

CHEMICAL BONDING

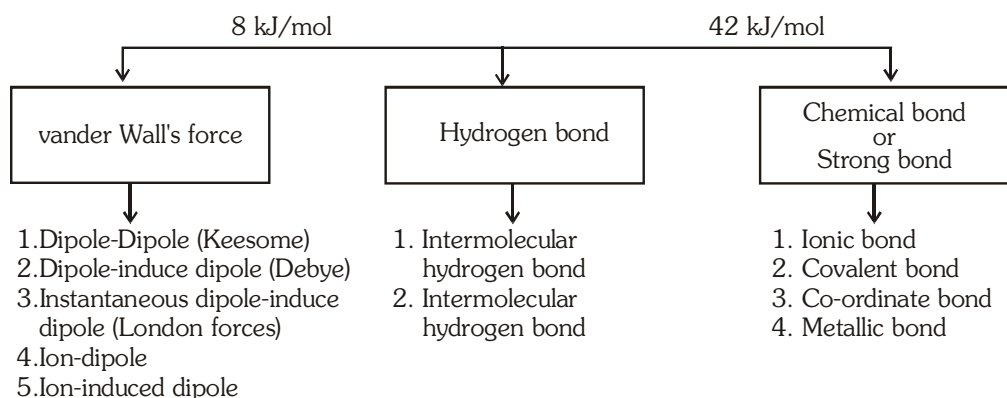
INTRODUCTION

- It is well known fact that except inert gases, no other element exists as independent atom under ordinary conditions.
- 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.
- A molecule will only be formed if it is more stable and has a lower energy, than the individual atoms.

Chemical Bond

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

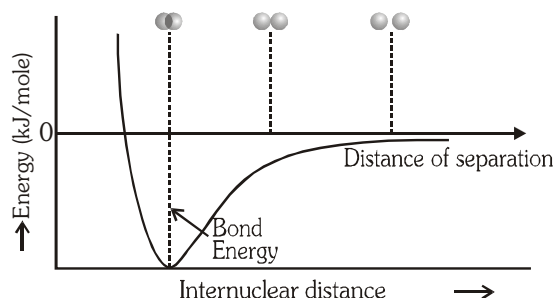
Classification of Bonds



Cause of Chemical Combination

(A) Tendency to acquire minimum energy

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



(B) Tendency to acquire noble gas configuration :

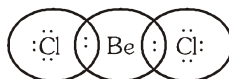
- Atom combines to acquire noble gas configuration.
- Only outermost electrons i.e. ns, np and (n-1)d shells electrons participate in bond formation.
- Inert gas elements do not participate in bond formation, as they have stable electronic configuration hence will have minimum energy. (Stable configuration $1s^2$ or ns^2np^6)

KOSSEL - LEWIS APPROACH TO CHEMICAL BONDING

- Every atom has a tendency to complete its octet in outermost shell
- H has the tendency to complete its duplet.
- To acquire inert gas configuration atoms lose or gain electron or share electron.
- The tendency of atoms to achieve eight electrons in their outer most shell is known as Lewis octet rule.



Obeys octet rule



Doesn't obey octet rule

Exception of Octet Rule

(a) Incomplete octet molecules :- or (electron deficient molecules)

Compound in which octet is not complete in outer most orbit of central atom.

Example - Halides of IIIA groups, BF_3 , AlCl_3 , BCl_3 , hydride of III A/ 13^{th} group etc.

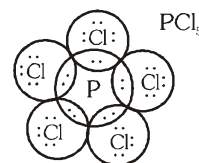


Other examples – BeCl_2 ($4e^-$), HgCl_2 ($4e^-$), $\text{Ga}(\text{CH}_3)_3$ ($6e^-$)

(b) Expansion of octet or (electron efficient molecules)

Compound in which central atom has more than $8e^-$ in outermost orbits.

Example - In PCl_5 , SF_6 and IF_7 the central atom P, S and I contain 10, 12, and 14 electrons respectively.



(c) Pseudo inert gas configuration :-

Cations which contain 18 electrons in outermost orbit

Ex. Ga^{+3} , Cu^+ , Ag^+ , Zn^{+2} , Cd^{+2} , Sn^{+4} , Pb^{+4} etc.

Electronic configuration of Ga - $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^1$

Electronic configuration of Ga^{+3} - $1s^2, 2s^2, 2p^6, \underline{3s^2 3p^6 3d^{10}}$
 $18e^-$

(d) Cations having electron between 9 to 17 in their outer most shell

Ex. Mn^{+2} , Fe^{+2} , Fe^{+3} , Ti^{+2} etc.

Electronic configuration of Fe - $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^6, 4s^2$

Electronic configuration of Fe^{+3} - $1s^2, 2s^2 2p^6, \underline{3s^2 3p^6 3d^5}$
 (less than $18e^-$)

(e) Odd electron molecules :-

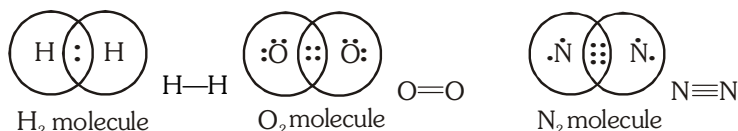
Central atom have an unpaired electron or odd no ($7e^-$, $11e^-$ etc) of electrons in their outer most shell.
 e.g. NO , NO_2 , ClO_2 etc.

VALENCY

It is defined as the combining capacity of the elements. The word valency is derived from an Italian word "Valentia" which means combining capacity.

Note : All the elements of a group have same valencies because they have same number of valence shell electrons.

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



- The shared pair of electrons should have opposite spins, and are localised between two atoms concerned.
- Sharing of electrons may occurs in three ways –

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

Examples - $\text{H}-\ddot{\text{N}}-\text{H}$ { Three single bonds (not triple bond)
 H

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

Orbital Concept of Covalent Bond

- One orbital can accommodate maximum 2 electrons with opposite spins like $\uparrow\downarrow$
- Half filled orbital or unpaired electron orbital share one electron from another atom, to complete its orbital.
- Tendency to complete orbital or to pair the electron is an essential condition of covalent bond.
Completion of octet is not the essential condition of covalent bond.
- **Covalency** : It is the number of covalent bonds which an atom makes in a molecule.
- If the outermost orbit has empty orbitals then covalent bonds are formed in excited state.

VARIABLE VALENCY IN COVALENT BONDS

- Variable valencies are shown by those elements which have empty orbitals in outermost shell.
- 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.
- The energy required for excitation of electrons is called promotion energy.
- Promotion rule – Excitation of electrons in the same orbit.

Example -

(a) Nitrogen \rightarrow Ground state

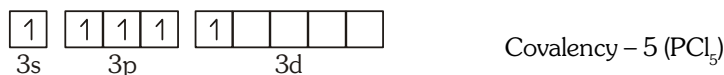


For Nitrogen \rightarrow Excited states are not possible due to absence of vacant orbital that's why (NCl_5) does not exist

(b) Phosphorus → Ground state



Phosphorus \rightarrow Excited state



Note :

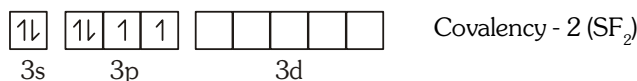
NCl_3 — exists

NCl_5 — doesn't exist (due to absence of d-orbitals in Nitrogen.) While PCl_3 and PCl_5 both exist because 3d orbitals are present in phosphorus.

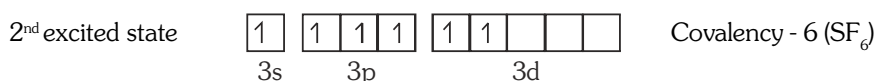
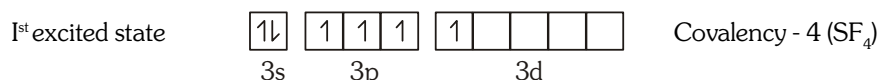
OF_2 — exists, but OF_4 and OF_6 doesn't exist due to absence of d-orbitals While SF_4 and SF_6 exist due to presence of d-orbital which are present in its valence shell.

- It can explain existence of molecules.

(c) Sulphur → Ground state.

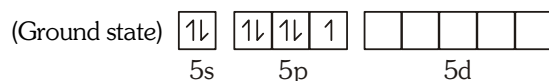


Sulphur → Excited state



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

(d) Iodine has three lone pair of electrons



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

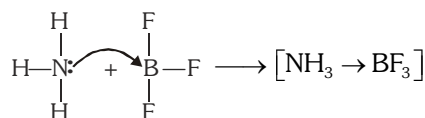
Variable Valencies are 1, 3, 5 and 7

CO-ORDINATE BOND

- (1) It is a covalent bond in which the shared e⁻ pair come from one atom is called coordinate bond.
- (2) Necessary conditions for the formation of coordinate bond are -
 - (a) Octet of donor atom should be complete and should have atleast one lone pair of electron.
 - (b) Acceptor atom should have deficiency of at least one pair of electron.

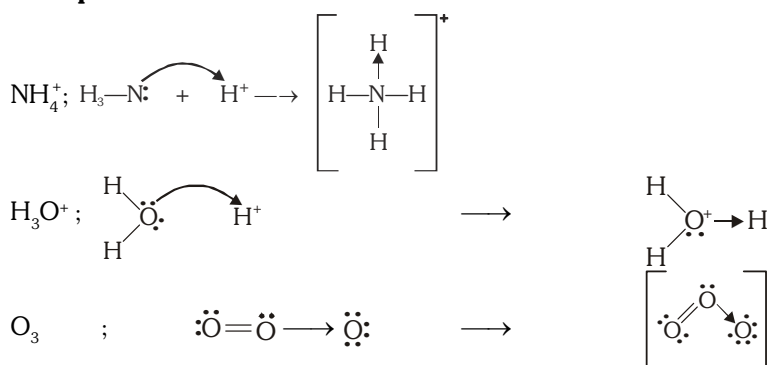


- (3) Atom which provide electron pair for sharing is called donor.
- (4) Other atom which accepts electron pair is called acceptor. That is why it is called donor-acceptor or dative bond.



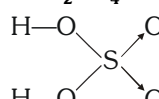
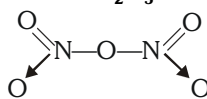
BF_3 is electron deficient compound.

Example :





Metal co-ordinate compounds -



Compounds in which Ionic, covalent and co-ordinate bonds are present, are as follows -



FORMAL CHARGE

The difference between the valence electrons in an isolated atom and the number of valence electrons assigned to that atom in a given Lewis structure is called that atom's formal charge. The formal charge, abbreviated FC, on an atom in a Lewis structure is given by the following relationship:

Formal charge on a atom in a Lewis structure

$$= (\text{total number of valence electrons in the isolated atom}) - (\text{Total number of nonbonding electrons})$$

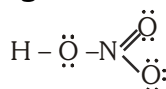
$$- \frac{1}{2} (\text{total number of bonding electrons}) \dots (i)$$

$$\text{or} \quad \text{FC} = (\text{Valence electrons}) - (\text{Nonbonding electrons}) - \frac{1}{2} (\text{bonding electrons})$$

$$= (\text{Valence electrons or group number}) - [(\text{Number of unshared } e\text{'s}) + (\text{Number of bonds})]$$

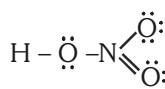
To find the formal charge, we count the bonding electrons as though they are equally shared between the two bonded atoms.

Q. Calculate the formal charges on the various atoms of nitric acid (HNO_3) molecule which has been described by the following Lewis structures:



I

or



II

The H atom : It has one valence electron, zero lone pair (or zero nonbonding electrons), and forms one bond (two bonding electrons).

$$\text{Substituting in Eq. (i), we write} \quad \text{FC} = (1) - (0) - \frac{1}{2}(2) = 0.$$

The O atom bonded to H: It has six valence electrons, two lone pairs (or four nonbonding electrons), and from two bonds (or four bonding electrons).

$$\text{Hence, we write} \quad \text{FC} = (6) - (4) - \frac{1}{2}(4) = 0.$$

The N atom: It has five valence electrons, zero lone pair (or zero nonbonding electrons), and forms four bonds (or has eight bonding electrons).

$$\text{Thus, we write} \quad \text{FC} = (5) - (0) - \frac{1}{2}(8) = +1$$

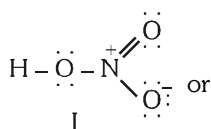
The end O atom in N = O: It has six valence electrons in the free state *but* in the Lewis structure (I or II), it has two lone pairs (or four nonbonding electrons) and forms two bonds (or has four bonding electrons).

$$\text{Thus, we can write} \quad \text{FC} = (6) - (4) - \frac{1}{2}(4) = 0$$

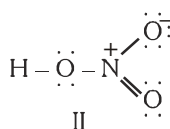
The end O atom in N - O : It has six valence electrons in the free state but in the Lewis structure (I or II), it has three lone pairs or six nonbonding electrons and forms one bond (or has two bonding electrons).

$$\text{thus, we write} \quad \text{FC} = (6) - (6) - \frac{1}{2}(2) = -1$$

We can now write the Lewis structures (I and II) for nitric acid molecule including the formal charges as



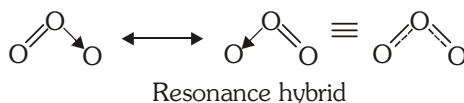
I



II

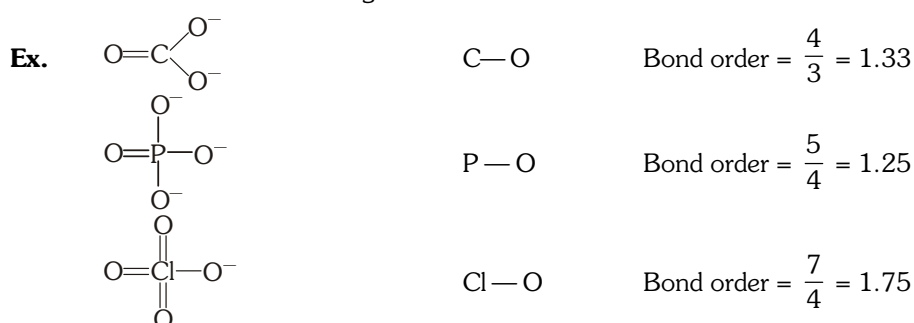
RESONANCE

- (a) It has been found that the observed properties of certain compounds cannot be satisfactorily explained by writing a single lewis structure. The molecule is then supposed to have many structures, each of which can explain most of the properties of the molecule but none can explain all the properties of the molecules. The actual structure is in between of all these contributing structures and is called resonance hybrid and the different individual structures are called resonating structures or canonical forms. This phenomenon is called resonance.
- (b) Let us discuss resonance in ozone, according to its resonance structure it should have one single bond ($\text{O}-\text{O} = 1.48\text{\AA}$) but experiments show that both the bonds are same which can be proved by its resonance hybrid as shown below.



Note : To calculate bond order in the polyatomic molecule or ion use following formula :

$$\text{Bond order} = \frac{\text{Total number of bonds in a molecule}}{\text{Resonating Structures}}$$



VALENCE BOND THEORY (VBT) :

- (A) It was presented by Heitler & London to explain how a covalent bond is formed.
It was extended by Pauling & Slater.
- (B) The main points of theory are –
- To form a covalent bond overlapping occurs between half filled valence shell orbitals of the two atoms.
 - Resulting bond acquires a pair of electrons with opposite spins to get stability.
 - Orbitals come closer to each other from the direction in which there is maximum overlapping
 - So covalent bond has directional character.
 - Strength of covalent bond \propto extent of overlapping.
 - Extent of overlapping depends on two factors.
 - Nature of orbitals – p, d and f are directional orbitals \rightarrow more overlapping
s-orbital \rightarrow non directional – less overlapping
 - 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.

$$1 - 1 > 1 - 2 > 2 - 2 > 2 - 3 > 3 - 3$$

$$1s - 2p > 2s - 2p > 3s - 3p$$

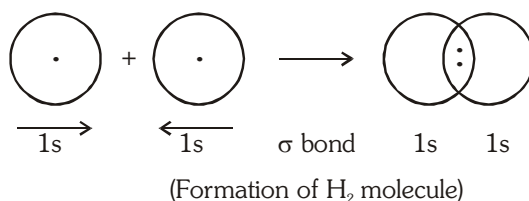
- (h) If n is same $2p - 2p > 2s - 2p > 2s - 2s$
- (i) Electron which is already paired in valency shell can enter into bond formation, if they can be unpaired first and shifted to vacant orbitals of slightly higher energy of the same energy shell.
- (j) This point can explain the trivalency of boron, tetravalency of carbon, pentavalency of phosphorus etc.
- (k) Two types of bonds are formed on account of overlapping.
- (A) Sigma (σ) bond (B) Pi (π) bond

Sigma (σ) Bond

- (a) Bond formed between two atoms by the overlapping of half filled orbitals along their axis (end to end overlap) is called sigma bond.
- (b) σ bond is directional.
- (c) σ bond do not take part in resonance.
- (d) Free rotation is possible about a single σ bond.
- (e) Maximum overlapping is possible between electron clouds and hence it is strong bond.
- (f) There can be only one σ bond between two atoms.

Sigma bonds are formed by four types of overlapping

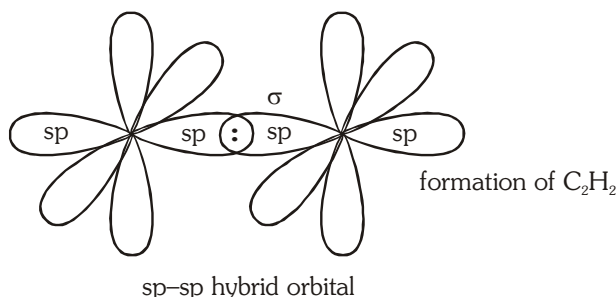
- (i) s - s overlapping – Two half filled s-orbitals overlap along the internuclear axis. Ex. H_2 molecule.



- (ii) s - p overlapping (Formation of HF) – When half filled s-orbital of one atom overlap with half filled p-orbital of other atom.

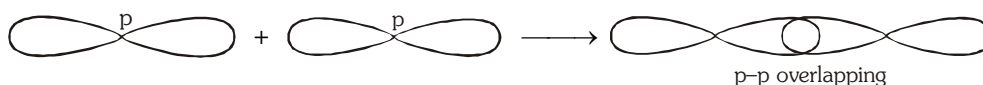


- (iii) Bond between two hybrid orbitals – $sp^3 - sp^3$, $sp^2 - sp^2$, $sp^3 - sp^2$, $sp^3 - sp$ etc.



Note : overlapping of hybrid orbitals form σ bond.

- (iv) p - p overlapping – (Coaxial) – It involves the coaxial overlapping between half filled p-orbitals of two different or same atoms.

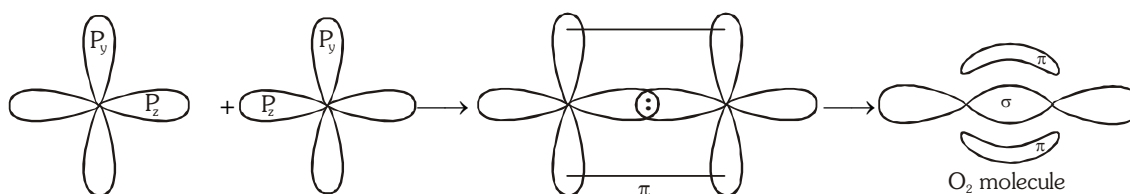


Ex. Formation of Cl_2 , F_2 , Br_2

Pi(π)-Bond

- (a) The bond formed by sidewise (lateral) overlapping are known as π bonds.
 (b) Lateral overlapping is only partial, so formed are weaker and hence more reactive than σ bonds (Repulsion between nucleus is more as orbitals have to come much close to each other for π bonds formation)

Example – Formation of O_2 molecule –



Note : Only two porbitals of oxygen atom have unpaired e^- in each orbital for bonding.

Electron configuration of oxygen is – $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$

- (c) Free rotation about a π bond is not possible.
 (d) π bond is weaker than σ bond (Bond energy difference is 63.5 KJ or 15 K cal/mole)
 (e) π bonds are less directional, so do not determine the shape of a molecule.
 (f) π bond takes part in resonance.
 (g) π bond formed by pure or unhybrid orbitals.

Comparison between σ and π bond

σ bond	π bond
1. Formed by axial overlapping	1. Formed by side by side overlapping
2. Involves s-s, s-p, p-p (axial) & hybrid orbitals	2. Involve p-p, p-d & d-d orbital
3. Extent of overlapping is more so stronger	3. Extent of overlapping is less so weaker
4. Free rotation around σ bond is possible	4. Free rotation around π bond is not possible
5. Hybridized or unhybridized orbital forms σ bond	5. Hybridized orbital never forms π bond
6. Independent existence of σ -bond.	6. No independent existence.

HYBRIDISATION

Consider an example of Be compound :-

If it is formed without hybridisation then $\text{Cl} \overset{\text{p}-\text{s}}{\text{---}} \text{Be} \overset{\text{p}-\text{p}}{\text{---}} \text{Cl}$

both the Be–Cl bonds should have different parameters and p–p bond strength > s–p bond strength. But practically bond strength and distance of both the Be–Cl bonds are same.

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

Hybridisation

- (1) It is introduced by Pauling, to explain equivalent nature of covalent bonds in a molecule.
- (2) **Definition** : Mixing of different shape 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.

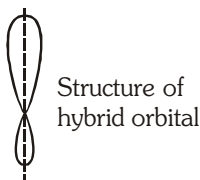
Now after considering s-p hybridisation in BeCl_2



(Bond strength of both the bonds will be equal)

Characteristic of Hybridisation

- (1) Hybridisation is a mixing of orbitals and not electrons. Therefore in hybridisation full filled, half filled and empty orbitals may take part.



- (2) Number of the hybrid orbitals formed is always be equivalent to number of atomic orbital which have taken part in the process of hybridisation.
- (3) Each hybrid orbital having two lobes, one is larger and other is smaller. Bond will be formed from large lobe.
- (4) The number of hybrid orbitals on central atom of a molecule or ion = number of σ bonds + lone pair of electron.
 - (i) The 1st bond between two atoms will be sigma.
 - (ii) The other bond between same two atoms will be pi bond.
 - (iii) The electron pair of an atom which do not take part in bond formation called as lone pair of electron.
- (5) One element can represent many hybridisation state depending on experimental conditions for example, C showing sp, sp^2 and sp^3 hybridisation in its compounds.
- (6) Hybrid orbitals are differentiated as sp, sp^2 , sp^3 etc.
- (7) The repulsion between $\text{lp} - \text{lp} > \text{lp} - \text{bp} > \text{bp} - \text{bp}$
- (8) 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.
 $\text{sp} < \text{sp}^2 < \text{sp}^3 < \text{sp}^3\text{d} < \text{sp}^3\text{d}^2 < \text{sp}^3\text{d}^3$

DETERMINATION OF HYBRIDISATION STATE

Number of hybrid orbital = number of σ bond around CA + number of lone pair on CA
(where CA = central atom)

Number of hybrid orbitals	Hybridisation
two	sp
three	sp^2
four	sp^3
five	sp^3d
six	sp^3d^2
seven	sp^3d^3

S.No.	Formula	Total pair of e^-		Hybridisation	Geometry	Ex.
		bp	lp			
1.	AB_2	2	0	sp	Linear	$BeCl_2, CO_2$
2.	AB_3	3	0	sp^2	Trigonal Planar	BCl_3, BF_3
3.	AB_4	4	0	sp^3	Tetrahedral	CH_4, CCl_4
4.	AB_5	5	0	sp^3d	Trigonal bipyramidal	PCl_5
5.	AB_6	6	0	sp^3d^2	Octahedral (Square bipyramidal)	SF_6
6.	AB_7	7	0	sp^3d^3	Pentagonal bipyramidal	IF_7

Position of lone pair & multiple bond

(i) $sp/sp^2/sp^3 = \text{Any where}$

(ii) $sp^3d = \text{equatorial}$

(iii) $sp^3d^2 = \text{axial (defined first)}$

(iv) $sp^3d \begin{cases} \text{Lone pair} = 1 \text{ then equatorial} \\ \text{Lone pair} = 2 \text{ then axial} \end{cases}$

(v) sp^3d hybridisation Axial bond length > equatorial bond length
 sp^3d^3 hybridisation Axial bond length < equatorial bond length } terminal atom same

Types of Hybridisation

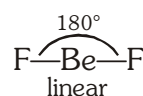
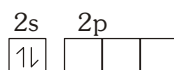
(A) sp hybridisation :

(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.

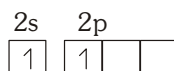
(b) These two sp hybrid orbitals are arranged in straight line & at bond angle 180° .

(c) s-character 50%

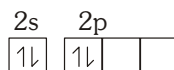
Be (ground state)



Be (excited state)



Be atom accepts two electrons
 from F in BeF_2 ,

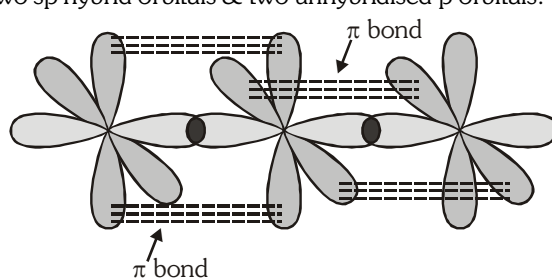


sp hybridisation



CO_2 Molecule ($O = C = O$) :

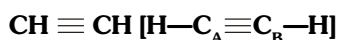
In CO_2 molecule, C has two sp hybrid orbitals & two unhybridised p orbitals.



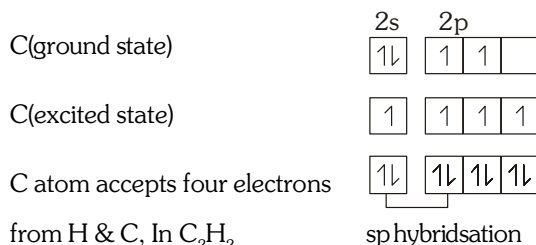
Molecular orbital picture of CO_2

Thus, CO_2 molecule is linear in shape & having 180° bond angle.

The bond length between C-O bond is reduced due to the presence of π bond.



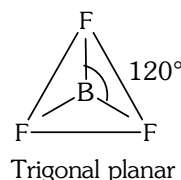
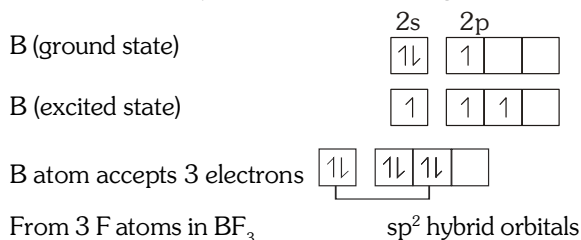
In $\text{CH} \equiv \text{CH}$ molecules, each C atom contains two sp hybrid orbitals & two unhybridised p orbitals



- sp hybrid orbital of each C overlaps to give sigma bond between C – C.
- The remaining one sp hybrid orbital of each C atom overlaps with s orbital of H, forming sigma bond between C – H.
- The two unhybridised p orbitals of each C atom (p_y and p_x) overlap laterally to form two $\pi(\pi)$ bonds.
- Therefore in $\text{H}-\text{C}_A \equiv \text{C}_B-\text{H}$
 - sigma bond between $\text{C}_A - \text{C}_B$ is formed sp – sp overlapping
 - sigma bond between $\text{C}_A - \text{H}$ is formed sp – s overlapping
 - sigma bond between $\text{C}_B - \text{H}$ is formed sp – s overlapping
 - π bond between $\text{C}_A - \text{C}_B$ is formed : $p_y - p_y, p_x - p_x$ overlapping
- Each C atom forms two sigma bonds but in C_2H_2 , total sigma bonds are 3
- Each C atom forms two π bonds. Total π bonds in C_2H_2 are two
- Total number of bonds in acetylene are : $3\sigma + 2\pi$ bond = 5 bonds.

(B) sp^2 Hybridisation :

- (a) In this hybridisation one s & two p orbitals are mixed to give three new sp^2 hybrid orbitals which are in same shape & equivalent energies.
- (b) These three sp^2 hybrid orbitals are at angle of 120° & giving trigonal planar shape.

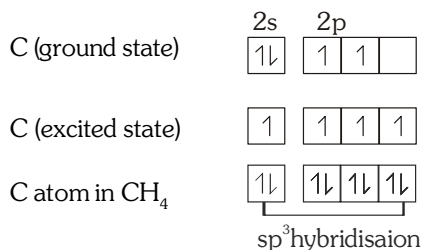


- (c) s - character 33.3 %

- SnX_2 having two σ bonds & one l.p. electron therefore hybridisation is sp^2
- The bond angle in SnX_2 will be less than 120° (due to presence of one l.p.e⁻).
- The shape of SnX_2 molecule is bent.

(C) sp^3 Hybridisation :

- (I) In this hybridisation one s orbital and 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.
- (II) The angle between hybrid orbitals will be $109^\circ 28'$ (6)



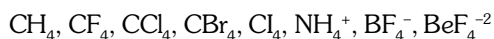
C atom share four electrons with four hydrogen atoms

(III) The shape obtained from these hybrid orbitals would be tetrahedron.

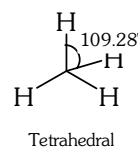
Three following examples represent this condition.

(a) Four sigma bonds with zero lone pair electron :

(I) The following examples represent this condition.

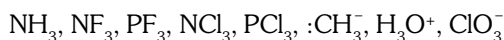


(II) In above compounds, bond angle is $109^\circ 28'$ & tetrahedron shape.



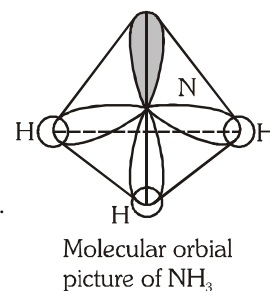
(b) Three sigma bonds & one lone pair of electron :

(I) This condition is shown by following compounds & ions.



(II) sp^3 hybridisation, pyramidal shape & bond angle will be less than $109^\circ 28'$.

Due to the presence of one lone pair electron on nitrogen it repels bond pair electron more therefore bond angle reduced from $109^\circ 28'$ to 107° . The repulsion between lp - bp > bp - bp.



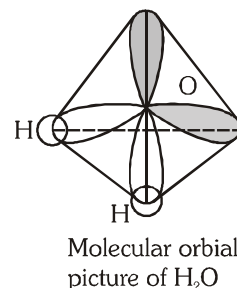
(c) Two sigma bonds & two lone pair of electrons :

(I) This condition is shown by following compounds and ions.



(II) In all above examples, the central atom showing sp^3 hybridisation, angular shape and bond angle will be either less than $109^\circ 28'$ or more than $109^\circ 28'$.

In H_2O the hybridisation on O atom is sp^3 , but due to presence of two lone pair electrons they repel each other

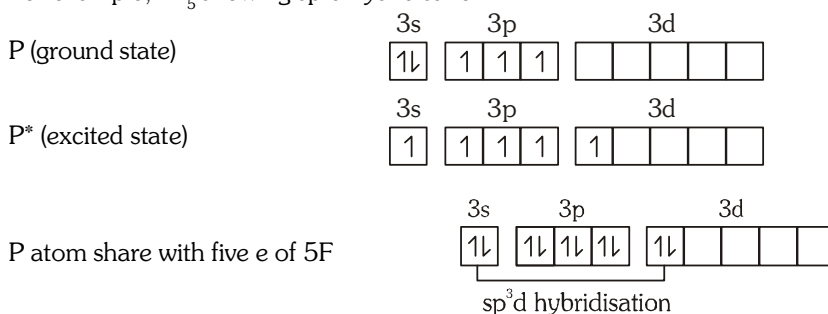


(D) sp^3d Hybridisation :

(I) 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.

(II) Out of these five hybrid orbitals, three hybrid orbitals are at 120° angle and two hybrid orbitals are perpendicular to the plane of three hybrid orbitals that is trigonal planar, the shape of molecule becomes trigonal bipyramidal.

For example, PF_5 showing sp^3d hybridisation



(III) In this hybridisation d_{z^2} orbital is hybridised with s and p orbitals.

In this way five sp^3d hybrid orbitals form five sigma bond with five F atoms and give a molecule of PF_5 , shape of this molecule is trigonal bipyramidal.

Two axial P–Cl bonds are longer than three equatorial P–Cl bonds due to repulsion between 3 equatorial bp of e^- and 2 axial b.p. of e^-

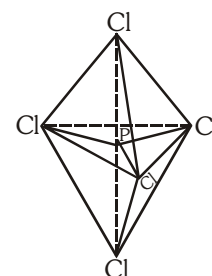
In above hybridisation, there are four conditions.

(a) Five sigma bonds and zero lone pair electron :

The following examples represent this conditions.

PCl_5 , PBr_5 , AsF_5 , $AsCl_5$, $SbCl_5$, SbF_5 etc.

The shape of all the above molecules is trigonal bipyramidal.



Structure of PCl_5

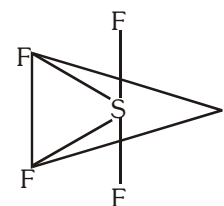
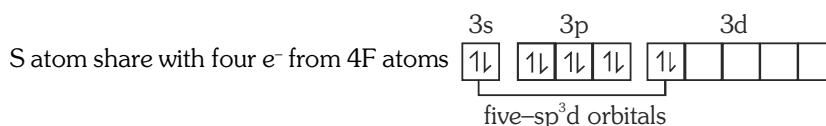
(b) Four sigma bonds and one lone pair of electron :

The following examples represent this condition.

SF_4 , SeF_4 , TeF_4 , PoF_4 , PF_4^- , SbF_4^- , SCl_4 , $SeCl_4$, $TeCl_4$ etc.

The shape of all above examples will be irregular tetrahedron or See-saw

Example SF_4



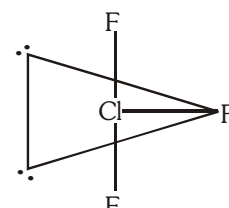
Structure of SF_4

(c) Three sigma bonds & two lone pair of electrons :

The following examples represent this condition.

ClF_3 , BrF_3 , IF_3 , $BrCl_3$, ICl_3 etc.

The shape of all above compounds is 'T' shape.



Structure of ClF_3

(d) Two sigma bonds & three lone pair of electrons :

The following examples represent this condition.

ICl_2^- , IBr_2^- , ClF_2^- , IF_2^- , BrF_2^- , XeF_2 , I_3^- , Br_3^-

The geometry of above examples will be linear shape.

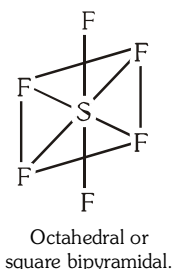
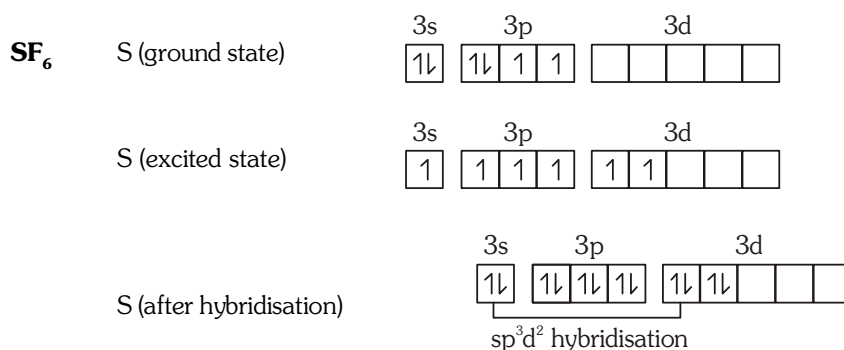
(E) sp^3d^2 Hybridisation :

- (I) In this hybridisation, one s-orbital, three p-orbitals & two d-orbitals (dz^2 , dx^2-y^2) are mixed to give six new hybrid orbitals known as sp^3d^2 hybrid orbitals.
- (II) The geometry of molecule obtained from above six hybrid orbitals will be symmetrical octahedral or square bipyramidal.

(III) The angle between all hybrid orbitals will be 90° .

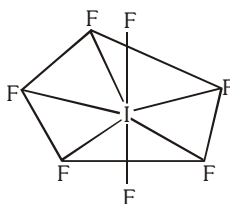
Example : SF_6 , AlF_6^{-3} , PF_6^- , ICl_5 , XeF_4 , XeOF_4 , ICl_4^- ,

(IV) Two 'd' orbital participates in the hybridisation are $d_{x^2-y^2}$ and d_{z^2} .



(F) sp³d³ Hybridisation :

- (I) In this hybridisation, one s-orbital, three p-orbitals & three d-orbitals are mixed to give seven new hybrid orbitals known as sp³d³ hybrid orbitals.
- (II) These seven sp³d³ orbitals are configured in pentagonal bipyramidal shape.
- (III) Five bond angles are of 72° and 10 bond angles of 90° .
- (IV) The following examples showing sp³d³ hybridisation - IF_7 & XeF_6 .



(Pentagonal biipyramidal)

VALENCE SHELL ELECTRON PAIR REPULSION THEORY (VSEPT)

- (a) If the central atom possess only bonded pairs of electrons along with identical atoms then shape of the compound is symmetrical and according to Sidgwick & Powl.

eg.	BF_3	—	120°	—	triangular
	CH_4	—	$109^\circ 28'$	—	tetrahedral
	CO_2	—	180°	—	linear

- (b) If the central atom possess bonded pair of electrons as well as lone pair of electron, then shape of the molecule will be unsymmetrical ie. the original bond angle will disturbed due to repulsion between lone pair of electrons.

Similarly on having different type of side atoms, molecule becomes unsymmetrical due to unequal force of repulsion between e^- . Order of repulsion is - [$\ell p - \ell p > \ell p - bp > bp - bp$]

$$\left[\text{Bond angle} \propto \frac{1}{\text{Number of lone pair of electrons}} \right]$$

- (c) By increasing one lone pair of electron, bond angle is decreased approx by 2.5° .

eg.:-	CH_4	NH_3	H_2O	→	sp^3
	109°	107°	105°		hybridisation

BOND PARAMETERS

Bond Length

The average distance between the nucleus of two atoms is known as bond length, normally it is represented in Å. eg. A — B

It depends mainly on electronegativities of constituent atoms.

Case -I. Electronegativity difference is zero then -

$$\text{Bond length} = r_A + r_B \quad \text{or} \quad d_{A-B} = r_A + r_B$$

where r_A = covalent radius of A

r_B = covalent radius of B

x_A = electronegativity of A

x_B = electronegativity of B

If $r_A = r_B$ then Bond length = $2r_A$ or $2r_B$

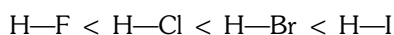
Example :- Cl—Cl

Case - II Electronegativity difference is not equal to zero then -

Bond length is given by Shomaker & Stevenson formula is - Bond length = $r_A + r_B - 0.09(x_A - x_B)$ Å
($x_A - x_B$) = Difference in electronegativities

Factors Affecting Bond Length

(a) **Δ electronegativity** :- Bond length $\propto \frac{1}{\Delta EN}$ (While B.E. $\propto \Delta EN$)



(b) **Bond order or number of bonds** :- Bond length $\propto \frac{1}{\text{Number of bonds or bond order}}$

Bond energy \propto Number of bond

ex.



Bond length

1.54 Å

1.34 Å

1.20 Å

← increasing

Bond energy

80

140

180-200 K.Cal.

→ increasing



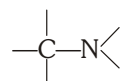
1.43 Å



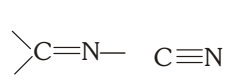
1.20 Å



1.13 Å



1.47 Å



1.28 Å



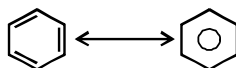
1.15 Å

(c) **Resonance** :- Due to resonance bond length affected

Ex.1. Benzene

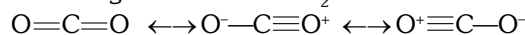
C—C bond length 1.54 Å

C=C bond length 1.34 Å



But bond length is between single and double bond is = 1.39 Å

Ex.2. Bond length of C—O in CO₂ is 1.15 Å Resonance occurs in CO₂ is as follows -



Bond length = 1.15 Å (Between double & triple bond)

(d) **Hybridization** :- Bond length $\propto \frac{1}{s \text{ character}}$

Example :-

Compound

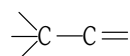
Hybridisation

Bond length

Ethane

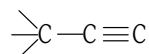
$\text{sp}^3\text{—sp}^3$

1.54 Å



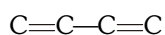
$\text{sp}^3\text{—sp}^2$

1.51 Å



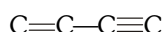
$\text{sp}^3\text{—sp}$

1.47 Å



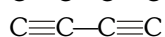
$\text{sp}^2\text{—sp}^2$

1.46 Å



$\text{sp}^2\text{—sp}$

1.42 Å



sp—sp

1.37 Å

s-character increases ↓

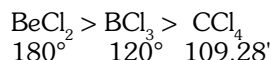
Bond Angle

The minimum angle between any two adjacent bonds is known as bond angle.

It is represented in degree (°), min (') and second (")

Factors affecting the bond angle -

Step I : Hybridisation or % 's' character : $\text{Bond angle} \propto \% \text{ s character}$



Step II : Lone pair

When hybridisation is same, lone pair are different.

$$\text{Bond angle} \propto \frac{1}{\text{No. of lone pair}}$$

Example :-

	CH_4		$\ddot{\text{N}}\text{H}_3$		$\text{H}_2\ddot{\text{O}}:$
Hybridisation	sp^3		sp^3		sp^3
Bond angle	109°	$>$	107°	$>$	105°
	No l.p.		one l.p.		two l.p.

- In the different molecules if central atom have same number of lone pair of electron then bond angle will depend on electronegativities of A & B.

Step III : Central Atom

$$\text{Bond angle} \propto \text{Electronegativity of central atom}$$

In AB_x type of molecules if side atoms are same and EN of central atom increases the bond angle increases.



- Electronegativity of 'O' > Electronegativity of 'S'
- Bond angle of $-\text{NH}_3 > \text{PH}_3 > \text{AsH}_3$

Example :-

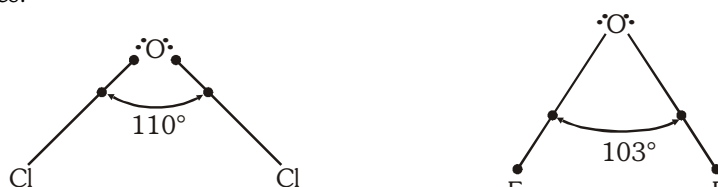
	$\ddot{\text{N}}\text{H}_3$	$\ddot{\text{P}}\text{H}_3$	$\ddot{\text{As}}\text{H}_3$
Bond angle	107°	93°	91°

$\xrightarrow{\text{Electronegativity decreasing. Bond angle will decrease}}$

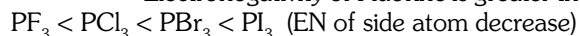
Step IV : Side atom

$$\text{Bond angle} \propto \frac{1}{\text{electronegativity of bonded atom}} \propto \text{size of side atom}$$

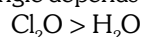
In AB_x type molecules, if central atoms are same and the EN of side atoms increases then bond angle decreases.

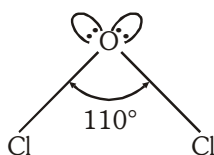
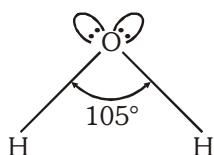


Electronegativity of Fluorine is greater than chlorine



Bond angle depends on size of side atom, On increasing size of side atom bond angle increases.





When hybridisation is same, lone pair are same, Central atom is same, bonded atoms are different.

sp^3	OF_2	103 - 105°	Electronegativity of bonded atom is decreasing
sp^3	Cl_2O	109 - 111°	
sp^3	Br_2O	116 - 118°	

Bond Energy (BE)

Bond energy may be defined as -

- Bond formation energy :- Energy released when any bond is formed is known as bond formation energy or bond energy.
- Bond dissociation energy :- Energy required to dissociate any bond is known as Bond dissociation energy. Calculation of released energy is more difficult than the dissociation energy therefore dissociation energy of bond is calculated and is assumed as bond energy or bond formation energy.

Case-I In diatomic molecule :

Bond energy = bond dissociation energy

Example:- $N_2 > O_2 > H_2 > F_2$

Case-II For polyatomic molecule :-

Bond energy \simeq Bond dissociation energy (D)

Factors Affecting The Bond Energy

- | | | | |
|--------------------------------|-------------------|------------------------|-------------------|
| (a) Δ Electronegativity | (b) Bond order | (c) Atomic size | (d) Bond polarity |
| (e) Resonance | (f) Hybridisation | (g) Lone pair electron | |

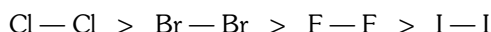
(a) Δ Electronegativity :- Bond energy $\propto \Delta EN$ eg. $HF > HCl > HBr > HI$

(b) Bond order :- Bond energy \propto Bond order.

eg. $C-C < C=C < C\equiv C$
 79 K. Cal., 143.3 K. Cal., 199.0 K. Cal.

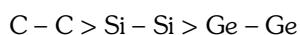
(c) Atomic size :- Bond energy $\propto \frac{1}{\text{Atomic size}}$ eg. $C\equiv C < C\equiv N < N\equiv N$

Exception :- In case of halogen group, order of bond energy is -



Because of higher electron density and small size of F atoms, repulsion between electrons of two F atoms, weakens the bond energy.

Other example $S-S > O-O$

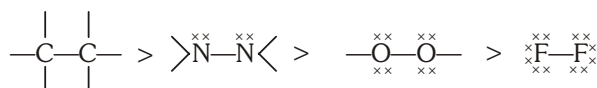


(d) Bond Polarity :- Bond energy \propto Bond polarity
 eg. $H-F > H-Cl > H-Br > H-I$

(e) Resonance :- Bond energy increases due to resonance.
 eg. In benzene bond energy of $C-C$ increases due to π electrons of $C=C$.

(f) Hybridisation :- Bond energy \propto s-character in hybrid orbitals.
 eg. $sp-sp > sp^2-sp^2 > sp^3-sp^3$
 s.character - 50 % 33.3 % 25 %

(g) Lone pair of electrons :- Bond energy $\propto \frac{1}{\text{lone pair of electrons}}$



Size of F and O atoms are small so their bond energy should be high (small atomic radius) but it is actually less, due to lone pair of electrons present on F and O atoms, which repels each other in F—F and —O—O—type of bonds.

Important Note (Summary) :

- (i) Bond strength \propto overlapping (if orbitals are given)
- (ii) Bond strength $\propto \frac{1}{\text{size of orbitals}}$
e.g. $1s - 2p > 1s - 3p > 1s - 4p$
- (iii) If orbitals are of same shell
Bond strength \propto extent of overlapping \propto directional properties

$$2p - 2p > 2s - 2p > \underbrace{2s - 2s}_{\text{Axial overlap}} > 2p - 2p \text{ (Side ways)}$$
- (iv) π -bond strength
 $2p\pi - 2p\pi > 2p\pi - 3d\pi > 2p\pi - 3p\pi > 3p\pi - 3p\pi$
- (v) O = O exist but S = S does not exist at room temperature.
- (vi) N \equiv N exist but P \equiv P does not exist at room temperature.
- (vii) O=C=O exist but O=Si=O does not exist.

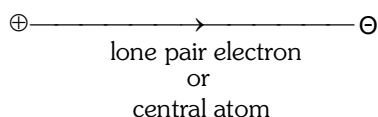
DIPOLE MOMENT

POLARITY OF BOND (IONIC NATURE IN COVALENT BOND)

- (a) Polarity of any polar covalent bond or molecule is measured in terms of dipole moment.
- (b) For measurement of extent of polarity, Pauling introduced the concept of dipole moment (μ).
The product of positive or negative charge (q) and the distance (d) between two poles is called dipole moment.

Here - $\mu = q \times d$ (magnitude of charge \times distance),

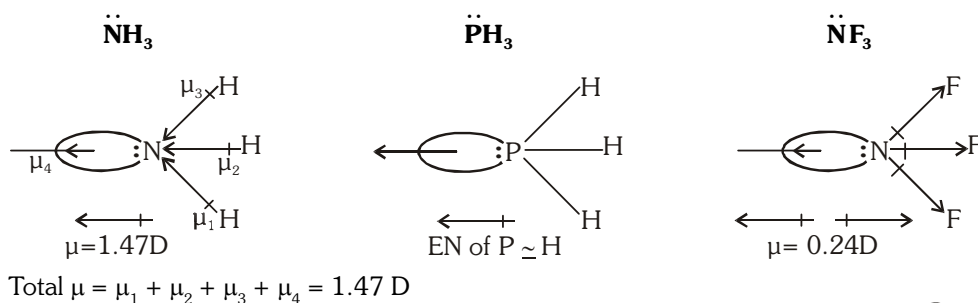
- (c) Dipole moment is a vector quantity i.e. it has both magnitude as well as direction.
- (d) Direction of dipole moment is represented by an arrow pointing from electro +ve to electro -ve element and from central atom to lone pair of electrons.



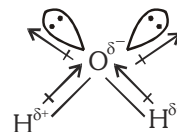
- (e) Unit of dipole moment is Debye
 $1 \text{ Debye} = 1 \times 10^{-18} \text{ e.s.u. cm} = 3.33 \times 10^{-30} \text{ coulomb metre}$
- (f) In the diatomic molecule μ depends upon difference of EN i.e. $\mu \propto \Delta \text{EN}$
order of μ , $\text{H-F} > \text{H-Cl} > \text{H-Br} > \text{H-I}$
 $\mu = 0$ for H-H , F-F , Cl-Cl , Br-Br , O-O
- (g) For polyatomic molecules μ depends on the vector sum of dipole moments of all the covalent bonds.
- (h) For PCl_5 and SF_6 , etc. $\mu = 0$ due to their symmetrical geometry (According to charge).
- (i) Benzene, naphthalene, diphenyl have $\mu = 0$ due to planar structure.
- (j) If the vector sum is zero, than compound is non-polar compound or symmetrical compound (and it is not essential that individual μ of every bond should be zero).

Example - BX_3 , CCl_4 , SiCl_4 , CH_4 , CO_2 , CS_2 , PCl_5 , SiH_4 etc.

In these examples the bond B—F, C—Cl, C—H, C—O, P—Cl etc. are polar even though compounds are non-polar.

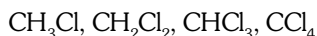


- (k) Dipole moment of H_2O is 1.85 D which is resultant μ of two O-H bonds.
 μ of $\text{H}_2\text{O} > \mu$ of H_2S because electronegativity of oxygen is higher than sulphur.



- (l) Angular structure of molecule have greater dipole moment.

Ex. Write the order of the dipole moment of following compounds ?



Sol. Right order is \longrightarrow CCl_4 $<$ CHCl_3 $<$ CH_2Cl_2 $<$ CH_3Cl
 $\mu = 0$ 1.02 1.55 1.93

Applications of Dipole Moment

(a) To determine polarity and geometry of molecule :-

If $\mu = 0$ compound is non polar and symmetrical

eg. CO_2 , BF_3 , CCl_4 , CH_4 , BeF_2 etc.

If $\mu \neq 0$ compound will be polar and unsymmetrical.

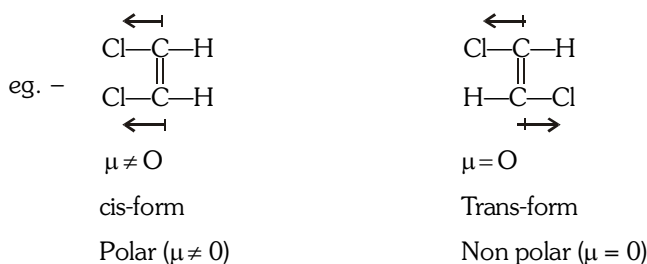
H_2O , SO_2 , NH_3 , Cl_2O , CH_3Cl , CHCl_3 etc.

(b) To calculate % ionic character :-

$$\% \text{ Ionic character} = \frac{\text{Experimental value of } \mu}{\text{Theoretical Value of } \mu} \times 100$$

(c) To distinguish cis form or trans form :-

- (I) Dipole moment of cis isomers is normally higher than trans isomers.



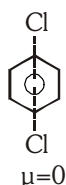
- (II) If two groups have opposite inductive effect then trans-isomer will have greater dipole moment.



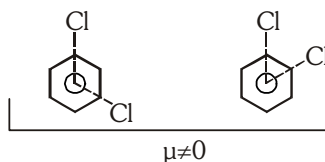
(d) To locate position of substituents in aromatic compounds.

$$\mu \propto \frac{1}{\text{Bond angle}}$$

(i) If same substituents are present in the symmetrical position μ of benzene ring compounds will be zero.



Angle 180°
p-dichloro benzene

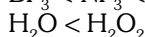
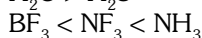
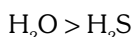
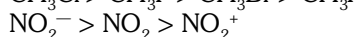
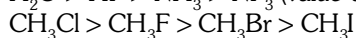
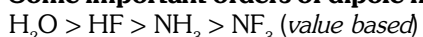


Angle 120°
m-dichloro benzene

Angle 60°
o-dichloro benzene

(ii) As angle between vector decreases value of μ increases.

● **Some important orders of dipole moments :**



MOLECULAR ORBITAL THEORY (MOT)

MOT put forward by Hund & Mulliken, which can be applied to explain the properties, which the old VBT (Valence bond theory) was unable to explain. eg. Paramagnetic nature of O_2 molecule, as per VBT ($:\text{O} = \text{O}:$) it should be diamagnetic.

Definition : The atomic orbital lose their identity during molecule formation (overlapping) and form new orbitals termed as molecular orbitals.

Characteristic of Molecular Orbitals

- (a) Molecular orbital formed by overlapping of atomic orbital of same energy.
- (b) Number of molecular orbital formed = number of atomic orbitals involved in overlapping.
- (c) Half of the molecular orbital have lower energy are called Bonding molecular orbital.
- (d) Half are of higher energy - termed as Antibonding molecular orbital.
- (e) Electronic configuration in various molecular orbital are governed by same three rules.
 - (1) Aufbau's rule
 - (2) Hund's rule
 - (3) Pauli's exclusion principle.
- (f) Wave function for bonding molecular orbital is $\psi_b = \psi_A + \psi_B$
- (g) Wave function for antibonding molecular orbital is $\psi_a = \psi_A - \psi_B$
 - ψ_A = wave function of atom A
 - ψ_B = wave function of atom B

Comparison of Bonding molecular orbital & Antibonding molecular orbital :

Bonding molecular orbital(BMO)

1. Bonding MO is the result of the linear combination of AO when their wave function are added

$$\psi_b = \psi_A + \psi_B$$

2. Generally it does not have nodal plane.
3. Electron density increases between two nuclei resulting attraction between two atoms.
4. Energy of BMO is less, hence stable.
5. Electron placed in a BMO stabilises a molecule.

Antibonding molecular orbital (ABMO)

1. ABMO is result of linear combination of AO when their wave function are subtracted

$$\psi_a = \psi_A - \psi_B$$

2. It always have a nodal plane between two nuclei of bonded atom.
 3. Electron density decreases in between two nuclei, leads to repulsion between two atoms.
 4. Energy of ABMO is high.
 5. Electron placed in the ABMO destabilises the molecule.
-

Notation of molecular orbitals

As atomic orbitals are known by letters s, p, d and f depending on their shapes. Similarly for molecular orbital

For bonding molecular orbital - σ, π etc.

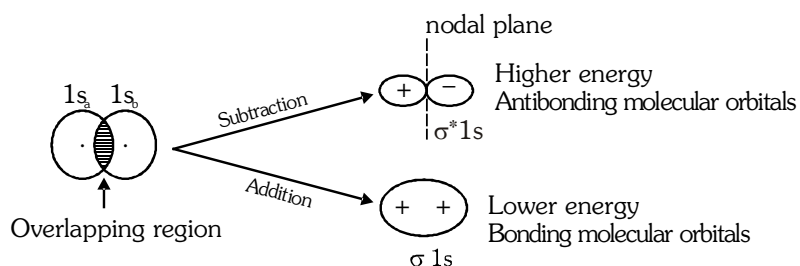
For antibonding molecular orbital - σ^*, π^* etc.

are used for different shapes of electron cloud.

SHAPES OF MOLECULAR ORBITALS (L.C.A.O. Method)

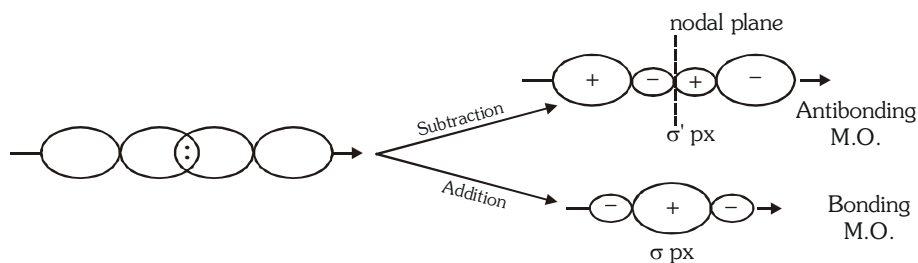
(A) (σ molecular orbital) :- It is formed by two ways -

(a) Combination of s-orbitals -



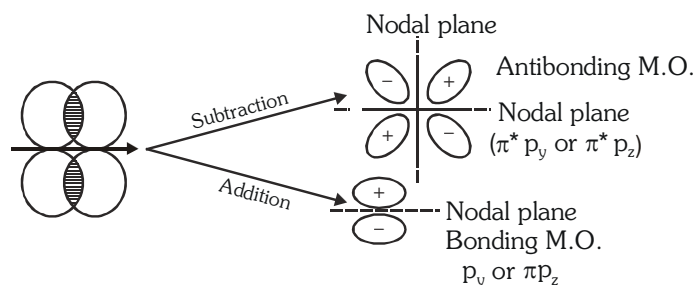
- $\sigma^* 1s$ have one nodal plane

(b) End on overlapping of p-orbitals - (Linearly) :-



- $\sigma^* p_x$ have one nodal plane

(B) π (pi) molecular orbitals :-



Positive sign, represent maximum probability finding of electrons.

$\pi^* p_y$ or $\pi^* p_z$ have two nodal plane

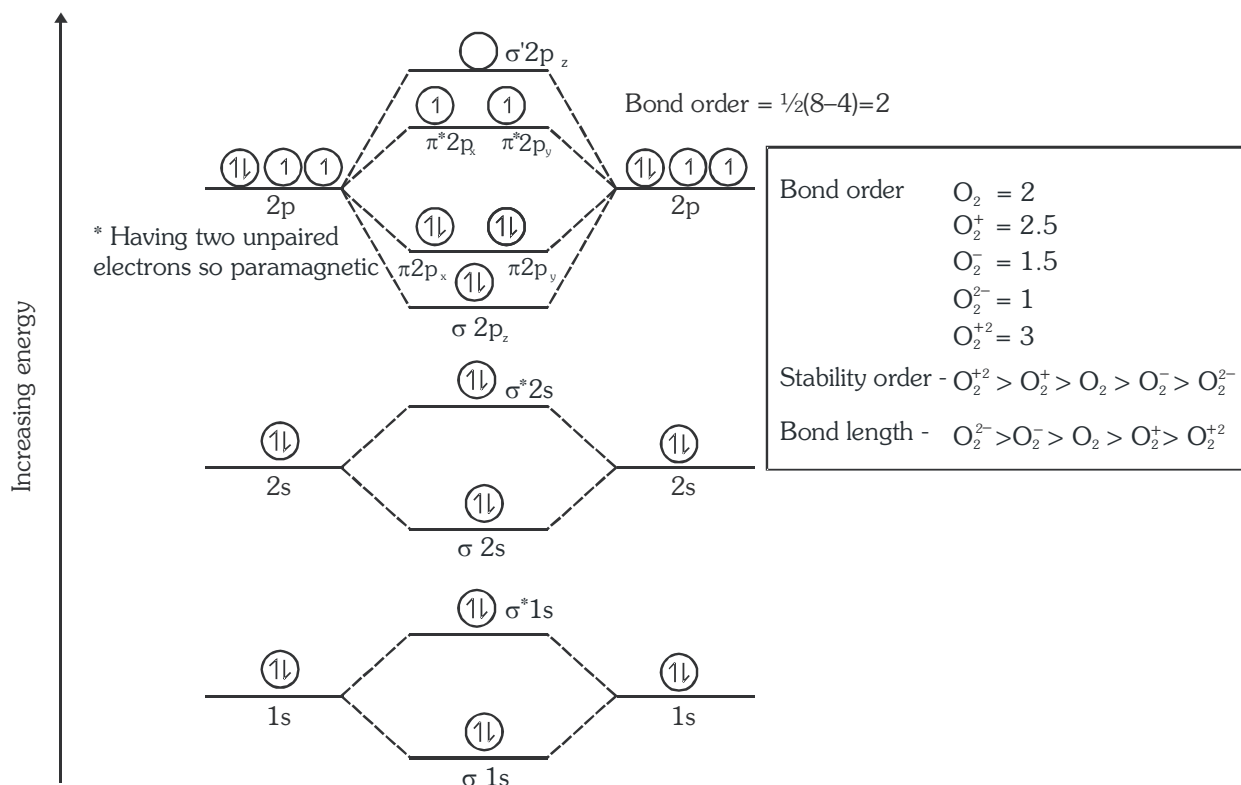
ENERGY LEVEL DIAGRAM OF MOLECULAR ORBITAL

(A) Energy level diagram for O_2, F_2, Ne_2 (Beyond N_2)

On the basis of Aufbau's rule - increasing order of energies of various molecular orbitals is -

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

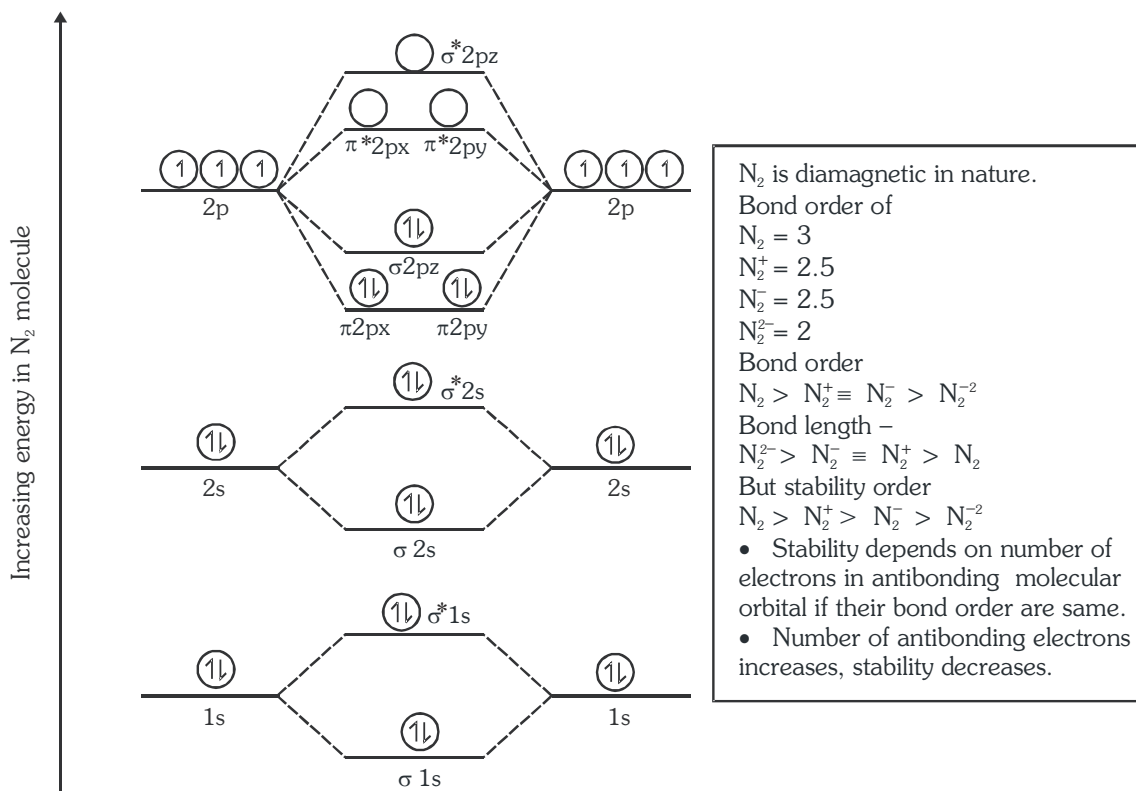
For O_2 molecule



(B) Energy level diagram for B_2 , C_2 and N_2 molecules (upto N_2)

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

For N_2 molecule



Electronic configuration of molecules and their related properties :-

For writing electronic configuration of diatomic molecules following two rules to be followed-

- Count the number of electrons present in two atoms and then fill in the appropriate energy level diagram according to Aufbau rule.
- The pairing in π 2px and π 2py or π^* 2px and π^* 2py will take place only when each molecular orbital of identical energy has one electron.

BOND ORDER

Bond order can be defined as :

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

N_b = No. of electron in bonding MO's

N_a = No. of electron in antibonding MO's

- If bond order = 0, it means species does not exist.
- Bond order of 1, 2 & 3 corresponds to a single bond, double & triple bond respectively.
- Bond order \uparrow stability of molecule \uparrow bond length \downarrow

MAGNETIC BEHAVIOUR

- If the molecule has one or more unpaired electron, it will be paramagnetic,
- If all the electrons are paired it will be diamagnetic.
- Magnetic strength can be calculated by using spin only formula of magnetic moment (μ).
- $\mu = \sqrt{n(n+2)}$ B.M. (where n = number of unpaired electron)

Ex. H_2 = Configuration : $\sigma_{(1s)}^2, \sigma_{(1s)}^{*0}$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2 - 0}{2} = 1,$$

Hence H – H (diamagnetic)

BONDING IN MOLECULES

(a) Hydrogen molecule

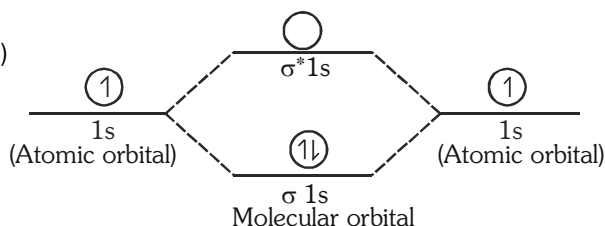
Having two H atoms with one electron each ($1s$)

M.O. configuration of $H_2 = (\sigma 1s)^2 (\sigma^* 1s)^0$

$$\begin{aligned} \text{Bond order} &= \frac{1}{2} [N_b - N_a] \\ &= \frac{1}{2} [2 - 0] = 1 \text{ ie. single bond.} \end{aligned}$$

Having paired electron so diamagnetic.

Stability \rightarrow quite stable (having single bond)



(b) H_2^+ ion —

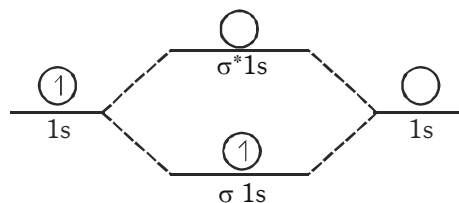
Configuration of $H_2^+ = (\sigma 1s)^1 (\sigma^* 1s)^0$

One electron in bonding molecular orbital.

So paramagnetic

$$\text{Bond order} = \frac{1}{2} [1 - 0] = \frac{1}{2}$$

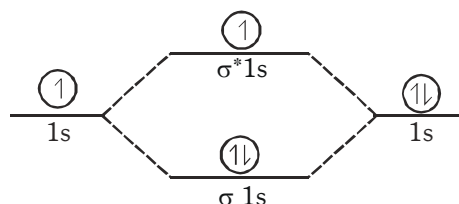
Less stable. (In comparison to H_2)



(c) H_2^- anion -

M.O. configuration - $(\sigma 1s)^2 (\sigma^* 1s)^1$

Paramagnetic



$$\text{Bond order} = \frac{1}{2} [2 - 1] = \frac{1}{2}$$

Stability is less than H_2^+ because H_2^- contain an ABMO electron

Stability order	$\text{H}_2 > \text{H}_2^+ > \text{H}_2^-$
Bond order	1.0 0.5 0.5

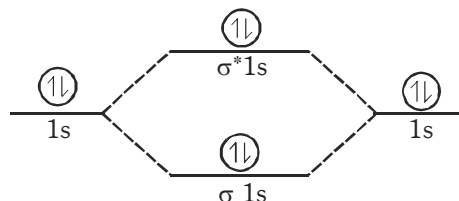
(d) Helium molecule (He_2)

M.O. configuration - $(\sigma 1s)^2(\sigma^* 1s)^2$

Diamagnetic

$$\text{Bond order} = \frac{1}{2} [2 - 2] = 0 \text{ (zero)}$$

- Bond order zero indicates no linkage between He atoms. Hence He_2 molecule does not exist.



Comparison between VBT and MOT

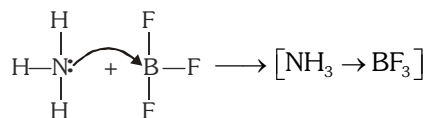
- | | |
|--|--|
| 1. According to VBT electron moves around only one nucleus | 1. According to MOT electron moves under influence of two or more nuclei |
| 2. Orbitals are monocentric | 2. Orbitals are polycentric |
| 3. According to VBT O_2 is diamagnetic | 3. According to MOT O_2 is paramagnetic |

CO-ORDINATE BOND

- (1) It is a covalent bond in which the shared e-pair come from one atom is called coordinate bond.
- (2) Necessary conditions for the formation of coordinate bond are -
 - (a) Octet of donor atom should be complete and should have atleast one lone pair of electron.
 - (b) Acceptor atom should have deficiency of at least one pair of electron.

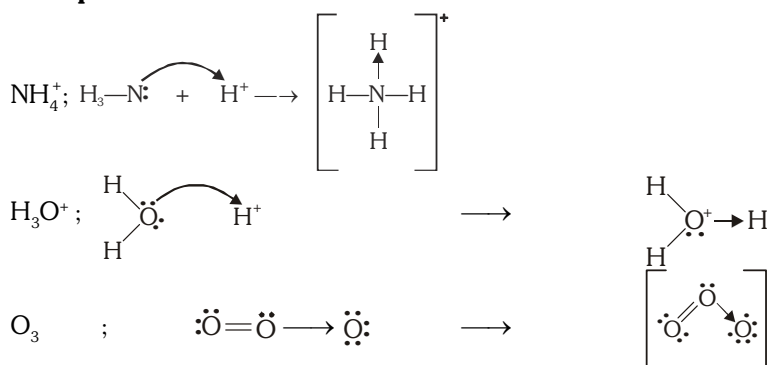


- (3) Atom which provide electron pair for sharing is called donor.
- (4) Other atom which accepts electron pair is called acceptor. That is why it is called donor-acceptor or dative bond.



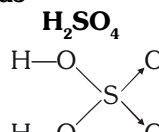
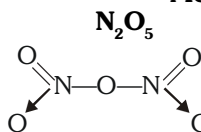
BF_3 is electron deficient compound.

Example :





Metal co-ordinate compounds -



Compounds in which Ionic, covalent and co-ordinate bonds are present, are as follows -
 NH_4Cl , CuSO_4 , $\text{K}_4[\text{Fe}(\text{CN})_6]$, Na_3PO_4 , KNO_3 , etc.

FORMAL CHARGE

The difference between the valence electrons in an isolated atom and the number of valence electrons assigned to that atom in a given Lewis structure is called that atom's formal charge. The formal charge, abbreviated FC, on an atom in a Lewis structure is given by the following relationship:

Formal charge on a atom in a Lewis structure

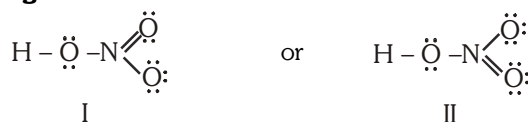
$$= (\text{total number of valence electrons in the isolated atom}) - (\text{Total number of nonbonding electrons}) - \frac{1}{2} (\text{total number of bonding electrons}) \dots (i)$$

$$\text{or} \quad \text{FC} = (\text{Valence electrons}) - (\text{Nonbonding electrons}) - \frac{1}{2} (\text{bonding electrons})$$

$$= (\text{Valence electrons or group number}) - [(\text{Number of unshared } e^-s) + (\text{Number of bonds})]$$

To find the formal charge, we count the bonding electrons as though they are equally shared between the two bonded atoms.

Q. Calculate the formal charges on the various atoms of nitric acid (HNO_3) molecule which has been described by the following Lewis structures:



The H atom : It has one valence electron, zero lone pair (or zero nonbonding electrons), and forms one bond (two bonding electrons).

$$\text{Substituting in Eq. (i), we write} \quad \text{FC} = (1) - (0) - \frac{1}{2}(2) = 0.$$

The O atom bonded to H: It has six valence electrons, two lone pairs (or four nonbonding electrons), and from two bonds (or four bonding electrons).

$$\text{Hence, we write} \quad \text{FC} = (6) - (4) - \frac{1}{2}(4) = 0.$$

The N atom: It has five valence electrons, zero lone pair (or zero nonbonding electrons), and forms four bonds (or has eight bonding electrons).

$$\text{Thus, we write} \quad \text{FC} = (5) - (0) - \frac{1}{2}(8) = +1$$

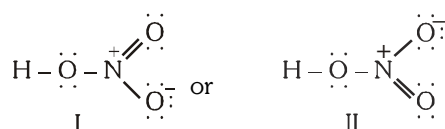
The end O atom in N = O: It has six valence electrons in the free state *but* in the Lewis structure (I or II), it has two lone pairs (or four nonbonding electrons) and forms two bonds (or has four bonding electrons).

$$\text{Thus, we can write} \quad \text{FC} = (6) - (4) - \frac{1}{2}(4) = 0$$

The end O atom in N - O : It has six valence electrons in the free state but in the Lewis structure (I or II), it has three lone pairs or six nonbonding electrons and forms one bond (or has two bonding electrons).

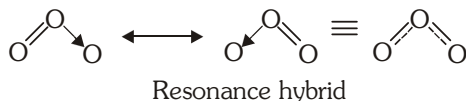
$$\text{thus, we write} \quad \text{FC} = (6) - (6) - \frac{1}{2}(2) = -1$$

We can now write the Lewis structures (I and II) for nitric acid molecule including the formal charges as



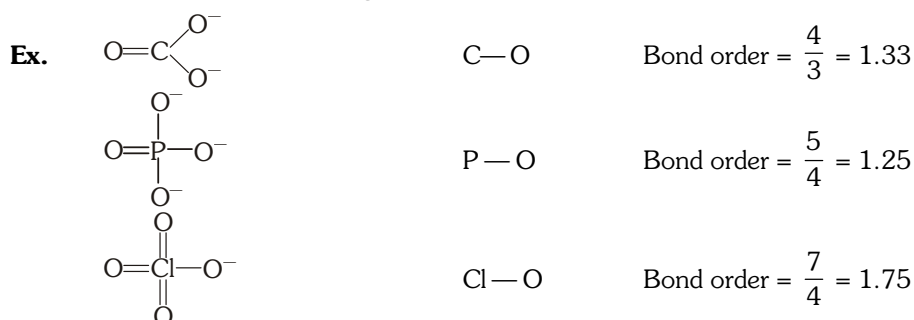
RESONANCE

- (a) It has been found that the observed properties of certain compounds cannot be satisfactorily explained by writing a single lewis structure. The molecule is then supposed to have many structures, each of which can explain most of the properties of the molecule but none can explain all the properties of the molecules. The actual structure is in between of all these contributing structures and is called resonance hybrid and the different individual structures are called resonating structures or canonical forms. This phenomenon is called resonance.
- (b) Let us discuss resonance in ozone, according to its resonance structure it should have one single bond ($\text{O}-\text{O} = 1.48\text{\AA}$) but experiments show that both the bonds are same which can be proved by its resonance hybrid as shown below.



Note : To calculate bond order in the polyatomic molecule or ion use following formula :

$$\text{Bond order} = \frac{\text{Total number of bonds in a molecule}}{\text{Resonating Structures}}$$



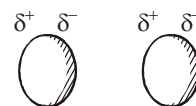
METALLIC BOND

- (1) The constituent particles of metallic solids are metal atoms which are held together by metallic bond.
- (2) In order to explain the nature of metallic bond Lorentz proposed a simple theory known as electron gas model or electron sea model.
- (3) A metal atom is supposed to consist of two parts, valence electrons and the remaining part (the nucleus and the inner shells) called kernel.
- (4) The kernels of metal atoms occupy the lattice sites while the space between the kernel is occupied by valence electrons.
- (5) Due to small ionisation energy the valence electrons or metal atoms are not held by the nucleus firmly. Therefore, the electrons leave the field of influence of one kernel and come under the influence of another kernel. Thus the electrons are not localised but are mobile.
- (6) The simultaneous attraction between the kernels and the mobile electrons which hold the kernel together is known as metallic bond.

WEAKER FORCES

Vander Waal's Forces

- (a) These are weak; non directional, non valence force of attraction among neutral species.
- (b) These are electrical in nature, due to induced polarity caused by temporary displacement of electrons towards one end of the inert atoms, becoming a temporary dipole.
- (c) This temporary dipole in one molecule can induce opposite dipoles in surrounding



molecule due to displacement of electrons, one end becomes -ve and other +ve.

These partially charged ends, induce surrounding molecules accordingly.

(d) Strength of vander waal force depends on ease of distortion of electron cloud.

$$\text{van der Waal's force} \propto \text{size of atom or molecule} \propto \text{atomic wt. or molecular weight.}$$

(e) Therefore m.p. and b.p. of noble gas elements (inert gas atom) and halogens increases down the group.

Types of van der Waal's Forces

(a) Keesom force or dipole dipole force - one dipole molecule orient the other dipole molecule, to bring opposite ends close to each other for attraction. This is called orientation effect. Example - HCl, H₂O, NH₃ etc.

(b) Debye force or dipole induce dipole force :- Forces which results from the interaction of a permanent dipole and induced dipole are called Debye force.

eg. When non-polar substance like benzene come in contact with polar molecules like NH₃, induced dipole moment in benzene appears (Induction effect).

(c) London dispersion force or Instantaneous dipole instantaneous induce dipole attraction :-

Due to vibration or moment to atom electron cloud and nuclei shifts temporarily towards opposite ends, leads to attraction between them, eg. In atoms of noble gases and halogens.

HYDROGEN BONDING

Definition

(a) It is an electrostatic attractive force between covalently bonded hydrogen atom of one molecule and an electronegative atom.

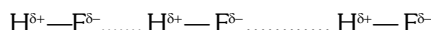


(b) It is not formed in ionic compounds.

(c) H-bond forms in polar covalent compounds, (not in non-polar).

(d) It is very weak bond but stronger than vander waal's force.

(e) It is also known as dipole-dipole attraction.



Main condition for H-bonding

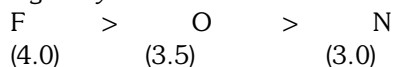
(a) H— should be covalently bonded with high electro -ve element like F, O, N.

(b) Atomic size of electro -ve element should be small.

Order of atomic size is -

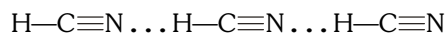


Order of electronegativity is -

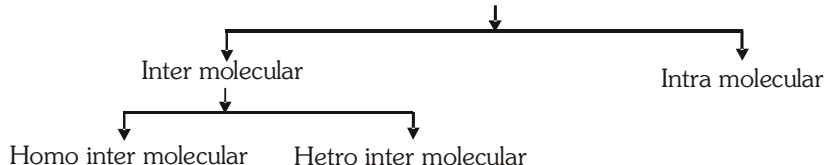


(c) Strength of H-bond \propto Electronegativity of Z (element) $\propto \frac{1}{\text{atomic size of Z}}$

(d) Hydrogen bonding occurs in HCN, due to (—C \equiv N) triple bond (sp hybridisation), electronegativities of carbon and nitrogen increases.



TYPES OF HYDROGEN BONDING



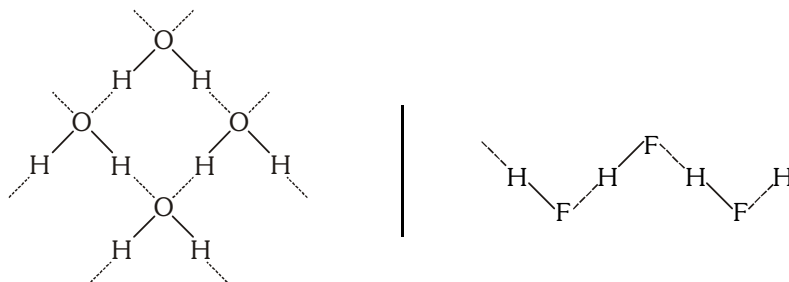
Intermolecular H-Bond

H-bond formation between two or more molecules of either the same or different compounds known as **Inter**

molecular H-bonding.

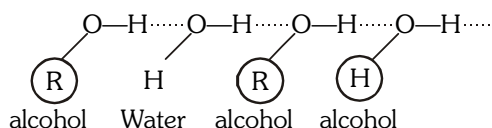
These are of two types :-

(i) **Homo intermolecular** :- H-bond between molecules of same compound.



(ii) **Hetro intermolecular** :- H-bond between molecules of different compounds

Eg. between alcohol and water



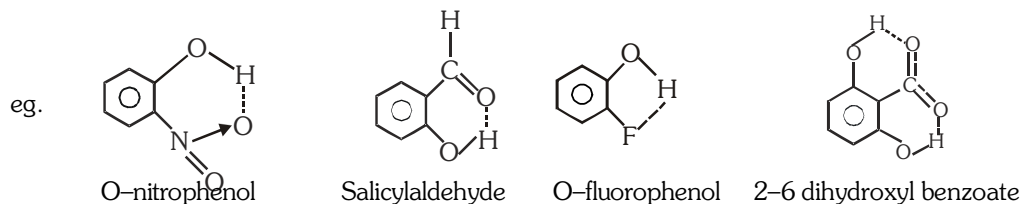
Intramolecular H-bond

It takes place within the molecule.

(a) H-bonded with electronegative element of a functional group, form H-bond with another electronegative element present on nearest position on the same molecule.

(b) This type of H-bond is mostly occurred in organic compounds (Aromatic)

(c) It results in ring formation (Chelation).



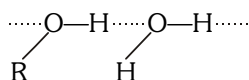
Effect of H-bond on Physical Properties

(A) Solubility

(a) Inter molecular H-bonding

(I) Few organic compounds (Non-polar) are soluble in water (Polar solvent) due to H-bonding.

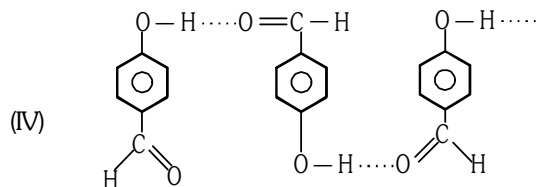
Ex. - Alcohol in water



Other examples - Glucose, Fructose etc. dissolve in water.

(II) Ketone, ether, alkane etc. are insoluble (no H-bond). Dimethyl ether is soluble in water while diethyl ether is partially soluble, due to bulky ethyl groups H-bonding interrupts.

(III) Solubility order- $\text{CH}_3\text{OCH}_3 < \text{CH}_3\text{OH}$

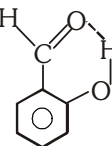


p-hydroxy benzaldehyde.

It can form H-bond with water molecule so it can dissolve.

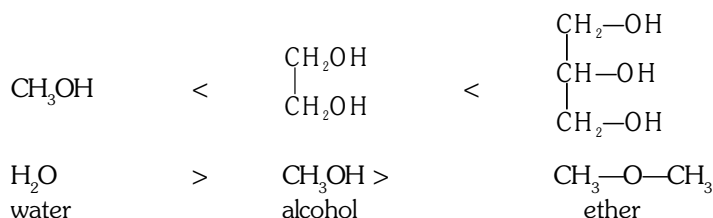
(b) Intra molecular H-bonding

- (I) It decreases solubility as it form chelate by H-bonding, so H- is not free for other molecule.
- (II) It can not form H-bond with water molecule so it can not dissolve.



(B) Viscosity

H-bond associates molecules together so viscosity increases.



(C) Surface Tension

Surface tension of a liquid \propto extent of H-bonding.

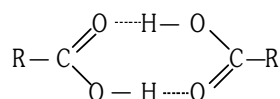
(D) Melting point and boiling point

- (I) Due to intermolecular H-bond M.P. & B.P. of compounds increases.
 $\text{H}_2\text{O} > \text{CH}_3\text{OH} > \text{CH}_3\text{—O—CH}_3$
- (II) Boiling points of VA, VIA, VIIA hydrides are as shown below :
 (Group 15 Hydrides) $\text{SbH}_3 > \text{NH}_3 > \text{AsH}_3 > \text{PH}_3$
 (Group 16 hydrides) $\text{H}_2\text{O} > \text{TeH}_2 > \text{SeH}_2 > \text{H}_2\text{S}$
 (Group 17 hydrides) $\text{HF} > \text{HI} > \text{HBr} > \text{HCl}$
- (III) But sudden increase in boiling point of NH_3 , H_2O and HF is due to H-bonding.
- (IV) $\text{H}_2\text{O} > \text{HF} > \text{NH}_3$ (BP comparison due to combined effect of strength and number of H bond)

Intramolecular H-bonding gives rise to ring formation, so the force of attraction among these molecules are vander waal force. So M.P. and B.P. are low.

(E) Molecular weight

Molecular wt. of CH_3COOH is double of its molecular formula, due to dimer formation occur by H-bonding.



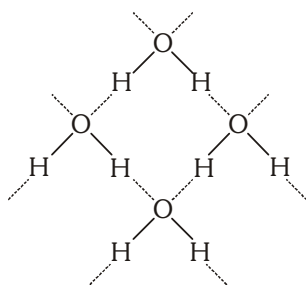
(F) Physical states

H_2O is liquid while H_2S is gas.

Water and Ice :- Both have H-bonding even then density of ice is less than water.

Volume of ice is more because of open cage like crystal structure, form by association of water molecules with the help of H-bond.

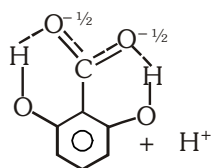
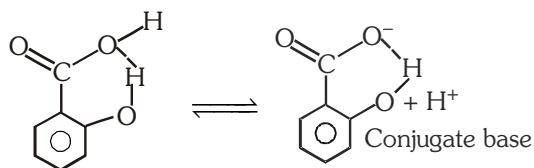
H_2O becomes solid due to four hydrogen bond among water molecule are formed in tetrahedral manner.



Effect of intramolecular H-bonding

Strength of acid

- (I) The formation of intramolecular H-bonding in the conjugate base of an acid gives extra stability to conjugate base and hence acid strength increases eg. Salicylic acid is stronger than benzoic acid
2, 6 - dihydroxy benzoic acid > salicylic acid > benzoic acid.

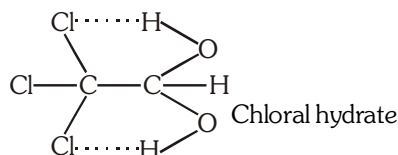


2, 6-dihydroxy benzoate ion.

- (II) C_2H_5SH is more acidic than C_2H_5OH . In C_2H_5OH , H-bond forms so H^+ is not free.
(III) HF is weaker acid than HI , due to H-bond in $H-F$, H^+ is not free

Stability of chloral hydrate

If two or more OH group on the same atom are present it will be unstable, but chloral hydrate is stable (due to H-bonding).



IONIC OR ELECTROVALENT BOND

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.

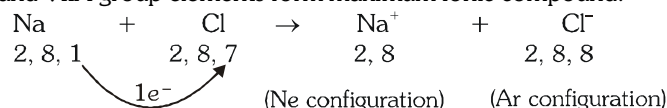
Electro +ve atom loses electron (group IA to IIIA)

Electro -ve atom gains electron (group VA to VIIA)

Electrostatic force of attraction between cation and anion is called ionic bond or electrovalent bond.

Nature of ionic bond \propto Electronegativity difference.

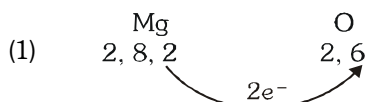
e.g. IA and VIIA group elements form maximum ionic compound.



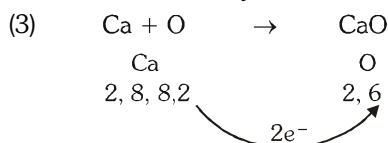
More the distance between two elements in periodic table more will be ionic character of bond.

Total number of electron lose or gained is called electrovalency.

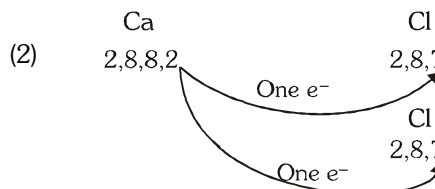
Example -



electrovalency of Mg = 2
electrovalency of O = 2



electrovalency of Ca = 2
electrovalency of O = 2



electrovalency of Ca = 2
electrovalency of Cl = 1

The force of attraction is equal in all direction so ionic bond is non-directional. A definite three dimensional

structure is formed called crystal lattice. Energy released during the formation of one mole crystal lattice is called lattice energy.

Ionic compound do not have molecular formula. It has only empirical formula.

e.g. NaCl is empirical formula of sodium chloride

Conditions for Forming Ionic Bonds

Formation of Ionic bond depends upon these three factors –

(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 Ionisation energy → Greater tendency to form cation.

e.g. $\text{Na}^+ > \text{Mg}^{+2} > \text{Al}^{+3}$
 $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ } Cation formation tendency

(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 → Greater tendency to form anion

$\text{Cl}^- > \text{F}^- > \text{Br}^- > \text{I}^-$
 $\text{F}^- > \text{O}^{-2} > \text{N}^{-3}$ } Anion formation tendency

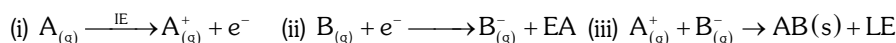
(c) Lattice energy - (Energy released) Amount of energy released when one mole of crystal lattice is formed

Higher lattice energy → Greater will be the stability or strength of ionic compound.
 or Amount of energy required to break the crystal.

(d) Overall lowering of energy :

Energy must be released during bond formation.

Energy changes are involved in the following steps –





This concludes that for lower value of IE and higher value of EA there is more ease of formation of the ionic compound which is summarised as Born Haber Cycle.

Representation of formula of compounds :

(1) Write the symbols of the ions side by side in such a way that positive ion is at the left and negative ion is at the right as $\text{A}^+ \text{B}^-$

(2) Write their electrovalencies in figure at the top of each symbol as $\text{A}^x \text{B}^y$

(3) Now apply criss cross rule as  , i.e. formula $\text{A}_y \text{B}_x$.

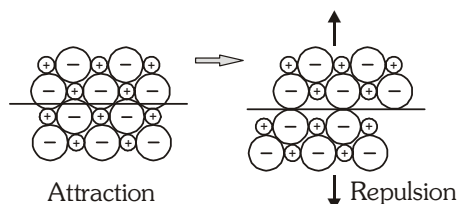
Examples : Calcium chloride  = CaCl_2

Properties of Ionic Compound

(a) Physical state –

Ionic compounds are hard, crystalline and brittle due to strong electrostatic force of attraction.

Brittleness →



{ Same charged ions comes nearer. So they repel each other. }

(b) Isomorphism –

(1) Two compounds are said to be isomorphous if they have similar no. of electrons i.e. similar configuration of their cation and anion.

(2) They have similar crystal structure.

Example –

	Na ⁺	F ⁻	Mg ⁺²	O ⁻²
Valency	+1,	-1	+2,	-2
electronic configuration	2, 8	2, 8	2, 8	2, 8
similarly		Ca ⁺²	2Cl ⁻¹	2K ⁺¹ S ⁻²
	2, 8, 8	2, 8, 8 } 2, 8, 8 }	2, 8, 8 } 2, 8, 8 }	2, 8, 8

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

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 Polar solvents like water.

Less soluble in non polar solvents like benzene.

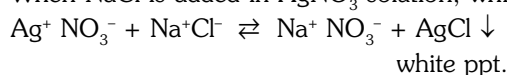
Ex. NaCl form a true solution in water but is colloid in benzene

(f) Ionic reaction –

(a) Ionic compounds shows ionic reaction and covalent compounds shows - molecular reaction.

(b) Ionic reactions are faster than molecular reaction because of free ions.

e.g. When NaCl is added in AgNO₃ solution, white ppt of AgCl is formed at once.



(g) Ionic bond non-directional and does not show stereo isomerism

Polarisation (Fajan's Rule) (Covalent Nature in Ionic Bond)

When a cation approaches an anion closely the positive charge of a cation attract the electron cloud of the anion towards itself, due to the electrostatic force of attraction between them.

At the same time cation also repel the positively charge nucleus of anion.

Due to this combined effect, cloud of anion is bulged or elongated towards the cation. This is called distortion, deformation or Polarisation of the anion by the cation and anion is called Polarised.

Polarisation Power

The ability of cation to polarised a nearby anion is called Polarisation power of cation.



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

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

Polarizability

Ability of an anion to get polarised by the cation.

Polarisation of anion causes some sharing of electron between the ions so ionic bond acquires certain covalent character.

[Polarisation \propto Covalent character]

Magnitude of polarisation depends upon a no. of factors, suggested by Fajan and are known as Fajan's

rule.

Fajan's Rule (Factors Affecting Polarisation)

(a) **Size of cation** : Polarisation of the anion increases as the size of cation decreases.

$$\text{Polarisation} \propto \frac{1}{\text{size of cation}}$$

eg.

In a group



-

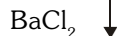
Size of cation increases

-

Covalent character decreases

-

Ionic character increases



Greatest polarising power of Be²⁺, shows its maximum covalent character

In a period — Na⁺, Mg²⁺, Al³⁺, Si⁴⁺

→

- Cation size decreases

- Covalent character increases

(b) **Size of anion** :- If the size of the anion increases for a given cation, the covalent character increases. Polarisation \propto size of anion.



-

size of anion increases

-

Covalent character increases

-

Ionic character decreases

(c) **Charge on cation** :-

$$\text{Polarisation} \propto \text{charge on cation}$$

$$\text{Polarisation (covalent character)} \propto \text{Charge on cation}$$

eg.



→

- Charge on cation increases

- Covalent character increases

(d) **Charge on anion** :-

$$\text{Polarisation} \propto \text{Charge of anion}$$



→

- Charge increases

- Covalent character increases



>



>



$$\text{Charge on anion} \propto \text{polarisation} \propto \text{covalent nature} \propto \frac{1}{\text{M.P.}}$$

(e) **Electronic configuration of cation** :-

Order of Polarisation power : $8e^- < (18+2)e^- < 18e^-$

$\text{CuCl} \longrightarrow \text{Cu}^+ \quad 2, 8, 18 \quad (\text{Covalent})$

$\text{NaCl} \longrightarrow \text{Na}^+ \quad 2, 8 \quad (\text{Ionic})$

Cu^+ and Na^+ both the cation (Pseudo inert & inert respectively) have same charge and size but polarising power of Cu^+ is more than Na^+ because -

$$\begin{array}{ccc} z_{\text{eff}} \text{ of } ns^2p^6 (\text{inert}) & < & z_{\text{eff}} \text{ of } ns^2p^6d^{10} (\text{pseudo inert}) \\ \text{Na}^+ & < & \text{Cu}^+ \\ (\text{Ionic}) & & (\text{Covalent}) \end{array}$$

So CuCl has more covalent character than NaCl .

Application of Fajan's Rule :

(i) To determine covalent and ionic character of molecule

greater the polarisation of anion greater will be the covalent character

Increasing order of covalent character :

- $\text{LiF} < \text{LiCl} < \text{LiBr} < \text{LiI}$
- $\text{CaCl}_2 < \text{FeCl}_2 < \text{FeCl}_3$
- $\text{SrCl}_2 < \text{SnCl}_2 < \text{CdCl}_2$
- $\text{SF}_2 < \text{SF}_4 < \text{SF}_6$
- $\text{Hg}_2\text{Cl}_2 < \text{HgCl}_2$
- $\text{ZnCl}_2 < \text{CdCl}_2 < \text{HgCl}_2$

(ii) Thermal Stability

It is the strength of a compound at high temperatures i.e. a molecule with more thermal stability has more resistance to decomposition at high temperatures.

- (1) For compounds having monoatomic anions, thermal stability is decided by the inter-ionic distance. As the inter ionic distance increases lattice energy decreases so thermal stability decreases and its vice versa.

- Ex.**
- (a) $\text{Li}_3\text{N} > \text{Na}_3\text{N} > \text{K}_3\text{N}$
 - (b) $\text{Li}_2\text{O} > \text{Na}_2\text{O} > \text{K}_2\text{O} > \text{Rb}_2\text{O} > \text{Cs}_2\text{O}$
 - (c) $\text{LiX} > \text{NaX} > \text{KX} > \text{RbX} > \text{CsX}$ (where $X = \text{F}, \text{Cl}, \text{Br}, \text{I}$)
 - (d) $\text{BeX}_2 > \text{MgX}_2 > \text{CaX}_2 > \text{SrX}_2 > \text{BaX}_2$ (where $X = \text{F}, \text{Cl}, \text{Br}, \text{I}$)
 - (e) $\text{Be}_3\text{N}_2 > \text{Mg}_3\text{N}_2 > \text{Ca}_3\text{N}_2 > \text{Sr}_3\text{N}_2 > \text{Ba}_3\text{N}_2$
 - (f) $\text{BeO} > \text{MgO} > \text{CaO} > \text{SrO} > \text{BaO}$

- (2) For the ionic compounds having polyatomic anions, Thermal stability depends on packing of the cations and anions. Larger anions are more stable with larger cations. hence for these anions, thermal stability increases down the group. For example

- Ex.**
- (a) $\text{LiClO}_3 < \text{NaClO}_3 < \text{KClO}_3 < \text{RbClO}_3 < \text{CsClO}_3$
 - (b) $\text{LiNO}_3 < \text{NaNO}_3 < \text{KNO}_3 < \text{RbNO}_3 < \text{CsNO}_3$
 - (c) $\text{LiOH} < \text{NaOH} < \text{KOH} < \text{RbOH} < \text{CsOH}$
 - (d) $\text{Li}_2\text{CO}_3 < \text{Na}_2\text{CO}_3 < \text{K}_2\text{CO}_3 < \text{Rb}_2\text{CO}_3 < \text{Cs}_2\text{CO}_3$
 - (e) $\text{Be}(\text{OH})_2 < \text{Mg}(\text{OH})_2 < \text{Ca}(\text{OH})_2 < \text{Sr}(\text{OH})_2 < \text{Ba}(\text{OH})_2$
 - (f) Super oxides, peroxides and ozonides of alkali & alkaline earth metals also have the same order.

Note :-

Heating Effect

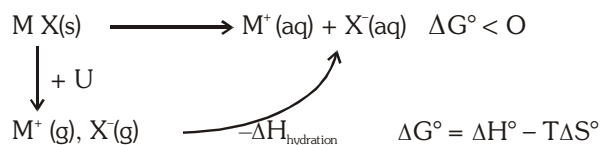
- (a) Metal carbonate $\xrightarrow{\Delta}$ metal oxide + CO₂
(Except the carbonate of Na⁺/K⁺/Rb⁺/Cs⁺, due to their greater ionic character)
- (b) Metal carbonate $\xrightarrow{<800^\circ\text{C}}$ metal oxide + SO₃
Metal carbonate $\xrightarrow{>800^\circ\text{C}}$ metal oxide + SO₂ + O₂
(Except the sulphate of Na⁺/K⁺/Rb⁺/Cs⁺, due to their greater ionic character)
- (c) Metal hydroxide $\xrightarrow{\Delta}$ metal oxide + H₂O
- (d) Metal bicarbonate $\xrightleftharpoons{\Delta}$ metal carbonate + CO₂ + H₂O
- (e) Ammonium salts having CO₃⁻², PO₄⁻³, SO₄⁻², X-anion (non oxidising or weak oxidising) gives NH₃ gas on decomposition.
Ammonium salt having Cr₂O₇⁻², ClO₃⁻¹, NO₂⁻¹, NO₃⁻¹ (strong oxidising anion) gives N₂ or N₂O gas on decomposition.
- (f) Metal nitrate $\xrightarrow{\Delta}$ metal oxide + NO₂ + O₂
Except : Na, K, Rb, Cs nitrate $\xrightarrow{\text{low temp.}}$ MNO₂ + 1/2 O₂
 \downarrow high temp. (>800°C)
M₂O + N₂ + O₂

Note :

- (i) Some less stable metal oxide like Ag₂O & HgO further decompose into metal & oxygen.
- (ii) Metal salts having high percentage of oxygen like KMnO₄, K₂Cr₂O₇ & KClO₃ give O₂ gas on decomposition.

(iii) Solubility in water :

Ionic compounds are more soluble in polar solvents and less soluble in non polar solvents.



For the solubility of ionic compounds in water, it is necessary that ΔG° must be negative.

Favourable conditions for solubility of ionic compound in water is

$$\Delta H_{\text{hydration}} > \Delta H_{\text{Lattice-energy}}$$

$$\text{LE} \propto \frac{1}{r^+ + r^-}, \quad \text{HE} \propto \frac{1}{r^+} + \frac{1}{r^-}$$

If lattice energy decreases, solubility increases

If hydration energy decreases, solubility decreases

Note : Some important solubility trends of ionic compounds.

- (1) In Sulphates of alkaline earth metals solubility decreases down the group



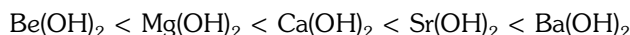
- (2) In Chlorides of alkaline earth metals solubility decreases down the group



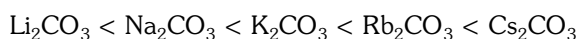
- (3) In Hydroxides of alkali metals solubility increases down the group



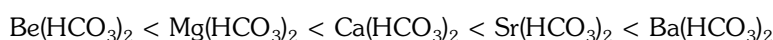
- (4) In Hydroxides of alkaline earth metals solubility increases down the group



- (5) In carbonates of alkali metals solubility increases down the group



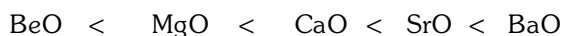
- (6) In HCO_3^- of alkaline earth metals solubility increases down the group



- (7) In F^- of alkali metals solubility increases down the group



- (8) In Oxides of alkaline earth metals solubility increases down the group.



(iv) Solubility of heavy metal salts

In heavy metal salts greater the covalent character the less will be the solubility in water.

$$\text{solubility} \propto \frac{1}{\text{cov. char.}}$$

Eg. (i) $\text{PbF}_2 > \text{PbCl}_2 > \text{PbBr}_2 > \text{PbI}_2$

(Anion size \uparrow , cov. char. \uparrow , solubility \downarrow)

(ii) $\text{ZnCl}_2 > \text{CdCl}_2 > \text{HgCl}_2$

$Z_{\text{eff}} \uparrow$, PP \uparrow , CC \uparrow , solubility \downarrow

(iii) $\text{ZnCl}_2 > \text{CdCl}_2 > \text{HgCl}_2$

$Z_{\text{eff}} \uparrow$, PP \uparrow , CC \uparrow , solubility \downarrow

(iv) $\text{AgF} > \text{AgCl} > \text{AgBr} > \text{AgI}$

Anionic Size \uparrow , PP \uparrow , CC \uparrow , solubility \downarrow

(v) Melting Point

Melting point of ionic compounds

The two factors which mainly influence the melting point of ionic compound are

- (i) Lattice enthalpy (ii) Polarisation

$$\text{M.P.} \propto \text{LE} \quad \text{when} \quad \left\{ \begin{array}{l} \text{Cation} = \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+ \\ \text{or} \\ \text{Anion} = \text{F}^-, \text{O}^{2-}, \text{N}^{3-}, \text{C}^{4-}, \text{H}^- \end{array} \right.$$

Melting point of ionic compound $>$ covalent compound

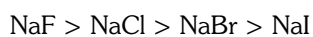
Examples



(ii) Polarisation

The increase of the covalent character is reflected in decreasing melting point of the compounds

$$\text{mp} \propto \frac{1}{\text{polarisation of anion}}$$



(vi) Colour of Compounds

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

$$\text{Colour intensity} \propto \phi(\text{Covalent character})$$

As polarisation increases from chloride to iodide, the colour of many metal halides are intensified, as for example :

