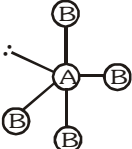
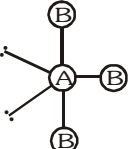
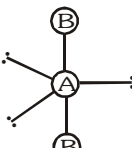

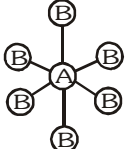
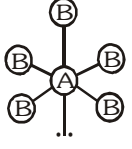
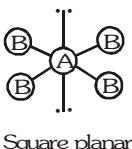
- (a) In this hybridisation, one s-orbital, three p-orbitals & three d-orbitals are mixed to give seven new hybrid orbitals known as  $sp^3d^3$  hybrid orbitals.
- (b) In this hybridisation d-orbitals used are  $d_{xy}$ ,  $d_{x^2-y^2}$  &  $d_{z^2}$  orbitals.
- (c) These seven  $sp^3d^3$  orbitals are configured in pentagonal bipyramidal shape.
- (d) Five bond angles are of  $72^\circ$  & ten bond angles of  $90^\circ$ .
- (e) The following examples showing  $sp^3d^3$  hybridisation -  $IF_7$  &  $XeF_6$ .



## VALENCE SHELL ELECTRON PAIR REPULSION THEORY (VSEPR)

- (a) Molecules having covalent bond have definite geometry as covalent bonding has directional characteristics. A simple theory was given for the molecular shape of the covalent molecules by Gillespie and Nyholm in 1957.
- (b) This theory predicts the shape of the molecule by considering the most stable configuration of the bond angles in the molecule. This theory states
- (i) Electron pairs in the valence shell of the central atom of a molecule, whether bonding or lone pairs are regarded as occupying localised orbitals. These orbitals arrange themselves in so as to minimize the mutual electronic repulsions.
- (ii) The magnitude of the different types of electronic repulsions follows the order given below:  
**lone pair-lone pair > lone pair - bonded pair > bonded pair - bonded pair**
- (iii) The electronic repulsion between two pairs of electrons will be minimum if they are as far apart as possible.
- (iv) The actual shape of the molecules containing lone pairs is a little distorted from the basic shape as in the  $\text{NH}_3$  and  $\text{H}_2\text{O}$  molecules, the bond angles are not  $109^\circ 28'$  but  $107^\circ$  and  $104.5^\circ$  respectively due to presence of one lone pair in  $\text{NH}_3$  and two lone pairs in  $\text{H}_2\text{O}$ .

Number of electron pairs	Molecule type	Electronic geometry	Bonding pair	Non-bonding pair (E)	Molecular geometry	Example
2	$\text{AB}_2$		2	0	 Linear	$\text{BeF}_2, \text{BeCl}_2$ Linear  etc
3	$\text{AB}_3$	 Trigonal planar	3	0	 Trigonal planar	
	$\text{AB}_2$	Trigonal planar	2	1	 Bent	 $\text{SO}_2, \text{O}_3$
4	$\text{AB}_4$	 Tetrahedral	4	0	 Tetrahedral	
	$\text{AB}_3\text{E}$	Tetrahedral	3	1	 Trigonal pyramidal	
	$\text{AB}_2\text{E}_2$	Tetrahedral	2	2	 Bent	

5	$AB_5$	 Trigonal bipyramidal	5	0	 Trigonal bipyramidal	$PCl_5$
	$AB_4E$	Trigonal bipyramidal	4	1	 See saw	$SF_4$
	$AB_3E_2$	Trigonal bipyramidal	3	2	 T-shaped	$ClF_3$
	$AB_2E_3$	Trigonal bipyramidal	2	3	 Linear	$XeF_2$
6	$AB_6$	 Octahedral	6	0	 Octahedral	$SF_6$
	$AB_5E$	Octahedral	5	1	 Square pyramidal	$BrF_5$
	$AB_4E_2$	Octahedral	4	2	 Square planar	$XeF_4$

### Determination of hybridisation state :

#### Method (I)

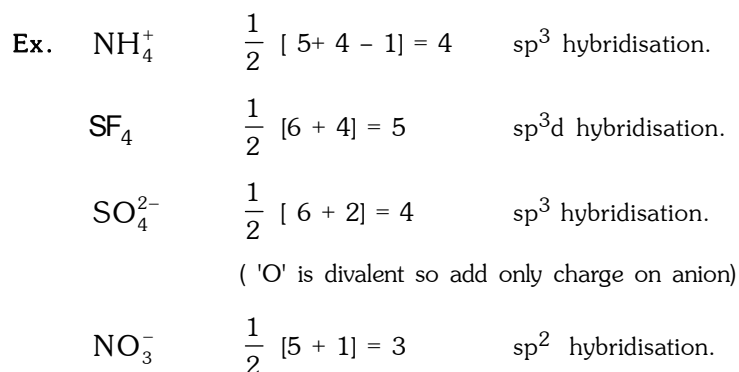
Count the following pair of  $e^-$  around the central atom :

- Count all pure  $\sigma$  bonded electron pairs (or  $\sigma$  bonds)
- Count all lone pair of electron
- Count all coordinate bond.
- Count all negative charge.

## Method (II)

To predict hybridisation following formulae may be used :

No. of hybrid orbital =  $\frac{1}{2}$  [Total number of valence  $e^-$  in the central atom + total number of monovalent atoms - charge on cation + charge on anion]



If such type of  $e^-$  pairs are -

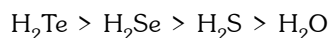
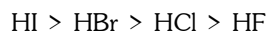
two	-	$\text{sp}$	hybridisation
three	-	$\text{sp}^2$	hybridisation
four	-	$\text{sp}^3$	hybridisation
five	-	$\text{sp}^3\text{d}$	hybridisation
six	-	$\text{sp}^3\text{d}^2$	hybridisation
seven	-	$\text{sp}^3\text{d}^3$	hybridisation

## BOND LENGTH

- (i) The internuclear distance between the two single covalently bonded atoms is called bond length or bond distance.
- (ii) If the electronegativities of both the atoms are equal, then the bond length is equal to the sum of the covalent radii of two bonded atoms.  $d_{A-A} = r_A + r_A$
- (ii) If the electronegativities of two bonded atoms differ, then the bond length is smaller than the sum of their covalent radii.  $d_{A-B} < r_A + r_B$

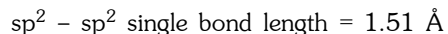
### Factors affecting bond length

- (i) **Size of atoms:**

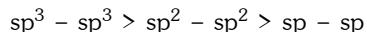
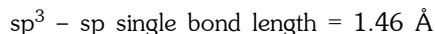


- (ii) **Hybridization state of the bonded atoms:** If the s-character in hybridization state of the bonded atoms increases, the C-H bond distance decreases.

Ex. In C - C single bond.



Bond length decreases in the order



- (iii) **Resonance or delocalisation of electrons of the bond:** Bond length between atoms are changed if a molecule shows resonance.

## BOND ANGLE

The angle between two bonds is known as bond angle.

### Factors affecting bond angle

- (i) **Hybridisation state of central atom:** Compounds having different hybridisation have different bond angle.

Ex.	BeH <sub>2</sub>	BH <sub>3</sub>	CH <sub>4</sub>
Hybridisation	sp	sp <sup>2</sup>	sp <sup>3</sup>
Bond angle	180°	120°	109°28'

- (ii) **Lone pair of electron:** If compounds have same hybridisation states then bond angle depends on lone pair of electron.

Ex.	CH <sub>4</sub>	NH <sub>3</sub>	H <sub>2</sub> O
Hybridisation	sp <sup>3</sup>	sp <sup>3</sup>	sp <sup>3</sup>
Lone pair e <sup>-</sup>	zero	one	two
Bond angle	109°28'	107°	105°

The different in bond angle is explained on the basis of following repulsion sequence

The repulsion between

**lone pair-lone pair > lone pair - bonded pair > bonded pair - bonded pair**

- (iii) **Electronegativity:** When compounds having same hybridisation state of central atom and some number of lone pair of electrons, then bond angle depends on electronegativity.

Bond angle  $\propto$  electronegativity

Ex.	H <sub>2</sub> O > H <sub>2</sub> S
	NH <sub>3</sub> > PH <sub>3</sub>

E.N. of oxygen is more than sulphur therefore the bond angle in H<sub>2</sub>O will be more than H<sub>2</sub>S.

- (iv) **Size of terminal atoms:** When size of terminal atoms increases, bond angle increases.

Ex.	OF <sub>2</sub> < Cl <sub>2</sub> O < Br <sub>2</sub> O
	PF <sub>3</sub> < PCl <sub>3</sub> < PBr <sub>3</sub>

## BOND ENERGY

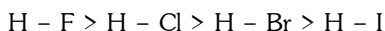
- (i) The amount of energy required to break one mole of the bond and separate the bonded atoms in the gaseous state is known as the bond energy of that particular bond.

- (ii) B.E. is expressed in KJ mol<sup>-1</sup> (in SI units) or in Kcal mol<sup>-1</sup>.

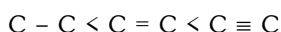
### Factors affecting bond energy

- (a) **Electronegativity difference of the bonded atoms :** As the EN difference of the bonded atoms increases the bond energy increases because the ionic nature of the bond increases.

Ex. Bond strength of hydrogen halides decreases in the order



- (b) **Bond Order** Bond energy  $\propto$  Bond order, therefore the increasing order of bond energy is

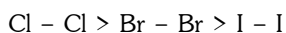


- (c) **Hybridisation state of the bonded atoms :** Bond energy  $\propto$  s-character

Ex.	-C - H < -C = H < -C $\equiv$ H
	sp <sup>3</sup> sp <sup>2</sup> sp

- (d) **Atomic size of bonded atoms :** Atoms with small atomic radii form stronger bonds because the extent of overlapping of atomic orbitals is more

**Ex.** B.E. of halogens is of the order



because their atomic sizes are in the order  $\text{Cl} < \text{Br} < \text{I}$ .

- (e) **Extent of overlapping of atomic orbitals:** A larger extent of overlapping of component atomic orbitals imparts great strength to the bond.
- (f) **Repulsion between the lone pairs of electrons of bonded atoms:**

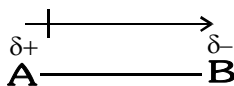
$$\text{Bond energy} \propto \frac{1}{\text{No. of lone pair of electron on the bonded atoms}}$$

**Ex.** the bond energies of the following single bonds having zero, one, two and three lone pair of electrons are in the order.



### DIPOLE MOMENTS & MOLECULAR POLARITY

- (a) The degree of polarity of covalent bond is given by the dipole moment ( $\mu$ ), which is the product of either charge ( $e$ ) and the distance ( $d$ ) between them.  $\mu = d \cdot e$ . 'e' is the order of magnitude of the electronic charge, i.e., about  $10^{-10}$  esu and  $d$  is the distance between the atomic centres, i.e., about  $10^{-8}$  cm.
- (b) Hence dipole moments may be expected to have value around  $10^{-10} \cdot 10^{-8} = 10^{-18}$  esu-cm. It is however, general practice to express dipole moments in **Debye units (D)**,  $1 \text{ D} = 10^{-18}$  esu-cm.



Electronegativity of A < Electronegativity of B

If the charge is in SI units (Coulombs) and  $d$  in metre,  $\mu$  will be coulomb-metre (cm) unit.

$$1\text{D} = 3.336 \cdot 10^{-30} \text{ cm}$$

- (c) Any covalent bond which has a certain degree of polarity will have a corresponding dipole moment, though it does not follow that compound containing such bonds will have dipole moment, for the polarity of the molecule as a whole is the vector sum of the individual bond moment.

$$\mu_{\text{resultant}} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta}$$

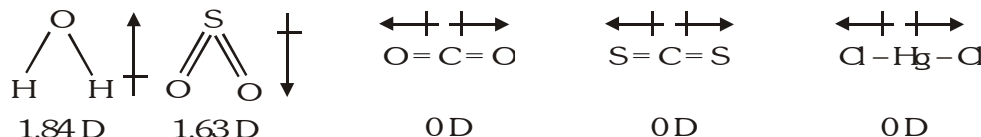
- (i) For example,  $\text{CO}_2$  is a linear molecule,  $\text{O} = \text{C} = \text{O}$ , so that the dipole moments of the two  $\text{C} = \text{O}$  bonds cancel out.
- (ii) The  $\text{C} \rightarrow \text{Cl}$  bond has a definite polarity and a definite dipole moment but carbon tetrachloride has zero dipole moment because it is a tetrahedral molecule, and the resultant of the 4  $\text{C} - \text{Cl}$  bond moments is zero.
- (iii) On the contrary  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  have definite dipole moments.
- (Order of dipole moment  $\text{CH}_3\text{Cl} > \text{CHCl}_3 > \text{CH}_2\text{Cl}_2 > \text{CCl}_4 = \text{CH}_4$ )

### **Application of Dipole Moment Measurements**

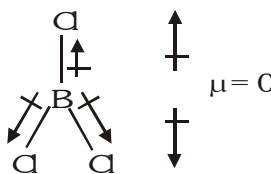
Dipole moment is a measure of the electrical dissymmetry (polarity) in the molecule and so its measurement provides valuable information concerning the shape of molecules. Conversely, when the symmetry of the molecules is known, dipole moment could be estimated fairly.

## 1. Inorganic substances:

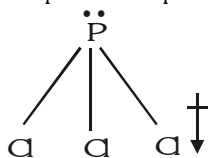
- (a) Monoatomic molecules such as He, Ne, etc., have zero dipole moment because they are symmetrical.
- (b) Diatomic molecules such as  $H_2$ ,  $Cl_2$  and  $N_2$  have no dipole moment; so these molecules are symmetrical.
- (c) Triatomic molecules some of these molecules possess zero dipole moment so they have a symmetrical linear structure, **Ex.**  $CO_2$ ,  $CS_2$ ,  $HgCl_2$ . Others like water and sulphur dioxide have definite dipole moments. They are said to have angular or bent structures. (V-shaped)



- (d) Tetratomic molecules some molecules like  $BCl_3$  have zero dipole moment. They are said to possess a flat and symmetrical (triangular) structure; other example are  $BF_3$ ,  $BBr_3$ ,  $CO_3^{2-}$ , and  $NO_3^-$

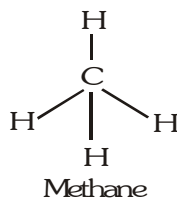


- (e)  $PCl_3$ ,  $AsCl_3$ ,  $NH_3$ ,  $PH_3$ ,  $AsH_3$ ,  $H_3O^+$  have appreciable dipole moment. They possess trigonal pyramidal structure.

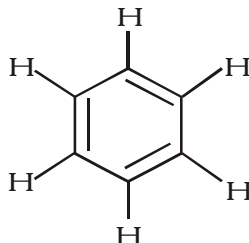


## 2. Organic substances

- (a) Methane and  $CCl_4$  have zero dipole moment. So they possess symmetrical tetrahedral structures with C atom at the centre of the tetrahedron.

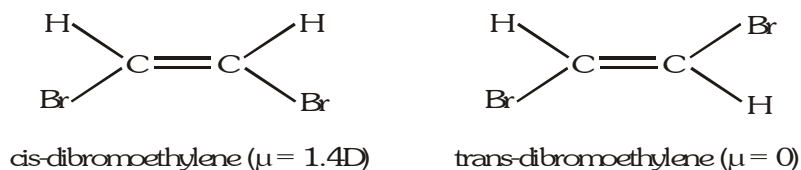


- (b) Benzene has zero dipole moment. All the 6C and 6H atoms are assumed to be in the same plane (symmetrical hexagonal structure).

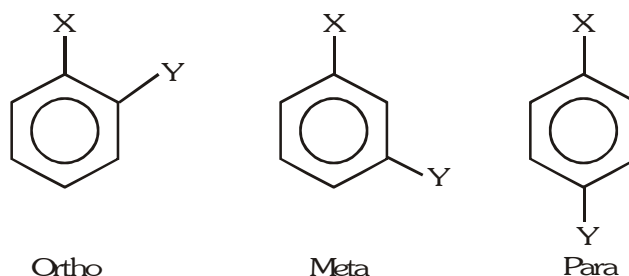


- (c) Measurement of dipole moments will enable us to detect cis-and trans isomers of organic compounds (you will learn about cis-trans or geometrical isomerism later in the organic chemistry).

The trans-isomer, which is symmetrical, has zero dipole moment while the cis-isomer has a definite dipole moment.



- (d) The dipole moments of the aromatic compounds present a very good illustration of dipole moment. We know that when substituted benzene is treated with reagent different products (namely ortho, meta and para products) are formed. The dipole moments of these products are different since the orientation of the groups is different. Let us take an example to clarify it. Let us take three isomers. o-nitrophenol, m-nitrophenol and p-nitrophenol. We also have three other isomers, o-aminophenol, m-aminophenol and p-aminophenol. We want to arrange these isomers in the order of their dipole moments.



In those cases where  $X = Y$ , the para isomer becomes symmetrical and have zero dipole moment. In order to find their dipole moment, we need to know about the nature of the groups linked to the benzene ring. In nitro phenols, one group (OH) is electron pushing and the other ( $\text{NO}_2$ ) is electron withdrawing while in aminophenols, both the groups (OH and  $\text{NH}_2$ ) attached are electron pushing. So, depending on the nature of the groups attached, the isomers have different dipole moment. Then calculation of dipole moment follows as:

**Case (i) :** When X and Y both are electron pushing or electron withdrawing.

Let the bond dipole of C-X bond is represented by  $\mu_1$  and that of C-Y bond by  $\mu_2$ . Now let us assume that the electgron pushing groups have +ve bond moment and the electron withdrawing groups have -ve bond moment. The net dipole moment is the resultant of two bond dipoles at different orientations.

$$\mu_{\text{ortho}} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos 60^\circ} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2} \frac{1}{2}$$

$$\therefore \mu_o = \sqrt{\mu_1^2 + \mu_2^2 + \mu_1\mu_2}$$

$$\mu_{\text{meta}} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos 120^\circ}$$

$$\therefore \mu_m = \sqrt{\mu_1^2 + \mu_2^2 - \mu_1\mu_2}$$

$$\mu_{\text{para}} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos 180^\circ} = \sqrt{\mu_1^2 + \mu_2^2 - 2\mu_1\mu_2}$$

$$\therefore \mu_p = \mu_1 - \mu_2$$

From the above expressions of  $\mu_o$ ,  $\mu_m$  and  $\mu_p$ , it is clear that when both X and Y are of the same nature i.e., both are electron withdrawing or both are electron pushing the para product has the least dipole moment and ortho product has the highest dipole moment. When  $X = Y$ ,  $\mu_1 = \mu_2$ , thus  $\mu_p$  would be zero.

**Case (ii) :** When X is electron pushing and Y is electron withdrawing or vice versa.

Let the bond moment of C-X dipole is  $\mu_1$  and that of C-Y dipole is  $\mu_2$ .

$$\begin{aligned} \mu_o &= \sqrt{\mu_1^2 + (-\mu_2)^2 + 2\mu_1(-\mu_2)\cos 60^\circ} = \sqrt{\mu_1^2 + \mu_2^2 - \mu_1\mu_2} \\ &= \sqrt{(\mu_1 + \mu_2)^2 - 3\mu_1\mu_2} \end{aligned}$$

$$\begin{aligned} \mu_{\text{meta}} &= \sqrt{\mu_1^2 + (-\mu_2)^2 + 2\mu_1(-\mu_2)\cos 120^\circ} = \sqrt{\mu_1^2 + \mu_2^2 + \mu_1\mu_2} \\ &= \sqrt{(\mu_1 + \mu_2)^2 - \mu_1\mu_2} \end{aligned}$$

$$\mu_{\text{para}} = \sqrt{\mu_1^2 + (-\mu_2)^2 + 2\mu_1(-\mu_2)\cos 180^\circ} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2} = \mu_1 + \mu_2$$

Looking at the expressions of  $\mu_o$ ,  $\mu_m$  and  $\mu_p$ , it is clear that the para isomer has the highest dipole moment and ortho has the least.



### 3. Dipole moment and percentage ionic character

The measured dipole moment of a substance may be used to calculate the percentage ionic character of a covalent bond in simple molecules.

1 unit charge = Magnitude of electronic charge =  $4.8 \times 10^{-10}$  e.s.u.

1 D =  $1 \times 10^{-18}$  e.s.u cm.

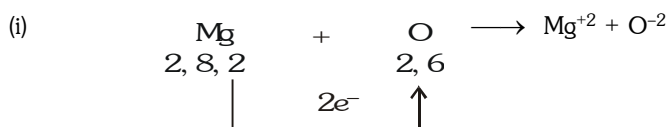
$$\therefore \% \text{ ionic character} = \frac{\text{Observed dipole moment}}{\text{Theoretical dipole moment}} \times 100$$

Theoretical dipole moment is confined when we assume that the bond is 100% ionic and it is broken into ions while observed dipole moment is with respect to fractional charges on the atoms of the bond.

#### ELECTROVALENT OR IONIC BOND

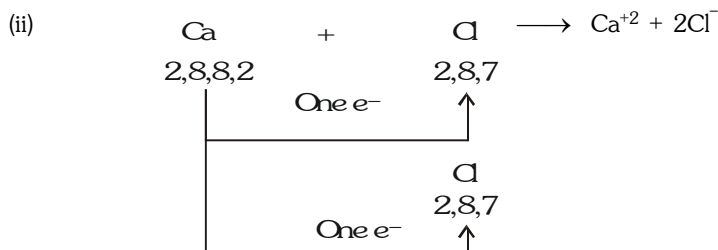
- (a) The chemical bond formed between two or more atoms as a result of the complete transfer of one or more electrons from one atom to another is called Ionic or electrovalent bond.
- (b) Electro positive atom loses electron (group IA to IIIA)
- (c) Electro negative atom gains electron (group VA to VIIA)
- (d) Electrostatic force of attraction between cation and anion is called ionic bond or electrovalent bond.
- (e) Total number of electron lose or gained is called electrovalency.

**Ex.**



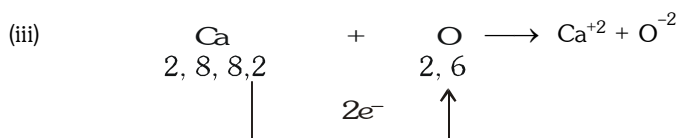
electrovalency of Mg = 2

electrovalency of O = 2



electrovalency of Ca = 2

electrovalency of Cl = 1



electrovalency of Ca = 2

electrovalency of O = 2

- (f) The force of attraction is equal in all direction so ionic bond is non-directional.
- (g) A definite three dimensional structure is formed called crystal lattice.
- (h) Ionic compound do not have molecular formula. It has only empirical formula.

**Ex.** NaCl is empirical formula of sodium chloride

## FORMATION OF IONIC COMPOUND - BORN HABER CYCLE

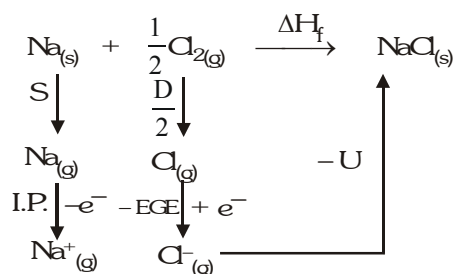
- (a) When elements react to form compounds,  $\Delta G$  (the free energy of formation) is negative. For a reaction to proceed spontaneously, the free energy of the products must be lower than that of the reactants.
- (b) Usually the energy changes are measured as enthalpy values  $\Delta H$ , and  $\Delta G$  is related to  $\Delta H$  by the equation

$$\Delta G = \Delta H - T\Delta S$$

In many cases enthalpy values are used instead of free energy values, and the two are almost the same if the term  $T\Delta S$  is small. At room temperature  $T$  is almost 300 K, so  $\Delta G$  and  $\Delta H$  are similar when the change in entropy  $\Delta S$  is very small. Entropy changes are large when there is a change in physical state, **Ex.** solid to liquid, or liquid to gas, but otherwise entropy changes are usually small.

- (c) A whole series of energy changes is involved when one starts from the elements and finishes with an ionic crystal. These changes are shown in the Born-Haber cycle.

Formation of NaCl (s) involves



thus 
$$S + \text{I.P.} + \frac{D}{2} - \text{EGE} - U = \Delta H_f$$

here  $S$  = heat of sublimation of Na(s)

I.P. = ionisation potential of Na(g)

$D$  = bond dissociation energy of  $\text{Cl}_2$

EGE = electron gain enthalpy of Cl(g)

$U$  = lattice energy

$\Delta H_f$  = enthalpy heat of formation of NaCl(s)

If lattice is  $\text{MgX}_2(\text{s})$  then

$$S + (\text{IP}_1 + \text{IP}_2) + D - 2\text{EGE} - U = \Delta H_f$$

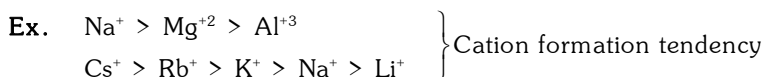
where  $(\text{IP}_1 + \text{IP}_2)$  = total ionisation energy to form  $\text{Mg}^{2+}_{(\text{g})}$  from  $\text{Mg}_{(\text{g})}$ .

## FACTORS FAVOURING IONIC BONDING

- (a) **Ionisation energy :**

Amount of energy required to remove an electron from the outermost orbit of an isolated gaseous atom to form the +ve ion or cation. (energy absorbed)

Lesser Ionization 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 -ve ion (anion) energy released.

Higher electron affinity  $\rightarrow$  Greater tendency to form anion

Ex.  $\text{Cl}^- > \text{F}^- > \text{Br}^- > \text{I}^-$

$\text{F}^- > \text{O}^{2-} > \text{N}^{3-}$

(c) **Lattice energy** - (Energy released)

The energy released in the formation of 1g mole electrovalent compound from isolated gaseous ions is called lattice energy (U) of that compound.

Higher lattice energy  $\rightarrow$  Greater will be the stability or strength of ionic compound.

**Factors affecting lattice energy :**

(i) Magnitude of charge  $\rightarrow U \propto z^+ z^-$  (Ionic charge)

Lattice energy  $\propto$  Magnitude of charge

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

- $\longrightarrow$
- Lattice energy increases
  - Size of cation decreases.

(ii) Size of Cation :- Lattice energy  $\propto \frac{1}{r^+ + r^-}$

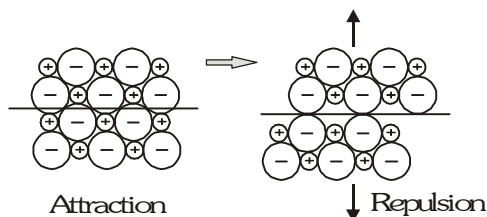
LiCl	NaCl	KCl	RbCl	CsCl
------	------	-----	------	------

- $\longrightarrow$
- Size of cation increasing
  - Size of anion is constant
  - Lattice energy decreases.

**PROPERTIES OF IONIC COMPOUND**

(a) **Physical state** - Ionic compounds are hard, crystalline and brittle due to strong electrostatic force of attraction.

Brittleness  $\rightarrow$  {Same charged ions comes nearer. So they repel each other}



(b) **Isomorphism** : Different ionic compounds, having same configuration/geometry of ions are isomorphs of each other and phenomenon is known as isomorphism

Ex. NaF, MgO,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . All alums  $\text{M}_2'\text{SO}_4 \cdot \text{M}_2''(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ .

(c) **Boiling point and melting point** -

Ionic compounds have high boiling point and melting point due to strong electrostatic force of attraction among oppositely charged ions.

(d) **Conductivity** - It depends on ionic mobility.

(i) In solid state - No free ions - Bad conductor of electricity.

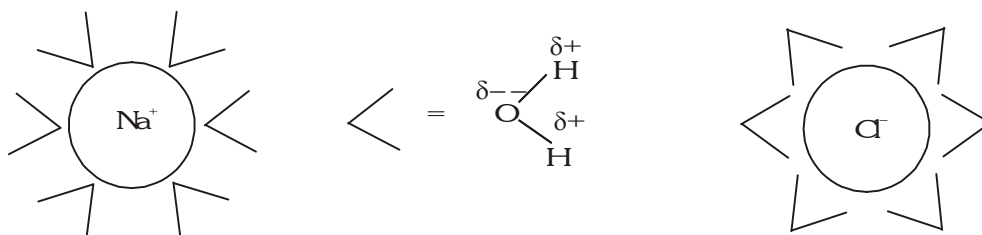
(ii) In fused state or aqueous solution Due to free ions - Good conductor of electricity.

**Conductivity order**                      Solid state < fused state < Aqueous solution

(e) **Solubility** – Highly soluble in water (Polar solvents) **Ex.** NaCl in water

(i) The  $\text{Na}^+$  ions get associated with -vely charged 'O' of water

(ii) And  $\text{Cl}^-$  ions associated with +vely charged 'H' of water.



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

(iv) The energy released due to interaction between solvent and solute is called solvation energy. If water is used as solvent it is called hydration energy.

(v) For an ionic compound to be soluble in water – Hydration energy > Lattice energy

$$\text{Lattice energy} \propto \frac{1}{\text{Solubility}}$$

$$\text{Hydration energy} \propto \text{Solubility.}$$

$$\text{Hydration energy (H)} \propto \frac{1}{r^+} + \frac{1}{r^-} \quad \{ r^+ \text{ \& } r^- \text{ are radius of cation and anion} \}$$

(vi) Hydration energy mainly depends on the cation radius because the value of  $\frac{1}{r^-}$  is negligible in comparison to  $\frac{1}{r^+}$

(vii) Down the group both the lattice energy & hydration energy decreases, if decrease in lattice energy is greater than hydration energy, solubility increases down the group and vice versa.

#### FACTOR AFFECTING SOLUBILITY :

(a) **Dielectric constant of solvent** –

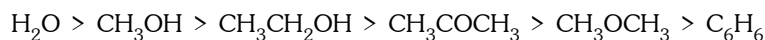
The capacity of solvent to neutralise the charge of ionic compounds is called Dielectric constant. It is represented by  $\epsilon$ .

(i) Water has maximum dielectric constant ( $\epsilon = 80$ )

( $\text{CH}_3\text{OH}$   $\epsilon = 35$ ) , (Acetone  $\epsilon = 21$ )

( $\text{C}_2\text{H}_5\text{OH}$   $\epsilon = 27$ ) , (Ether  $\epsilon = 4.1$ )

(Benzene  $\epsilon = 2.3$ )



(ii) Ionic compounds are more soluble in the solvents, having high dielectric constant.

(iii)  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  have high dielectric constant but these are not a good solvent due to oxidising nature.

(b) **Size of ion** :

(i) Keeping size of cation constant, the lattice energy decreases with the increase of anionic radius.

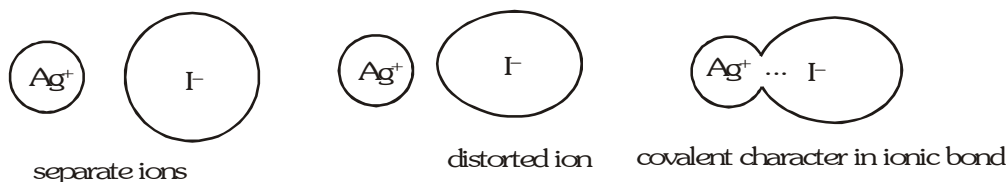
Hence order of solubility of  $\text{LiX}$  in water is  $\text{LiF} < \text{LiCl} < \text{LiBr} < \text{LiI}$

$$\text{As solubility} \propto \frac{1}{\text{lattice energy}}$$

- (ii) In LiI covalent nature is more according to Fajan's rule but  $HE > LE$  therefore LiI is more soluble in water.
  - (iii) Keeping size of anion constant, the hydration energy decreases with the increase of cationic radius. Hence order of solubility of  $MSO_4$  will be –  $BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$  ( Exception of Fajan's rule)
  - (iv) If size of cation and anion is very large, solubility decreases from top to bottom.
  - (v) Solubility decreases in a period (as ionic nature decreases and covalent nature increases)
- $NaCl > MgCl_2 > AlCl_3$

### TRANSITION FROM IONIC TO COVALENT BOND – FAJANS' RULE

- (a) Just as a covalent bond may have partial ionic character an ionic bond may also show a certain degree of covalent character. When two oppositely charged ions approach each other closely, the cation would attract the electrons in the outer shell of the anion and simultaneously repel its nucleus. This produces distortion or polarization of the anion, which is accompanied by some sharing of electrons between the ions, i.e., the bond acquires a certain covalent character. The formation of a covalent bond between two ions may be illustrated with reference to formation of AgI.



- (b) **FACTORS INFLUENCING ION – DEFORMATION OR INCREASING COVALENT CHARACTER**

- (i) **Large charge on the ions:**

The greater the charge on the cation, the more strongly will it attract the electrons of the anion. For example,  $Al^{3+}$  can distort  $Cl^-$  ion more than  $Na^+$  ion. So aluminium chloride is a covalent compound whereas NaCl,  $AlF_3$ , AgF are ionic.

- (ii) **Small cation and large anion:**

For a small cation, the electrostatic force with which its nucleus will attract the anion will be more. Moreover a large anion cannot hold the electrons in its outermost shell, especially when they are attracted by a neighbouring cation. Hence there will be increased covalent character with a small cation and a large anion, as in AgI.

- (iii) **Cation with a pseudo-inert gas type of electronic configuration:**

A cation with a 18 electron in outermost shell such as  $Ag^+$  ( $[Kr] 4d^{10}$ ) polarizes anions more strongly than a cation with a 8 electron arrangement as in  $K^+$ . The 'd' electrons in  $Ag^+$  do not screen the nuclear charge as effectively as the 's' and 'p' electron shell in  $K^+$ . Thus AgI is more covalent than KI, although  $Ag^+$  and  $K^+$  ions are nearly of the same size. Cuprous and mercurous salts are covalent.

The above statements regarding the factors, which influence covalent character, are called Fajans' rules. It can thus be seen easily that there is nothing like a purely ionic compound or a purely covalent compound.

Polarisation power of a cation is usually called ionic potential or charge density.

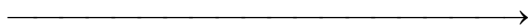
$$\text{Ionic potential } \phi (\text{phi}) = \frac{\text{Charge on cation}}{\text{Size of cation}}$$

## APPLICATION OF THE CONCEPT OF POLARISATION :

(a) To determine covalent and ionic character of molecule : -

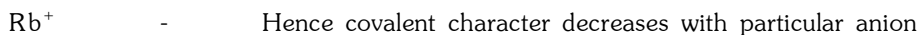
$$\phi \propto \frac{\text{Covalent character}}{\text{Ionic character}}$$

From left (larger size) to right (smaller size) in a period  $\phi$  increases so covalent character increases.



- charge increases
- size decreases  $\phi$  increases
- Covalent character increases with particular anion

From top to bottom in a group  $\phi$  decreases so covalent, character decreases.



(b) To determine nature of oxide : -

$$\sqrt{\phi} < 2.2 \quad (\text{Basic oxides})$$

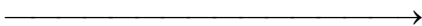
$$\sqrt{\phi} = 2.2 \text{ to } 3.2 \quad (\text{Amphoteric oxides})$$

Neutral oxides doesn't react with acid & base eg. H<sub>2</sub>O, CO etc.

Amphoteric oxides (Al<sub>2</sub>O<sub>3</sub> etc.) reacts with acid & base

$$\sqrt{\phi} > 3.2 \quad (\text{Acidic oxide})$$

Ex. Li<sub>2</sub>O, Na<sub>2</sub>O, K<sub>2</sub>O, Rb<sub>2</sub>O, Cs<sub>2</sub>O



- $\sqrt{\phi}$  decreases
- Basic character increases

(c) To determine conductivity of metal halides (MX)

If  $\sqrt{\phi} < 2.2$  MX - ionic nature

If  $\sqrt{\phi} > 2.2$  MX - covalent nature

(d) **Formation of complex compounds :-**

Smaller the cation, more will be the tendency of forming complex compounds.

High value of  $\phi$  shows tendency of forming complex compounds.

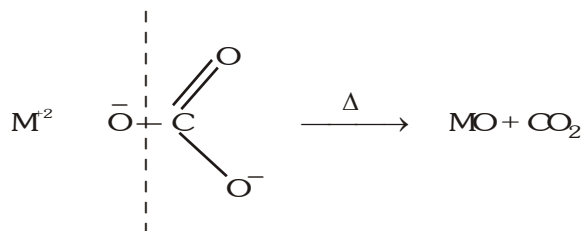
If  $\phi$  is low  $\rightarrow$  No or less tendency of forming complex compounds.

- s-block metals (larger size) doesn't have the tendency to form complex compounds.

Exceptions - Li, Be, Mg (small size)

- d-block metals have the tendency to form complex compounds (small in size, high charge).

(e) **To determine thermal stability of metal carbonates :** stability  $\propto \frac{1}{\phi}$  (Covalent nature)

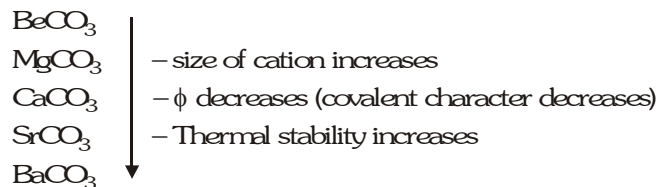


More smaller the size of metal cation, its polarisation capacity increases - strength of M—O bond increases and C—O bond decreases. So thermal stability of carbonates decreases.



From top to bottom thermal stability of carbonates increases (as size of cation increases)

(Ionic character increases or covalent character decreases)



(f) **To explain colour of compounds : -**

More the covalent character, more will be the colour intensity.

Colour density  $\propto \phi$  (Covalent character)

Ex.	AgCl	AgBr	AgI
	(White)	(Light yellow)	(Dark yellow)
	SnO <sub>2</sub>	SnS <sub>2</sub>	
	(White)	(Yellow)	

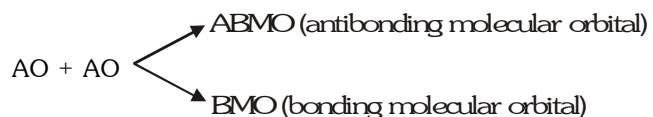
(g) **To explain diagonal relationship :-**

Since the value of  $\phi$  for Be<sup>2+</sup> is almost of the same order as that of diagonally situated Al<sup>3+</sup>. Hence have many similar properties. Similarly value of  $\phi$  for Li<sup>+</sup> is equal to Mg<sup>+2</sup>, so have diagonal relationship.

## MOLECULAR ORBITAL THEORY (MOT):

Given by hund & Mulican

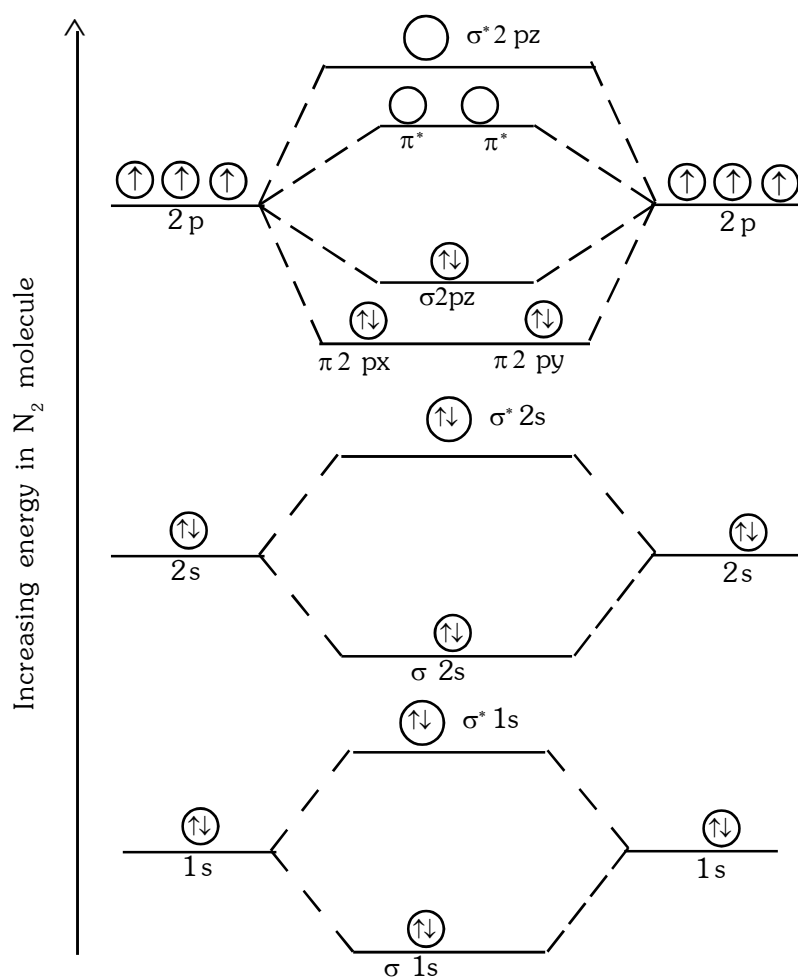
- (a) Two atomic orbital come nearer & then overlap each other to form two molecular orbitals (MO)
- (b) Combination of two atomic orbital (AO) forms two molecular, orbital (MO):



- (c) Both orbitals can be filled by electrons according to Aufbau principle.
- (d) Energy of BMO < Energy of ABMO.
- (e) Order of energy in molecular orbitals of di-atomic molecules.
- (i) From  $H_2$  to  $N_2$ :

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \pi 2p_z = \pi 2p_y < \sigma 2p_x < \pi^* 2p_z = \pi^* 2p_y < \sigma^* 2p_x$$

**For  $N_2$  molecule**

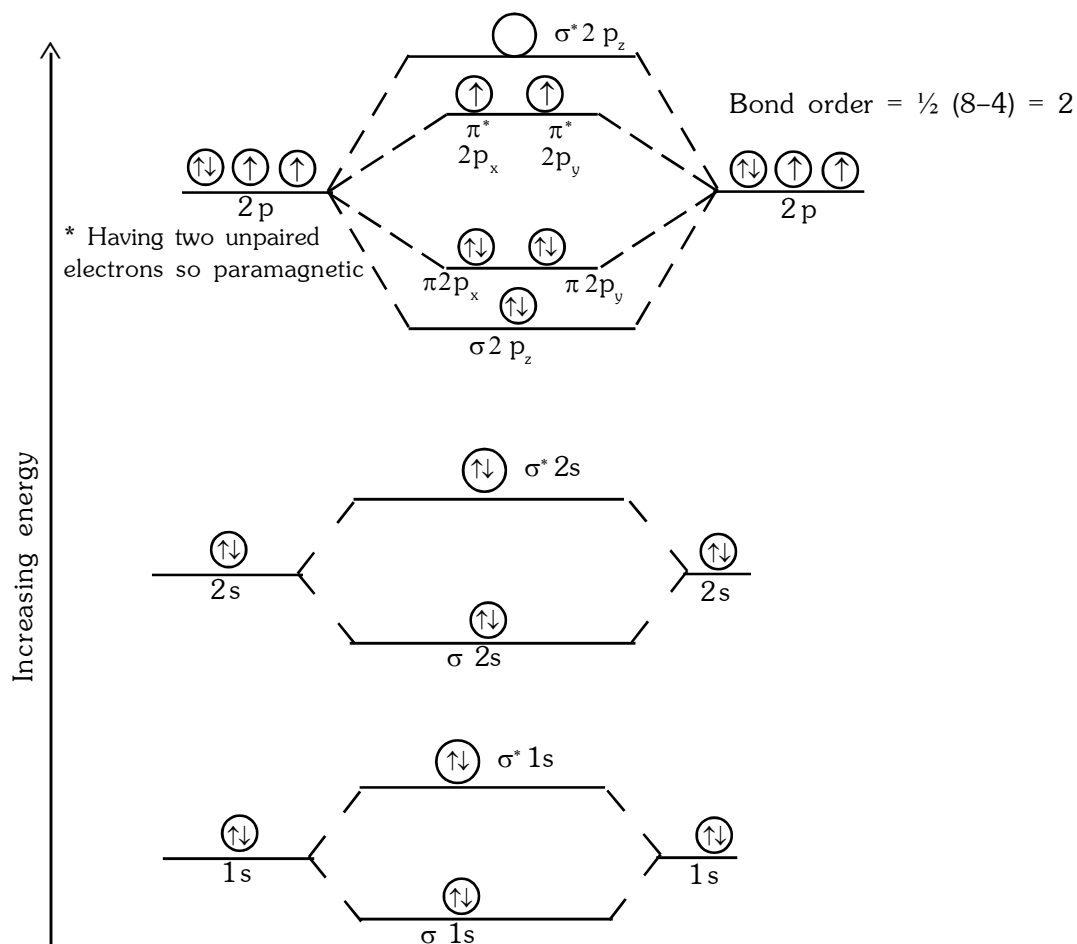




(ii) For  $O_2$  &  $F_2$ :

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_x < \pi 2p_z = \pi 2p_y < \pi^* 2p_z = \pi^* 2p_y < \sigma^* 2p_x$$

For  $O_2$  molecule



$\sigma^*, \pi^* =$  antibonding molecular orbital

$\sigma, \pi =$  bonding molecular orbital

$$\text{Bond order} = \frac{N_b - N_a}{2}$$

$N_b =$  No. of electron in bonding MO's

$N_a =$  No. of electron in antibonding MO's

(g) If bond order = 0, it means species does not exist.

(h) Bond order of 1, 2 & 3 corresponds to a single bond, double & triple bond respectively.

(i) Bond order  $\uparrow$  stability of molecule  $\uparrow$  bond length  $\downarrow$

(j) If the molecule has one or more unpaired electron, it will be paramagnetic, while if all the electrons are paired it will be diamagnetic.

**Ex.**  $H_2 =$  Configuration :  $\sigma (1s)^2 \sigma^* (1s)^0$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2 - 0}{2} = 1, \quad \text{Hence H - H (diamagnetic)}$$

## MO Electronic Configuration of Some Molecules

Molecule or ion	Total no. of electrons	MO configuration	Bond order behaviour	Magnetic
H <sub>2</sub>	2	(σ 1 s) <sup>2</sup>	1	Diamagnetic
H <sub>2</sub> <sup>+</sup>	1	(σ 1 s) <sup>1</sup>	0.5	Paramagnetic
H <sub>2</sub>	3	(σ 1 s) <sup>2</sup> , (σ * 1 s) <sup>1</sup>	0.5	Paramagnetic
He <sub>2</sub>	4	(σ 1 s) <sup>2</sup> , (σ * 1 s) <sup>2</sup>	0	Diamagnetic
N <sub>2</sub>	14	KK (σ 2s) <sup>2</sup> , (σ * 2s) <sup>2</sup> , (π 2p <sub>y</sub> ) <sup>2</sup> =(π 2p <sub>z</sub> ) <sup>2</sup> , (σ 2p <sub>x</sub> ) <sup>2</sup>	3	Diamagnetic
O <sub>2</sub>	16	KK (σ 2s) <sup>2</sup> , (σ * 2s) <sup>2</sup> (σ 2p <sub>x</sub> ) <sup>2</sup> , (π 2p <sub>y</sub> ) <sup>2</sup> =(π 2p <sub>z</sub> ) <sup>2</sup> (π * 2p <sub>y</sub> ) <sup>1</sup> (π * 2p <sub>z</sub> ) <sup>1</sup>	2	Diamagnetic
O <sub>2</sub> <sup>+</sup>	15	Remove one electron from π * 2p <sub>z</sub> from O <sub>2</sub>	2.5	Paramagnetic
O <sub>2</sub> <sup>2+</sup>	14	Same as that of N <sub>2</sub>	3	Diamagnetic
O <sub>2</sub>	17	KK (σ 2s) <sup>2</sup> , (σ * 2s) <sup>2</sup> (σ 2p <sub>x</sub> ) <sup>2</sup> , (π 2p <sub>y</sub> ) <sup>2</sup> , (π 2p <sub>z</sub> ) <sup>2</sup> (π * 2p <sub>y</sub> ) <sup>2</sup> , (π * 2p <sub>z</sub> ) <sup>1</sup>	1.5	Paramagnetic
O <sub>2</sub> <sup>2-</sup>	18	KK (σ 2s) <sup>2</sup> , (σ * 2s) <sup>2</sup> (σ 2p <sub>x</sub> ) <sup>2</sup> (π 2p <sub>y</sub> ) <sup>2</sup> , (π 2p <sub>z</sub> ) <sup>2</sup> (π * 2p <sub>y</sub> ) <sup>2</sup> , (π * 2p <sub>z</sub> ) <sup>2</sup>	1	Diamagnetic
F <sub>2</sub>	18	Same as above	1	Diamagnetic
Ne <sub>2</sub>	20	18 as above and (σ * 2p <sub>x</sub> ) <sup>2</sup>	0	Diamagnetic
CO	14	Same as in N <sub>2</sub>	3	Diamagnetic
NO	15	Same as in O <sub>2</sub> <sup>+</sup>	2.5	Paramagnetic
NO <sup>+</sup>	14	Same as in N <sub>2</sub>	3	Diamagnetic
NO <sup>2+</sup>	13	KK(σ 2s) <sup>2</sup> (σ * 2s) <sup>2</sup> (σ 2p <sub>x</sub> ) <sup>2</sup> (π 2p <sub>y</sub> ) <sup>1</sup> , (π 2p <sub>z</sub> ) <sup>1</sup>	2.5	Paramagnetic
NO <sup>-</sup>	16	Same as in O <sub>2</sub>	2	Paramagnetic
CN	13	Same as in NO <sup>2+</sup>	2.5	Paramagnetic
CN <sup>-</sup>	14	Same as in N <sub>2</sub>	3	Diamagnetic

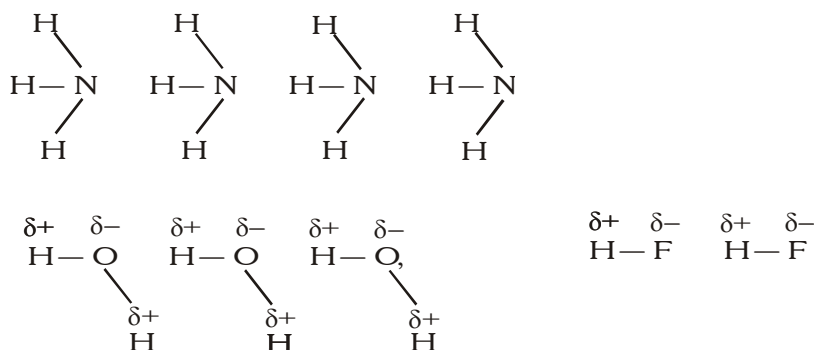
### HYDROGEN BOND

- (a) An atom of hydrogen linked covalently to a strongly electronegative atom can establish an extra weak attachment to another electronegative atom in the same or different molecules. This attachment is called a hydrogen bond.
- (b) To distinguish from a normal covalent bond, a hydrogen bond is represented by a broken line,  
e.g. X – H ... Y where X and Y are two electronegative atoms. The strength of hydrogen bond is quite low about 2-10 kcalmol<sup>-1</sup> or 8.4-42 kJmol<sup>-1</sup>.

(c) Conditions of hydrogen bonding:

- (i) The molecule must contain a highly electronegative atom linked to H-atom. (If E.N.  $\uparrow$  polarity of bond  $\uparrow$ )
- (ii) The size of the electronegative atom should be small. (size  $\downarrow$  electrostatic attraction  $\uparrow$ )

**Ex.**



(d) Strength of H-bond :

H ..... F      bond dissociation energy =  $41.8 \text{ kJ mol}^{-1}$

H ..... O      bond dissociation energy =  $29.3 \text{ kJ mol}^{-1}$

H ..... N      bond dissociation energy =  $12.6 \text{ kJ mol}^{-1}$

(e) Effect of H-bond

- (i) It causes the association of many molecules.
- (ii) Due to hydrogen bond molecules are associated and show high molecular weight.
- (iii) M.P. & B.P. of the molecules increases
- (iv) Viscosity & surface tension of the molecules increases.
- (v) The compounds which can form H-bond with the covalent molecules are soluble in such solvents.

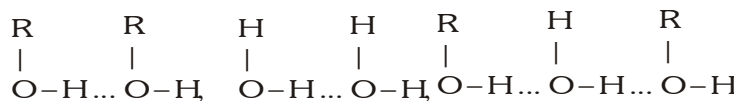
Examples : Alcohol & Ammonia are water soluble.

**Type of H-bonding :**

- (a) Intermolecular
- (b) Intramolecular

**(a) Intermolecular H-bond:**

- (i) This type of H-bonding takes place between two molecules. **Ex.** ROH,  $\text{H}_2\text{O}$ , R - OH &  $\text{H}_2\text{O}$



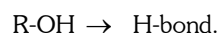
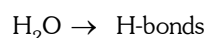
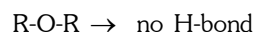
- (ii) In such compounds molecular wt., M.P. & B.P. are high.
- (iii) Extent of H-bonding  $\uparrow$  viscosity & density  $\uparrow$ .

**(b) Intramolecular Bond:**

- (i) It is the H-bonding in the same molecule of a compound. The bonding also known as chelation.
- (ii) Solubility in water, M.P. & B.P. of these compounds decreases.
- (iii) The value of acid strength of acid depends on the relative stability of the acid and its conjugated base if the intermolecular H-bonding stabilises the conjugate base then, the acid strength increase and if the conjugate acid is stabilised in this way then the acid strength decreased.

**H-bond has serious consequences on the physical properties. These are –**

- (i)  $\text{H}_2\text{O}$  is liquid at room temperature whereas  $\text{H}_2\text{S}$  is gas at room temperature although  $\text{H}_2\text{S}$  has greater molecular weight.
- (ii) Ice is lighter than water, although it solid because in ice  $\text{H}_2\text{O}$  molecules are extending their H-bonds to full length and six water molecules produce a cage like structure which is porous in nature leading to smaller mass and larger volume, thus lowering the density.
- (iii) Alcohols have higher boiling points than corresponding alkanes and there of the same molecular mass. This can be explained by the intermolecular H-bonds existing among the  $\text{R-OH}$  molecules whereas ethers and hydrocarbon are not capable to have such strong intermolecular forces. thus they have lower boiling points.

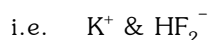


- (iv) Alcohol and water are miscible in any proportion due to formation of H-bonds.
- (v) Ammonia is excessively soluble in water whereas other gases are partially soluble. This is due to the tremendous capacity of  $\text{NH}_3$  molecule to generate 4-H-bonds.



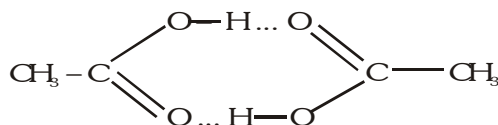
- (vi) Solubility order of different amines and ammonia in water follows the order  $\text{NH}_3 > \text{RNH}_2 > \text{R}_2\text{NH}$ . This can be explained by the capacity of these elements to form H-bonds.

- (vii)  $\text{KHF}_2$  exists whereas  $\text{KCl}_2$ ,  $\text{KBr}_2$ ,  $\text{KI}_2$  do not because  $\text{KHF}_2$  is constituted by 2 ions

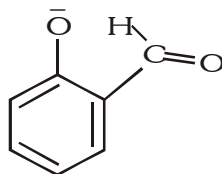


$\text{KHF}_2$  is a red orange coloured solid.

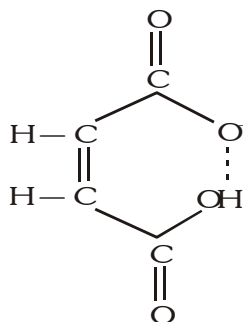
- (viii) o-nitro phenol is steam volatile and less  $\text{H}_2\text{O}$  soluble than its corresponding para isomer because in o-nitro phenol, intra molecular H-bond exists which reduces the capacity of the molecule to produce intermolecular H-bonds with other molecules like water. This brings intermolecular forces among the o-nitrophenol molecules resulting into high volatility.
- (ix) Acetic acid has a molecular weight of 60 in benzene and it shows a very high boiling points. This is due to dimerization of molecule.



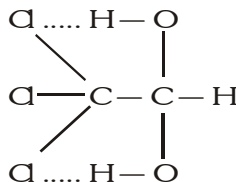
- (x) Salicylic acid has very high acidity due to chelation of salicylate ion through the H-bond



- (xi) Chelation means to grab atoms in vicinity as much as possible.
- (xii) Maleic acid has greater acidity than fumaric acid. This can also be explained by chelation of monomaleate anion which has a H-bond between carboxylate anion and the unionized carboxylic acid.

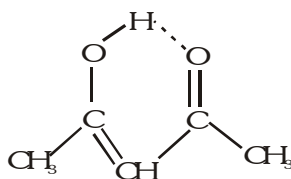


- (xiii) Normally when 2 hydroxyl groups are present on the same carbon atom i.e. gem diols are unstable, but "chloralhydrate" is a stable molecule due to formation of H-bond.



- (xiv)  $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$

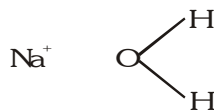
In the above compound, (acetyl acetone) enol form is stable because of the intramolecular H-bond.



## VANDER WALL'S FORCES

- (a) These are the weakest type of inter molecular forces that exist among the molecules which bring significant change in physical properties.
- (b) These are non-directional, non-valence cohesive forces. These attractive forces being played between the two molecules are independent of the presence of other molecules.
- (c) Solid, liquid or gaseous states of many molecules are explained on the basis of inter molecular forces other than covalent, ionic or metallic bonds. Although inert gases do not form any type of bond but may exist in liquid and solid states. This shows that the atoms of inert gases are attracted by each other through some type of inter molecular forces. These intermolecular forces are called Vander Walls forces and may be of the following types:

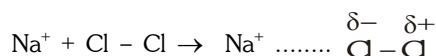
- (d) **Ion-dipole attraction** : Polar molecules are attracted by ions. The negative pole is attracted by cation and positive pole attracted by the anion. This type of attraction is called ion dipole attraction, ion-dipole attraction is observed generally in the process of solvation when sodium chloride ( $\text{Na}^+ \text{Cl}^-$ ) is dissolved in water because negative poles of water aggregate around  $\text{Na}^+$  ions and positive poles around  $\text{Cl}^-$  ions.



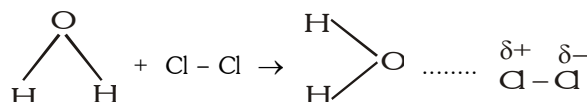
- (e) **Dipole-dipole attraction** : The force of attraction between the oppositely charged poles of two polar molecules (for example :  $\text{H}_2\text{O}$ ,  $\text{H-F}$ ,  $\text{NH}_3$  etc.) is called dipole-dipole attraction. This type of attraction is weaker than the ion-dipole attraction.



- (f) **Ion-induced dipole attraction** : When non polar molecules come in contact with ions, its electron cloud gets polarised and the oppositely charged end of it is attracted by the ion. For example attraction between  $\text{Na}^+$  and  $\text{Cl}_2$  molecule.



- (g) **Dipole-induced dipole attraction** : This type of cohesive forces occurs in a mixture of polar and non polar molecules. The former induce polarity in non polar molecules by disturbing their electron system. for example force of attraction between  $\text{Cl}_2$  and  $\text{H}_2\text{O}$ .



- (h) **Induced-Induced dipole** : The weak intermolecular forces operating in similar non polar gaseous molecules are called London forces. These forces are very weak in nature and exists only at low temperature. For example weak intermolecular forces in  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{N}_2$ , molecules and in noble gases.

