CHEMICAL BONDING

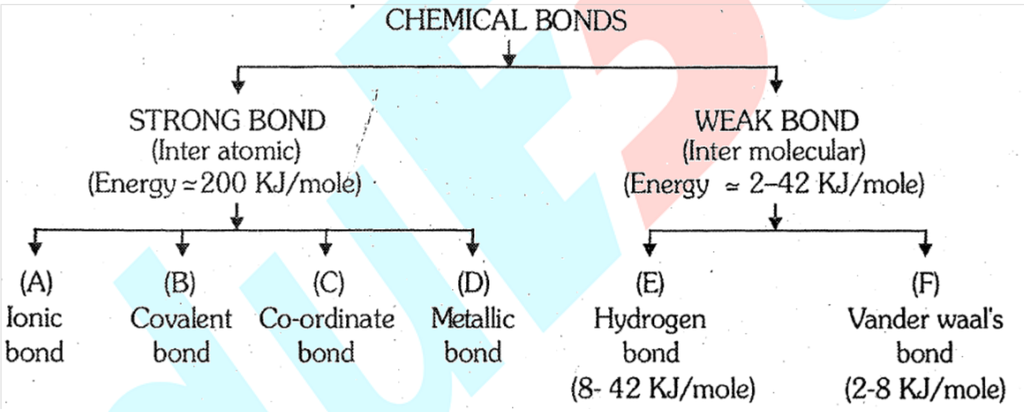
2.0 INTRODUCTION

- 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 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 energy a Strength of the bond.
- Therefore molecules are more stable than atoms.

Classification of Bonds



Cause of Chemical Combination

(A) Tendency to acquire minimum energy

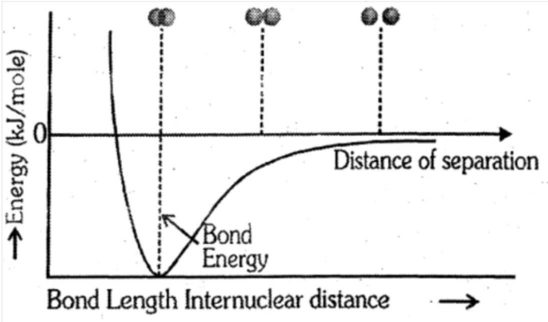
(a) When two atoms approaches to each other. Nucleus of one atom attracts the electron of another atom.

(b) Two nuclei and electrons of both the atoms repells each other.

(c) If net result is attraction, the total energy of the system (molecule) decreases and a chemical bond forms.

(d) So Attraction α 1/energy α Stability.

(e) Bond formation is an exothermic process



(B) Tendency to acquire noble gas configuration:

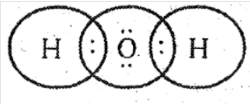
(a) Atom combines to acquire noble gas configuration.

(b) Only outermost electrons i.e. ns, np and (n–1)d shells electrons participate in bond formation.

(c) 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)

2.1 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 loose 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 defficient molecules)

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

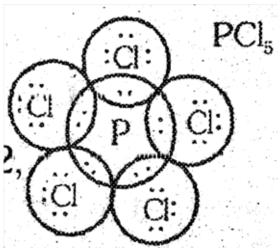
Example- Halides of IIIA groups, BF_3, $AlCl_3$, BCl_3, hydride of IIIA/13th group etc.

Other examples – $BeCl_2$ ($4e^-$), $ZnCl_2$ ($4e^-$), $Ga(CH_3)_3$ ($6e^-$)

(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- $1s^2,2s^22p^6,3s^23p^63d^{10},4s^24p^1$

Electronic configuration of Ga^{+3} – 1s2, 2s2, 2p6, $\underbrace{3s^2 3p^6 3d^{10}}_{18e^-}$

(d) Cations having electron between 9 to 1 7 in their outer most shell

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

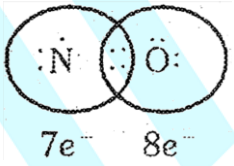
Electronic configuration of Fe- $1s^2,2s^22p^6,3s^73p^63d^6,4s^2$

Electronic configuration of Fe^{+3} - $1s^2,2s^22p^6$, $\underbrace{3s^2 3p^6 3d^5}_{(\text{less than } 18e^-)}$

(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.

Old concept : Given by : **Frankland**

Valency with respect to Hydrogen : Valency of H = 1

It is defined as the number of hydrogen attached with a particular element

	IA	IIA	IIIA	IVA	VA	VIA	VIIA
	NaH	MgH_2	AlH_3	SiH_4	PH_3	H_2S	HCl
Valency	1	2	3	4	3	2	1

Note : Valency w.r.t. H across the period increases upto 4 and then again decreases to 1.

Valency with respect to oxygen : Valency of 'O' = 2

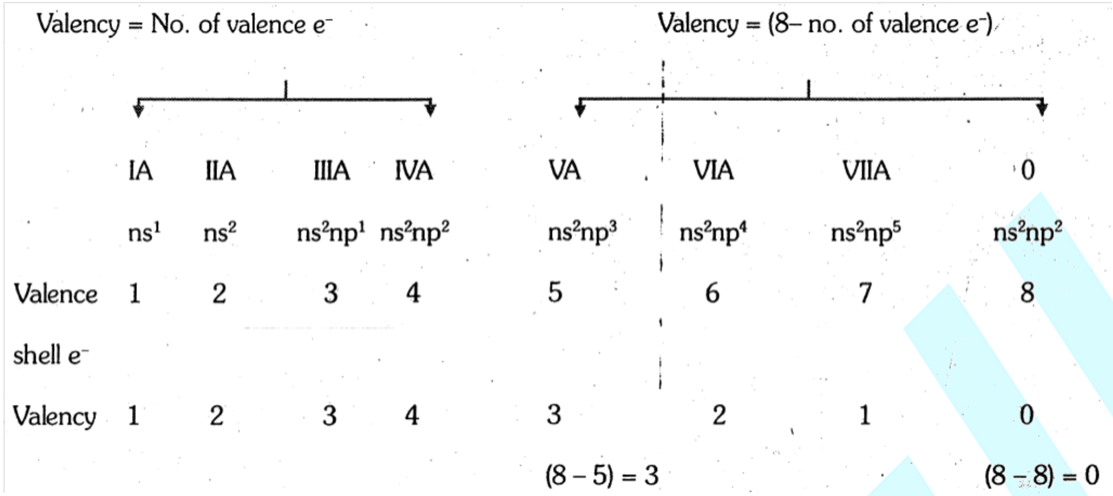
It is defined as twice the number of oxygen atoms attached with a particular atom .

	IA	IIA	IIIA	IVA	VA	VIA	VIIA
	Na_2O	MgO	$Al2O_3$	SiO_2	P_2O_5	SO_3	Cl_2O_7
Valency	1	2	3	4	5	6	7

Note: Valency with respect to oxygen increases from 1 to 7 across the period. Valency w.r.t. 'O' is equal to the group number .

New concept : This concept is based on the electronic configuration. According to this concept valency for IA to IVA group elements is equal to number of valence shell e^- and from VA to zero group, it is -

[8- (number of valence e^-)]



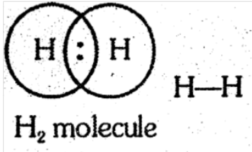
Valency = No. of valence e^- | Valency = (8– no. of valence e^-)

	IA	IIA	IIIA	IVA	VA	VIA	VIIA	0
	ns^1	ns^2	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^2
Valence shell e^-	1	2	3	4	5	6	7	8
Valency	1	2	3	4	3	2	1	0
					(8 – 5) = 3			(8 – 8) = 0

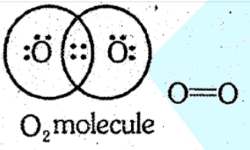
Note : All the elements of a group have same valencies because they gave same number of valence shell electrons.

2.2 COVALENT BOND

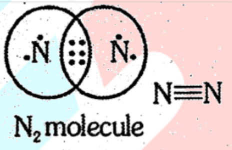
- A covalent bond is formed by the mutual sharing of electrons between two atoms of electro negative elements to complete their octet. (Except H which completes its duplet)



H_2 molecule



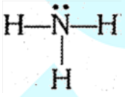
O_2 molecule



N_2 molecule

- 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 -  $H-\overset{\cdot\cdot}{\underset{|}{N}}-H$ $\underset{}{H}$ {Three single bonds (not triple bond)}

N≡N Triple bond. (not three single bonds) O=O Double bond (Not two single bonds) H–O–H (Two single bonds)

Orbital Concept of Covalent Bond

- One orbital can accommodate maximum 2 electrons with opposite spins like $\boxed{\uparrow\downarrow}$
- 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.

2.3 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.

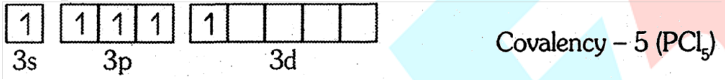
Example-

(a) Nitrogen → Ground state

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

(b) Phosphorus → Ground state

Phosphorus → Excited state



Note:

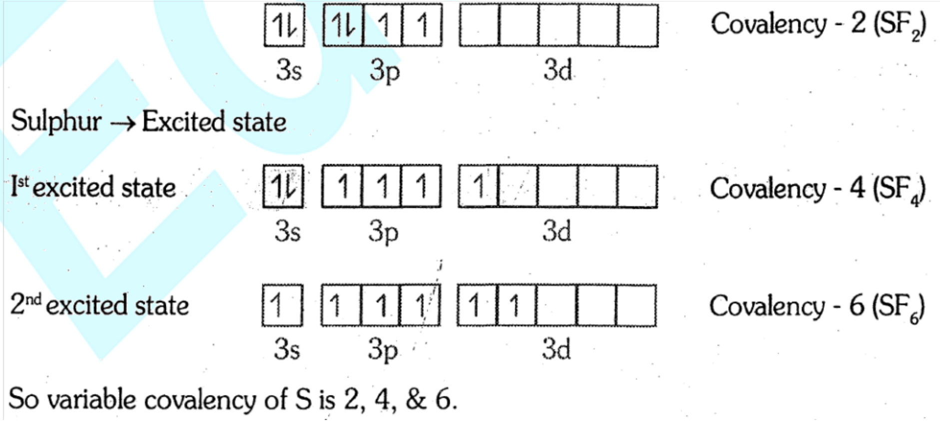
NCl_3 – exists

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.

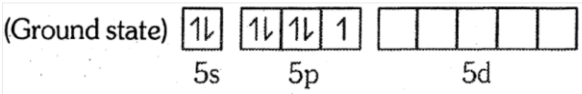
(c) Sulphur → Ground state



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

2.4 CHARACTERISTIC OF COVALENT COMPOUND

(a) Physical state :- Covalent compounds are found in all the three states - Gas, Solid & Liquid.

Separate molecules – In gaseous state
Associate molecules – In liquid & solid state ·
(Due to strong vander waal's force and hydrogen bonding among the molecules.)
As the molecular weight increases physical state changes -

eg.	F_2 and Cl_2	Br_2	I_2, At_2
	gas	liquid	solid

$\longrightarrow$

Top to bottom in a group. Vander waal's force increases between the molecules.

(b) Covalent solid :- Those solids in which atoms are linked together by covalent bonds, forms infinite three dimensional giant structure.
eg. Diamond, Graphite, AlN, SiC, SiO_2 etc.
Molecular solid :- Discrete (separate) molecules are formed by covalent bonds and then the, molecules associates due to intermolecular force of attraction. (van der Waal force)
eg. Solid I_2, dry ice (Solid CO_2) etc.

(c) Conduttivity:- Mastly covalent compounds are bad conductor of electricity. But few polar covalent compounds due to self ionisation can conduct electricity, eg. H_2O, liquid NH_3 etc.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$2NH_3 \rightarrow NH_4^+ + NH_2^-$$

Free ions are formed which can conduct electricity.
Exceptions :- Graphite, HCl in water.

(d) Solubility :- Non polar compounds are soluble in non polar solvents. Non polar compounds forms vander waal bond with non polar solvent molecules.
Non polar solvents are C_6H_6, CCl_4 etc.

(e) Isomerism :- Covalent bond is rigid and directional, so it shows isomerism.
eg. Organic compounds.

(f) Reaction :- Reaction between covalent compounds are slow Because it involves breaking of old bonds and formation of new bonds.

BEGINNER'S BOX-1

1. Which condition favours the bond formation:
(1) Maximum attraction and maximum potential energy
(2) Minimum attraction and minimum potential energy
(3) Minimum potential energy and maximum attraction

(4) Number of the above

2. Which one at the following element will never obey octet rule:
(1) Na (2) F (3) S (4) H

3. Which is not an exception to octet rule ?
(1) BF_3 (2) $SnCl_4$ (3) BeI_2 (4) ClO_2

4. An oxide of chlorine which is an odd electron molecule is:
(1) ClO_2 (2) Cl_2O_6 (3) Cl_2O_7 (4)Cl_2O

2.5 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 –

(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) Strength of covalent bond $\propto$ extent of overlapping.

(f) Extent of overlapping depends on two factors.

(i) Nature of orbitals - p, d and fare directional orbitals → more overlapping
s-orbital → non directional - less overlapping

(ii) NatUre of overlappirig - 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.

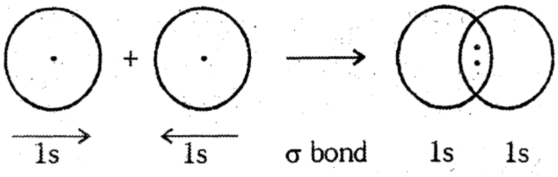
(d) Free rotation is possible about a single σ bond.

(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

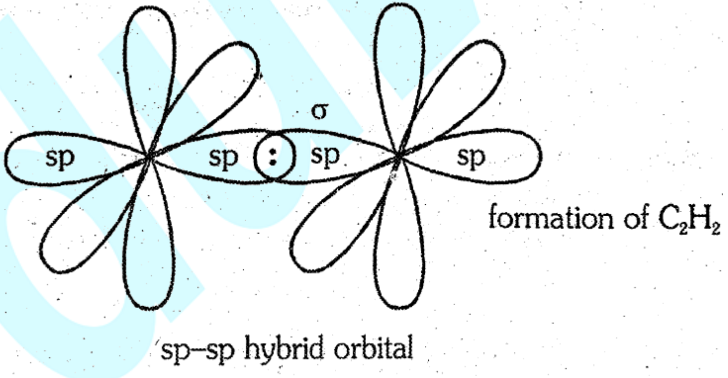
(i) s-s overlapping - Two half filled s-orbitals overlap along the internuclear axis. Ex. H_2 molecule.



(Formation of H_2 molecule)

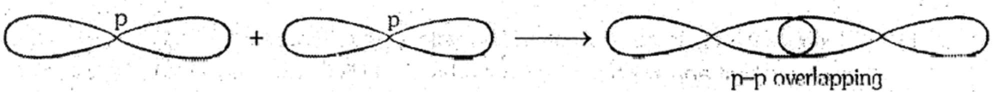
(ii) s-p overlapping (Formation of HF) – When half ill s-orbital of one atom overlap with half filled p-orbital of other atom.

(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.



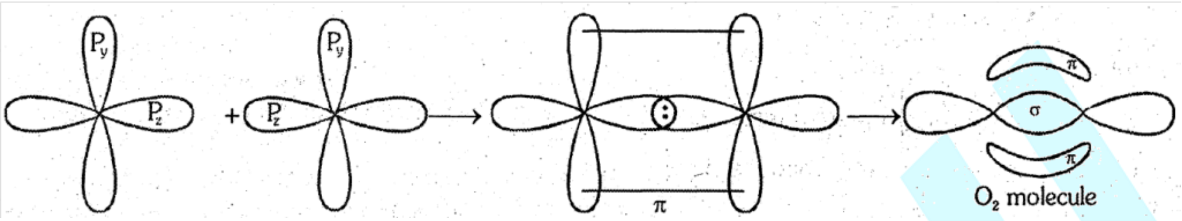
Ex. Formation of Cl_2, F_2, Br_2

Pi(π) – Bond

(a) The bond formed by sidewise (lateral) overlapping are known as n 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 n 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- $1s^2\ 2s^2 2p_x{}^2\ p_y{}^1\ p_z{}^1$

(b) 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.

BEGINNER'S BOX-2

1. According to the valence bond theory, when a covalent bond is formed between two reacting atoms, the potential energy of the system becomes-

(1) negative (2) positive (3) minimum (4)maximum

2. The strongest covalent bond is formed by the overlap of – (If considering for same shell)

(1) sand p orbitals (2) s and s orbitals

(3) p and d orbitals (4) p and p collateral orbitals

3. In a triple bond there is sharing of :-

(1) 3-electrons (2) 4-electrons

(3) Several electrons (4) 6-electrons

4. Which of the following configuration shows second excitation state of Iodine:-

5. Variable covalency is exhibited by:-

(1) P and S (2) N and O (3) N and P (4) F and Cl

6. Which of the following bonds will have directional character

(1) Ionic bond (2) Metallic bond

(3) Covalent bond (4) Both covalent & metallic

7. Number of σ and π bonds present in

CH_3–CH=CH–C=CH are-

(1) 10 σ , 3π (2) 10 σ, 2π (3) 9σ, 2π (4) 8σ, 3π

8. Which of the following statements regarding covalent bond is not true ?

(1) The electrons are shared between atoms

(2) The bond is non-directional

(3) The strength of the bond depends upon the extent of overlapping

(4) The bond formed may or may not be polar

9. Predict the nature of bond

Orbitals	Internuclear axis	Bond
s + s	any axis	....
s + px	x-axis	....
s + py	y-axis	....
s + px	z-axis	....
px + px	x-axis	....
py + pz	y-axis	....
pz + pz	z-axis	....
px + px	y or z-axis	....
py + py	x or z axis	....
pz + pz	x or y axis	....

2.6 HYBRIDISATION

Consider an example of Be compound :-

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

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.

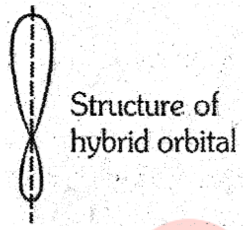
Now after considering s-p hybridisation in $BeCl_2$

$Cl\overset{p-s}{—}Be\overset{p-p}{—}Cl$

(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 Ist 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 lp-lp > lp-bp > bp-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.

$sp < sp^2 < sp^3 < sp^3d < sp^3d^2 < sp^3d^3$

DETERMINATION OF HYBRIDISATION STATE

Method (I) : Number of hybrid orbital = number of cr bond + number of lone pair [surrounding the central atom]

Method (II) : To predict hybridisation following formulae may be used :

$$\text{Number of hybrid orbital} = \frac{1}{2}\,[Ve^- + SA \pm C]$$

[Ve^- = Total number of valence e^- in the central atom, SA = total number of monovalent atoms; C = charge]

Eg. NH_4^+ $\frac{1}{2}$ [5 + 4 – 1] = 4 sp^3 hybridisation.

SF_4 $\frac{1}{2}$ [6 + 4] = 5 sp^3d hybridisation.

SO_4^{2-} $\frac{1}{2}$[6 + 2) = 4 sp^3 hybridisation

('O' is divalent so add only charge on anion)

NO_3^- $\frac{1}{2}$[5 + 1] = 3 sp^2 hybridisation

If such type of e^- pairs are -

two - sp hybridisation ..

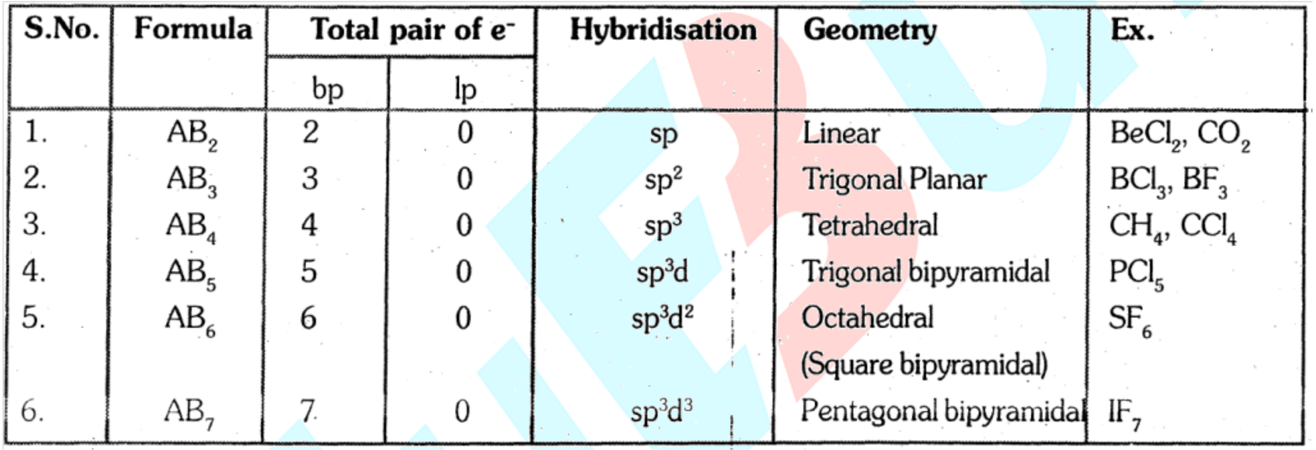
three - sp^2 hybridisation

four - sp^3 hybridisation

five - sp^3d hybridisation

six - sp^3d^2 hybridisation

seven - sp^3d^3 hybridisation



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) $sp/sp^2/sp^3$ = Any where

(ii) sp^3d = equatorial

(iii) sp^3d^2 = axial (defined first)

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

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

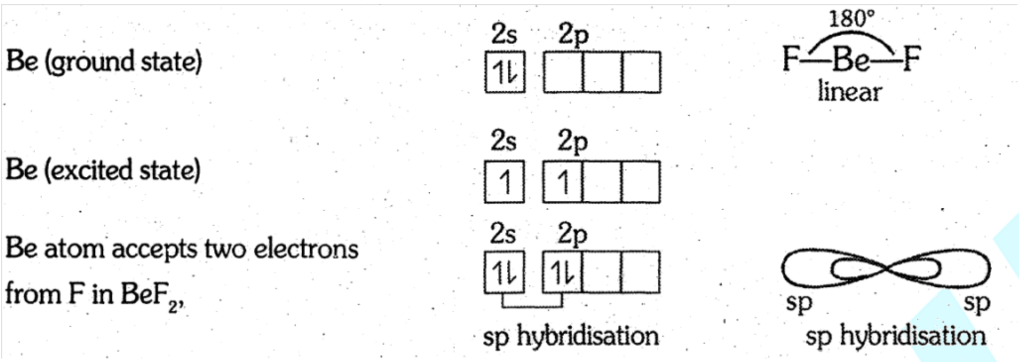
Type of Hybridisation

(A) sp bybridisation :

(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.

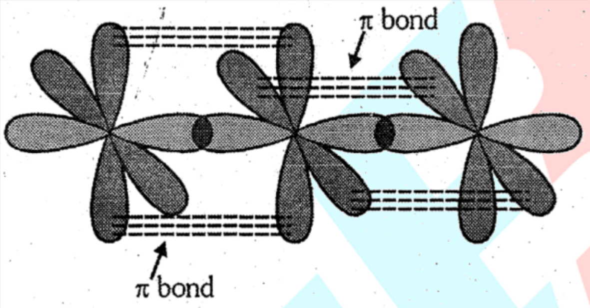
(b) These two sp hybrid orbitals are arrange in straight line & at bond angle 180°.

(c) s-character 50%



CO_2 Molecule (O=C=O) :

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



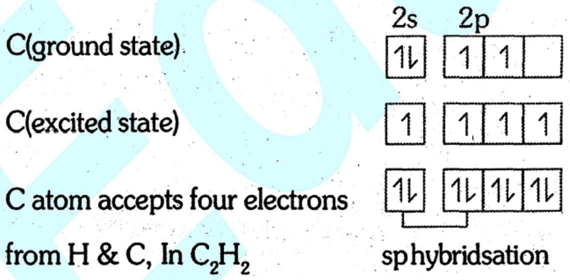
Molecular orbital picture of CO_2

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

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

CH≡CH[H–C_A= C_B–H]

In CH≡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(π) bonds.

Therefore in H–C_A ≡ C_B–H

sigma bond between C_A–C_B is forrned sp- sp overlapping

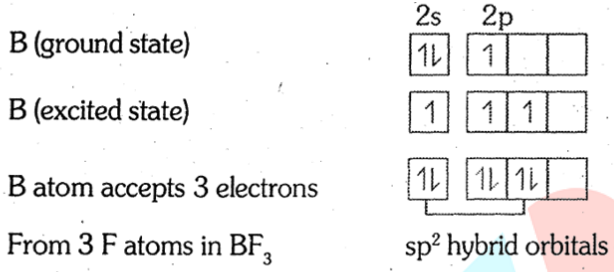
sigma bond between C_A–H is formed sp-s overlapping
sigma bond between C_B–H is formed sp-s overlapping
pi bond between C_A–C_B is formed : P_y- $P_{y'}$ P_x - $P_{x'}$ overlapping

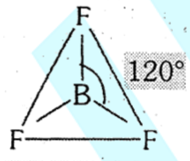
- Each C atom forms two sigma bonds but in C_2H_2, total sigma bonds are 3
- Each C atom forms two π bonds. Total. π bonds in C_2H_2 are two
- Total number of bonds in acetylene are: 3σ + 2π bond = 5 bonds .

(B) sp^2 Hybridisation :

(a) In this hybridisation one s & two p orbitails are mixed to give three new sp^2 – hybrid orbitails which are in same shape & equivalent energies.

(b) These three sp^2 hybrid orbitals are at angle of 120° & giving trigonal planar shape.





Trigonal planar

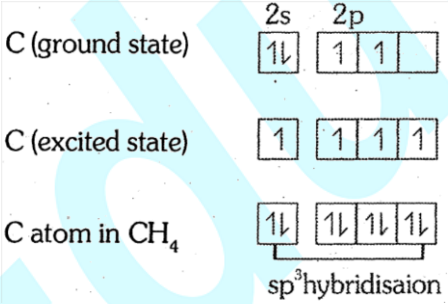
(c) s - character 33.3 %

- 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 $e^{\ominus}$)
- 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° 28' (6)



C atom share four electrons with four hydrogen atoms

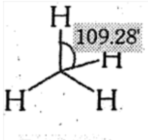
(III) The shape obtained from these hybrid orbitals would be tetrahedron.

Three following examples represent this condition.

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

(I) The following examples represent this condition.
CH_4, CF_4, CCl_4, CBr_4, Cl_4, NH_4^+, BF^{4-}, BeF_4^{-2}

(II) In above compounds, bond angle is 109° 28' & tetrahedron shape.



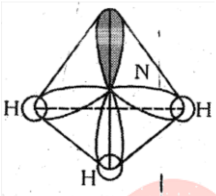
Tetrahedral

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

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

NH_3, NF_3, PF_3, NCl_3, PCl_3, $:CH_3^-$, H_3O^+, ClO_3^-

(II) sp^3 hybridisation, pyramidal shape & bond angle will be less than 109° 28'. Due to the presence of one lone pair electron on nitrogen it repels bond pair electron more therefore bond angle reduced from 109° 28 to 107°. The repulsion between lp- bp > bp-bp.



Molecular orbial picture of NH_3

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

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

H_2O, OCl_2,OBr_2, OF_2, OI_2 etc .

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

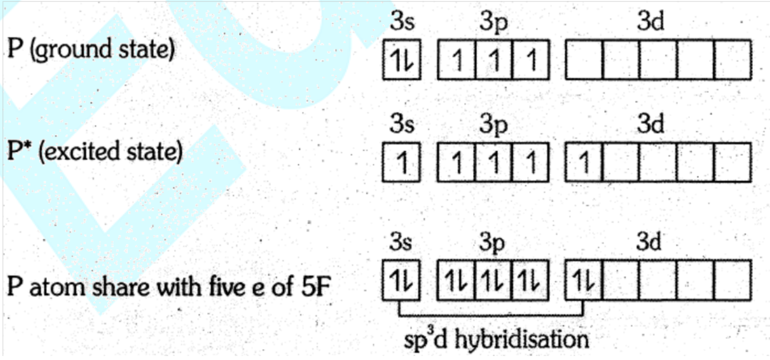
In H_2O the hybridisation on O atom is sp^3, but due to presence of two lone pair electrons they repell each other

(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 hybridization



(III) In this hybridisation d_{z^2} orbital is hybridisedwith sand 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^-

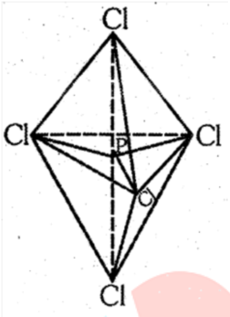
In above hybridisation, there1are four conditions.

(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

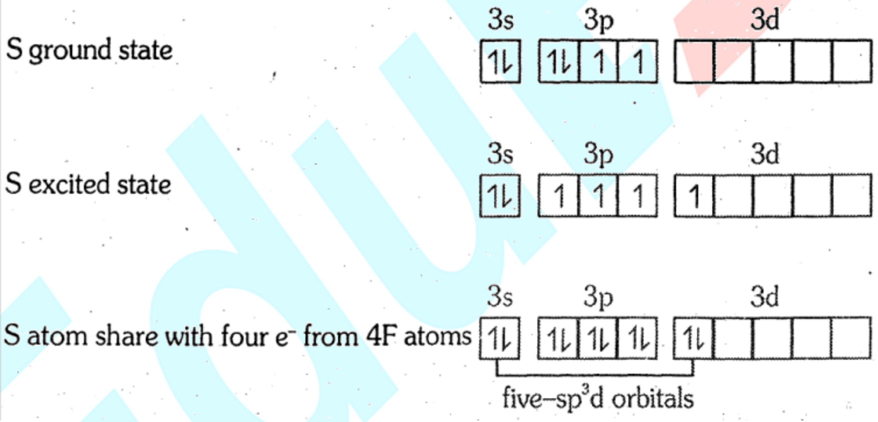
(b) Four sigma bonds and one lone pair of electron:

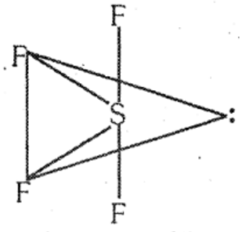
The following examples represent this condition.

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





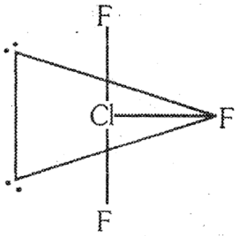
Structure of SF_4

(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^-, CIF_2^-, IF_2^-, BrF_2^-, XeF_2, I_3^-, Br_3^-

The geometry of above examples will be linear shape.

(E) sp^{3}d^2 Hybridisation :

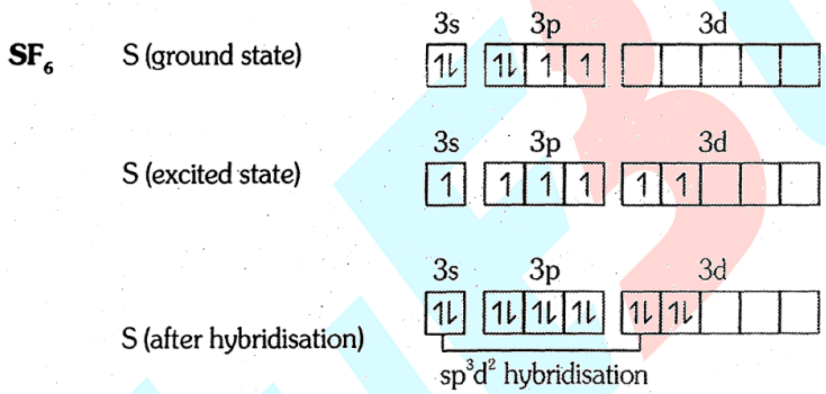
(I) In this hybridisation, one s- orbital, three p-orbitals & two d-orbitals (dz^2, dx^2-y^2) are mixed to give six new hybrid orbitals known as sp^{3}d^2 hybrid orbitals.

(II) The geometry of molecule obtained from above six hybrid orbitals will be symmetrical octahedral or square bipyrarnidal.

(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}.



Octahedral or square bipyramidal.

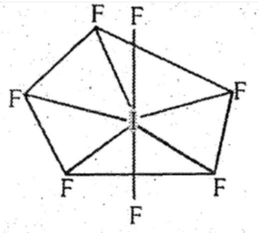
(F) sp^{3}d^3 Hybridisation :

(I) In this hybridisation, one s-orbital, three p-orbitals & three d-orbitals are mixed to give seven new hybrid orbitals known as sp^{3}d^3 hybrid orbitals.

(II) These seven sp^{3}d^3 orbitals are configurated in pentagonal bipyramidal shape.

(III) Five bond angles are of 72° and 10 bond angles of 90°.

(IV) The following examples showing sp^{3}d^3 hybridisation - IF_7 & XeF_6.



(Pentagonal biypyramidal)

EXAMPLES ON sp^3d HYBRIDISATION

Example	σ bond	l.p.e.	Hybridisation	Bond angle	Shape
PCl_5	5	-	sp^3d	120°, 180° & 90°	Trigonal bipyramidal
SF_4	4	1	sp^3d	< 180°,< 90°,< 120°	Irregular tetrahedron
ClF_3	3	2	sp^3d	87.6°	T-shape
IF_3	3	2	sp^3d	87.6°	T-shape
ICl_3	3	2	sp^3d	87.6°	T-shape
Br_3^-	2	3	sp^3d	180°	Linear
ICl_2^-	2	3	sp^3d	180°	Linear
XeF_2	2	3	sp^3d	180°	Linear
PCl_4^+	4	-	sp^3		Tetrahedron
NH_4^+	4	-	sp^3		Tetrahedron
NF_3	3	1	sp^3		Pyramidal
H_3O^+	3	1	sp^3		Pyramidal
SO_3^{2-}	3	1	sp^3		Pyramidal
XeO_3	3	1	sp^3		Pyramidal
H_2O	2	2	sp^3		Angular (V)
NH_2^-	2	2	sp^3		Angular (V)
OF_2	2	2	sp^3		Angular (V)
Cl_2O	2	2	sp^3		Angular (V)
Diamond	4	-	sp^3		Tetrahedron
SiO_2	4	-	sp^3		Tetrahedron
SiC	4	-	sp^3		Tetrahedron
NO_3^-	3	-	sp^2	120°	Trigonal planar
SO_2	2	1	sp^2	<120°	Angular (V)
HCO_3^-	3	-	sp^2	120°	Trigonal planar
$SnCl_2$	2	1	sp^2	<120°	Angular (V)
NO_2^+	2	-	sp	180°	Linear
N_3^-	2	-	sp	180°	Linear

BEGINNER'S BOX-3

1. Which of the following is incorrect about hybridization?

(1) The concept of hybridization is not, applied to isolated atoms.

(2) Hybridization is the mixing of at least two non-equivalent atomic orbitals.

(3) The number of hybrid orbitals generated is more than the number of pure atomic orbitals that participate in the hybridization process.

(4) Hybridization requires an input of energy.

2. The hybridization state of the central atom in $HgCl_2$ is-

(1) sp (2) sp^2 (3) sp^3 (4) dsp^2

3. The hybridization state of the central atom in AlI_3 is-
(1) dsp^2 (2) sp^3 (3) sp^2 (4) sp

4. In C_3O_2, the hybridization state of C is-
(1) sp^2 (2) sp (3) sp^3 (4) dsp^2

5. By hybridization, we mean the hybridization of-
(1) electrons (2) atomic orbitals (3) atoms (4) protons

6. The d- orbitals involved in sp^3d hybridisation is :-
(1) $d_{x^2-y^2}$ (2) d_{z^2} (3) d_{xy} (4) d_{xz}

7. A sp^3 hybrid orbital contains:-
(1) $\frac{3}{4}$ s- character (2) $\frac{1}{4}$ p- character
(3) $\frac{3}{4}$ p – character (4) $\frac{1}{2}$ s - character.

8. In the protonation of NH_3 molecule, following statement is true:-
(1) A covalent bond is formed
(2) Hydrogen bond is formed
(3) Hybridisation state of N is changed
(4) Shape of NH_3 molecule is changed

9. The shape of sulphate ion is :-
(1) Hexagonal (2) Square planar
(3) Trigonal bipyramidal (4) Tetrahedral

10. In which following compound, central atom has four bond pair and one lone pair :-
(1) NH_4^+ (2) ICl_4^- (3) SF_4 (4) XeF_4

11. In which molecule s - p overlapping occurs ?
(1) CH_4 (2) NH_3 (3) H_2O (4) None of these

Hybridisation in solid state :

- Compounds which change their structure in solid state.

$2PCl_5(s) \longrightarrow PCl_4^+ + PCl_6^-$

$PBr_5(s) \longrightarrow PBr_4^+ + Br^-$

$PF_5(s) \cancel{\longrightarrow} PF_4^+ + PF_6^-$

$IF_5(\ell) \longrightarrow IF_4^+ + IF_6^-$

$N_2O_5(s) \longrightarrow NO_2^+ + NO_3^-$

$N_2O_4(s) \longrightarrow NO^+ + NO_3^-$

$XeF_6(s) \longrightarrow XeF_5^+ + F^-$

$Cl_2O_6(s) \longrightarrow ClO_2^+ + ClO_4^-$

$I_2Cl_6(s) \longrightarrow ICl_2^+ + ICl_4^-$

$3I_2(s) \longrightarrow I_3^+ + I_3^-$

Hybridisation in radicals :

Radical	**Hybridisation**
CH_3	....
CH_3	....
ClO_3	....
NO_2	....

Existence and Nonexistence :

Identify existing I non existi.ng compounds/ions

(a) PCl_6^- (b) NH_5 (c) PH_5 (d) $(CCl_6)^{2-}$ (e) $(SiF_6)^{2-}$ (f) $(SiCl_6)^{2-}$
(g) $ClBr_7$ (h) SH_6 (i) XeH_4 (j) $XeOF_4$ (l) ClF_3 (m) BH_4^-
(n) $(PI_6)^-$

2. 7 VALENCE SHFLL ElECTRON PAIR REPULSION TIIEORY(VSEPRT)

(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° 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 - [lp- lp > lp - lp > bp - bp]

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

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

eg.:- CH_4	NH_3	H_2O	$\longrightarrow$	sp^3
109°	107°	105°		hybridization

2.8 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 -

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

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 2_B

Example : - Cl–Cl

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

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

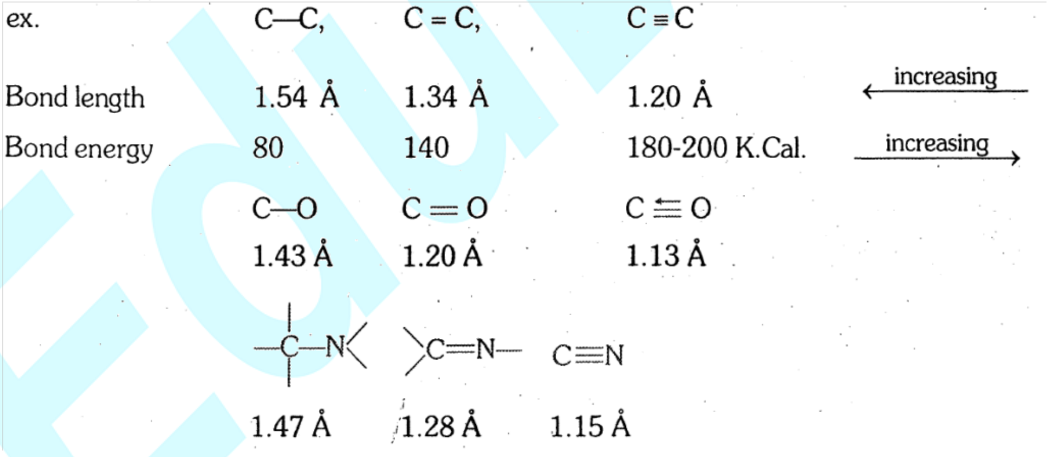
Factors Affecting Bond Length

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

H–F < H–Cl < H–Br < H–l

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

Bond energy $\propto$ Number of bond



ex.	C—C,	C = C,	C ≡ C	
Bond length	1.54 Å	1.34 Å	1.20 Å	← increasing
Bond energy	80	140	180-200 K.Cal.	increasing →
	C—O	C = O	C ≡ O	
	1.43 Å	1.20 Å	1.13 Å	
	$-\overset{\vert}{\underset{\vert}{C}}-N<$	$>C=N-$	$C\equiv N$	
	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 CO_2 is 1.15 Å Resonance occurs in CO_2 is as follows

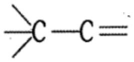
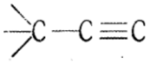
$O=C=O \longleftrightarrow O^{-}–C\equiv O^{+} \longleftrightarrow O^{+}\equiv C–O^{-}$

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

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

Example :-

s–character increases ↓

Compound	Hybridisation	Bond length
Ethane	$sp^3 — sp^3$	1.54 Å
	$sp^3 — sp^2$	1.51 Å
	$sp^3 — sp$	1.47 Å
$C=C—C=C$	$sp^2 — sp^2$	1.46 Å
$C=C—C\equiv C$	$sp^2 — sp$	1.42 Å
$C\equiv C—C\equiv C$	$sp — sp$	1.37 Å

Bond Angle

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

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

Factors affecting the bond angle –

Step I : Hybridisation or % 's' character : Bond angle ∝ % s character

$BeCl_2$	>	BCl_3	>	CCl_4
180°		120°		109.28'

Step II : Lone pair

When hybridization is same, lone pair are different.

$$\text{Bond angle} \propto \frac{1}{\text{Number of lone pair}}$$

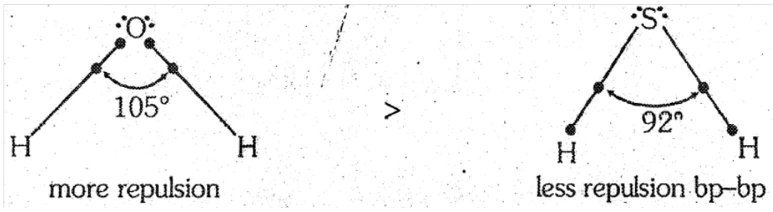
Example :-	CH_4		$\ddot{N}H_3$		$H_2\ddot{O}:$
Hybridisation	sp^3		sp^3		sp^3
Bond angle	109	>	107	>	105
	No l.p.		one l.p.		two l.p.

- 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

Bond angle ∝ 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 – $NH_3 > PH_3 > AsH_3$

Example :-

	$\ddot{N}H_3$	$\ddot{P}H_3$	$\ddot{As}H_3$
Bond angle	107°	93°	91°

$\longrightarrow$

- Electronegativity decreasing.
- Bond angle will decrease

Step IV : Side atom

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

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

Electronegativity of Fluorine is greater than chlorine

$PF_3 < PCl_3 < PBr_3 < PI_3$ (EN of side atom decrease)
$OF_2 < Cl_2O < Br_2O$
$SF_2 < SCl_2 < SBr_2$

Bond angle depends on size of side atom, on increasing size off side atom bond angle increases.
$Cl_2O > H_2O$

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

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

Bond Energy (BE)

Bond energy may be defined as -

(a) Bond formation energy :- Energy released when any bond is formed is known as bond formation energy or bond energy.

(b) 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 $\propto$ 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) ΔElectronegativity :- Bond energy $\propto \Delta$EN eg. HF > HCl > HBr > HI

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

eg	C–C	<	C=C	<	C≡C
	79 K.Cal.		143.3 K.Cal.		199.0 K. Cal.

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

Exception :- In case of halogen group, order of bond energy is-
Cl–Cl > Br–Br > F–F > I–I

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
C–C > Si–Si > Ge–Ge

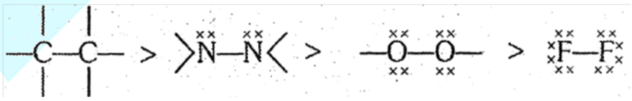
(d) Bond Polarity :- Bond energy $\propto$ Bond polarity
eg. H–F > H–Cl > H–Br > H–I

(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 $\propto \dfrac{1}{\text{lone pair of electrons}}$



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 repells each other in F–F and –O– type of bonds.

Important Note (Summary) :

(i) Bond strength $\propto$ overlapping (if orbitals are given)

(ii) Bond strength $\propto \dfrac{1}{\text{size of orbitals}}$

e.g. 1s-2p > 1s-3s > 1s-4p

(iii) If orbitals are of same shell

Bond strength $\propto$ extent of overlapping $\propto$ directional properties

$$\underbrace{2p - 2p > 2s - 2p > 2s - 2s}_{\text{Axial overlap}} > 2p - 2p \text{ (Side ways)}$$

(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=N exist but P=P does not exist at room temperature.

(vii) O=C=O exist but O=Si =O does not exist.

BEGINNER'S BOX-4

1. Which of the following molecules has the longest nitrogen-nitrogen bond?

(1) N_2H_4 (2) N_2

(3) N_2F_2 (4) All have equal bond lengths

2. Which of the following molecules has the highest value of carbon-carbon bond energy ?

(1) C_2H_4 (2) C_3H_8 (3) C_2H_2 (4) C_2H_6

3. Which of the following has the shortest bond length ?

(1) Br_2 (2) F_2 (3) Cl_2 (4) I_2

4. In ethene, the carbon-, carbon bond distance is-

(1) 154 pm (2) 120 pm (3) 134 pm (4) 142 pm

5. Carbon-halogen bond is strongest in the following

(1) CH_3Cl (2) CH3Br (3) CH_3F (4) CH_3I

6. The correct order of bond length is

(1) C–C < C=C < C≡C (3) C≡C < C=C < C–C

(3) C=C < C≡C < C–C (4) C=C < C–C < C≡C

7. The F–F bond is weak because :

(1) The repulsion between the nonbonding pairs of electrons of two fluorine atoms is large

(2) The ionization energy of the fluorine atom is very low

(3) The length of the F-F bon1 much larger than the bond lengths in other halogen molecules

(4) The F-F bond distance is small and hence the internuclear repulsion between the two F atoms is very low

8. The correct order of decreasing bond energy is:-

(1) O–O > S–S > Se–Se (2) C–C > Si– Si > Ge–Ge

(3) F–F > O–O > N–N (4) F–F > Cl–Cl > Br–Br

9. The bond length does not affected by:-

(1) Electron affinity (2) Bond order

(3) Hybridisation (4) Resonance

10. In allene structure three carbon atoms are joined by:

(1) Three sigma bonds and three pi bonds (2) Two sigma bonds and one pi bond

(3) Two sigma bonds and two pi bonds (4) Three pi bonds only

2.9 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.

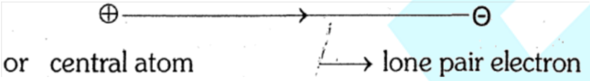
(b) For measurement of extent of polarity, Pauling introduced the concept of dipole moment (μ).

The product of positive or negative charge (q) and the distance (d) between two poles is called dipole moment.

Here- $\vec{\mu}$ = q×d (magnitude of charge × 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 Debye = 1 × 10^{-18} e.s.u. cm = 3.33 × 10^{-30} coulomb metre

(f) In the diatomic molecule ll depends upon difference of EN i.e. μ α ΔEN

order of μ, H–F > H–Cl > H–Br > H–I

μ = 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,

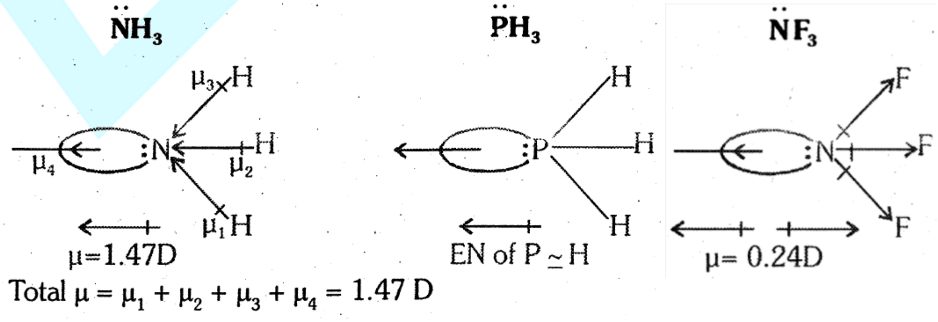
(h) For PCl_5 and SF_6, etc. μ = 0 due to their symmeterical geometry.

(i) Benzene, naphthalene, diphenyl have μ = 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).

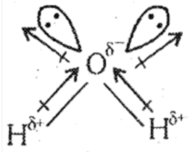
Example- BX_3, CCl_4, $SiCl_4$, CH_4, CO_2 CS_2, PCl_5, SiH_4 etc.

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 H_2O > μ of H_2S because electro negativity 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?

CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4

Sol. Right order is ⟶ $CCl_4 < CHCl_3 < CH_2Cl_2 < CH_3Cl$

$\mu = 0$ 1.02 $CHCl_3$ 1.93

Applications of Dipole Moment

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

If μ = 0 compound is. non polar and symmetrical

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

If μ ≠ 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 :-

$$\% \text{ Ionic character} = \frac{\text{Exerimental value of } \mu}{\text{Theoritical value of } \mu} \times 100$$

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

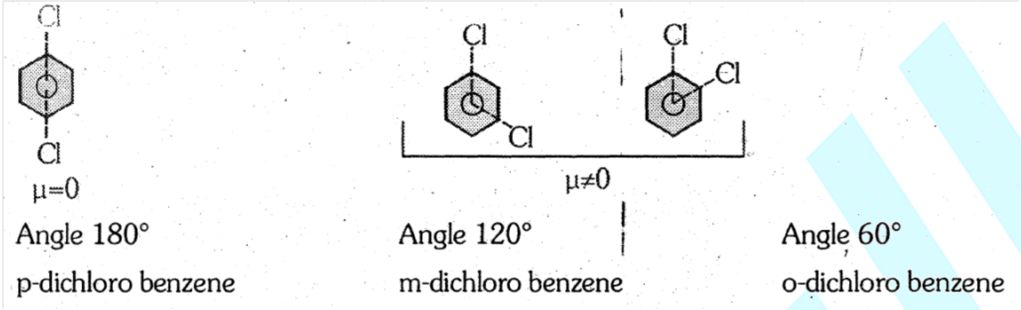
(I) Dipole moment of cis isomers is normally higher than trans isomers.

(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.

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

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



(II) As angle between vetor decreases value of μ increases.

Illustrations

Illustrations 1. Calculate the μ of HCl > if bond distance is 1.34 Å, charge = 4.8×10^{-10} esu and calculate % ionic character if experimental value of m = 1.08 D?

Solution $\mu = q \times d = 4.8 \times 10^{-10} \times 1.34 \times 10^{-8}$

$\mu = 6.4 \times 10^{-18}$ esu cm.

$$\%\ \text{Ionic character} = \frac{1.08 \times 10^{-18}}{6.4 \times 10^{-18}} \times 100 = 16.79\ \%$$

GOLDEN KEY POINTS

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

$H_2O > HF > NH_3 > NF_3$ (value based)	$H_2O > H_2S$
$CH_3Cl > CH_3F > CH_3Br > CH_3I$	$BF_3 < NF_3 < NH_3$
$NO_2^- > NO_2 > NO_2^+$	$H_2O < H_2O_2$

BEGINNER'S BOX-5

1. Which of the following contains polar arid nonpolar bonds?
(1) H_2O_2 (2) CH_4 (3) HCN (4) NH_4Cl

2. Carbon tetrachloride has no net dipole moment because of-
(1) Similar electron affinitie of C and Cl (2) its regular tetrahedral geometry
(3) its planar geometry (4) similar sizes of C and Cl atoms

3. Which of the following molecules is nonpolar?
(i) $PbCl_4$ (ii) BF_3 (iii) $SnCl_2$ (iv) CS_2
(1) (i), (ii), (iii) (2) (i), (ii), (iii), (iv) (3) (i), (ii), (iv) (4) (ii), (iii), (iv)

4. Which of the following has the highest dipole moment.?
(1) o-Dichlorobenzene (2) m-Dichlorobenzene
(3) p-Dichlorobenzene (4) All have equal values

5. Both CO_2 and H_2O contain polar covalent bonds but CO_2 is nonpolar while $H_2O$is polar because-

(1) H atom is smaller than C atom

(2) CO_2 is a linear molecule while H_2O is an angular molecule

(3) O–H bond ~s more polar than C–H bond

(4) CO_2 contains multiple bonds while H_2O has only single bonds

2.10 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 (**:**O=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.

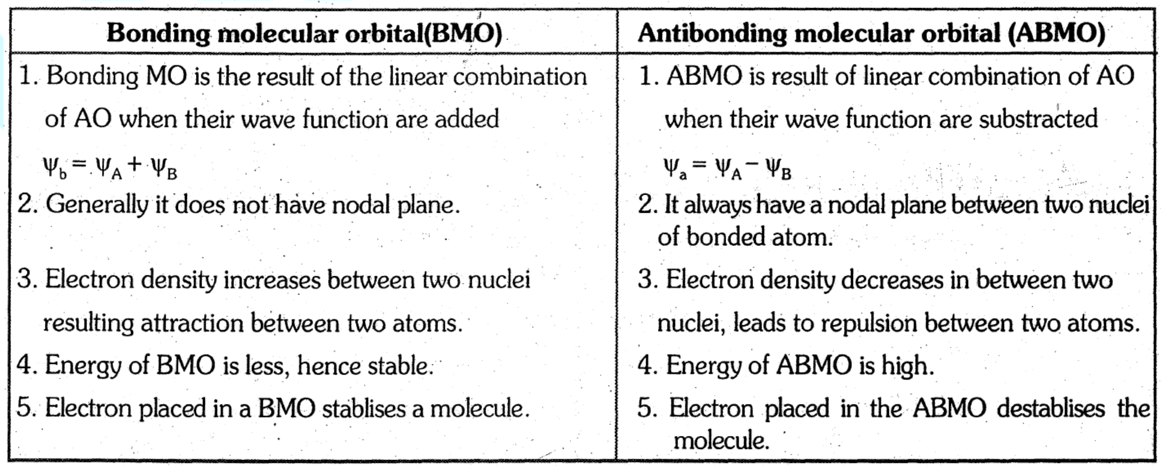
(f) Wave function for bonding molecular orbital is $\psi_b = \psi_A + \psi_B$

(g) Wave function for antibonding molecular orbit 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)	Antibonding molecular orbital (ABMO)
1. Bonding MO is the result of the linear combination of AO when their wave function are added $\psi_b = \psi_A + \psi_B$	1. ABMO is result of linear combination of AO when their wave function are substracted $\psi_a = \psi_A - \psi_B$
2. Generally it does not have nodal plane.	2. It always have a nodal plane between two nuclei of bonded atom.
3. Electron density increases between two nuclei resulting attraction between two atoms.	3. Electron density decreases in between two nuclei, leads to repulsion between two atoms.
4. Energy of BMO is less, hence stable.	4. Energy of ABMO is high.
5. Electron placed in a BMO stablises a molecule.	5. Electron placed in the ABMO destablises 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 - σ, π etc.

For bonding molecular orbital - σ, π* etc.

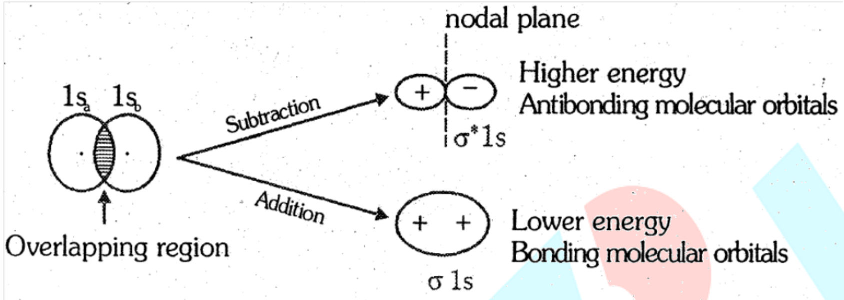
For antibonding molecular orbital- σ*, π* etc.

are used for different shapes of electron cloud.

Shapes of Molecular Orbitals (L.C.A.O. Method)

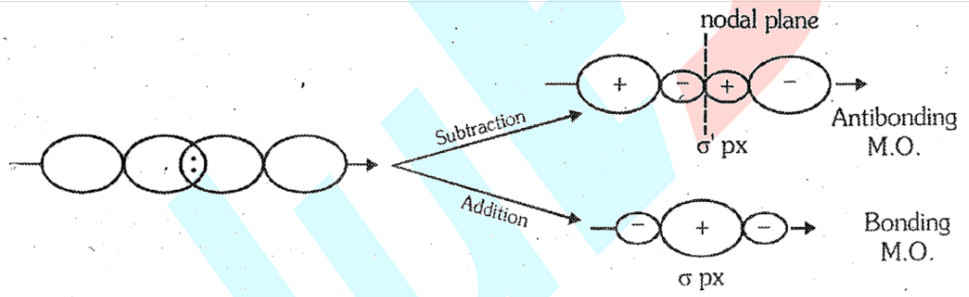
(A) (σ molecular orbital) :- It is formed by two ways -

(a) Combination of s-orbitals –



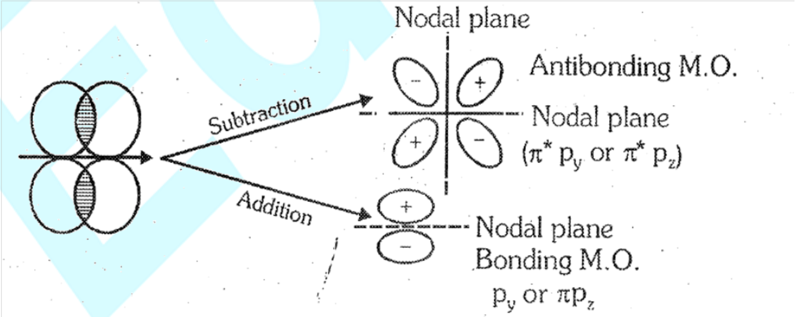
- σ* 1s have one nodal plane

(b) End on overlapping of p-orbitals – (Lineraly) :-



- σ* p_x have one nodal plane

(B) π(pi) molecular orbitals : -



Positive sign, represent maximum probability finding of electrons.

π* p_y or π* p_z have two nodal plane

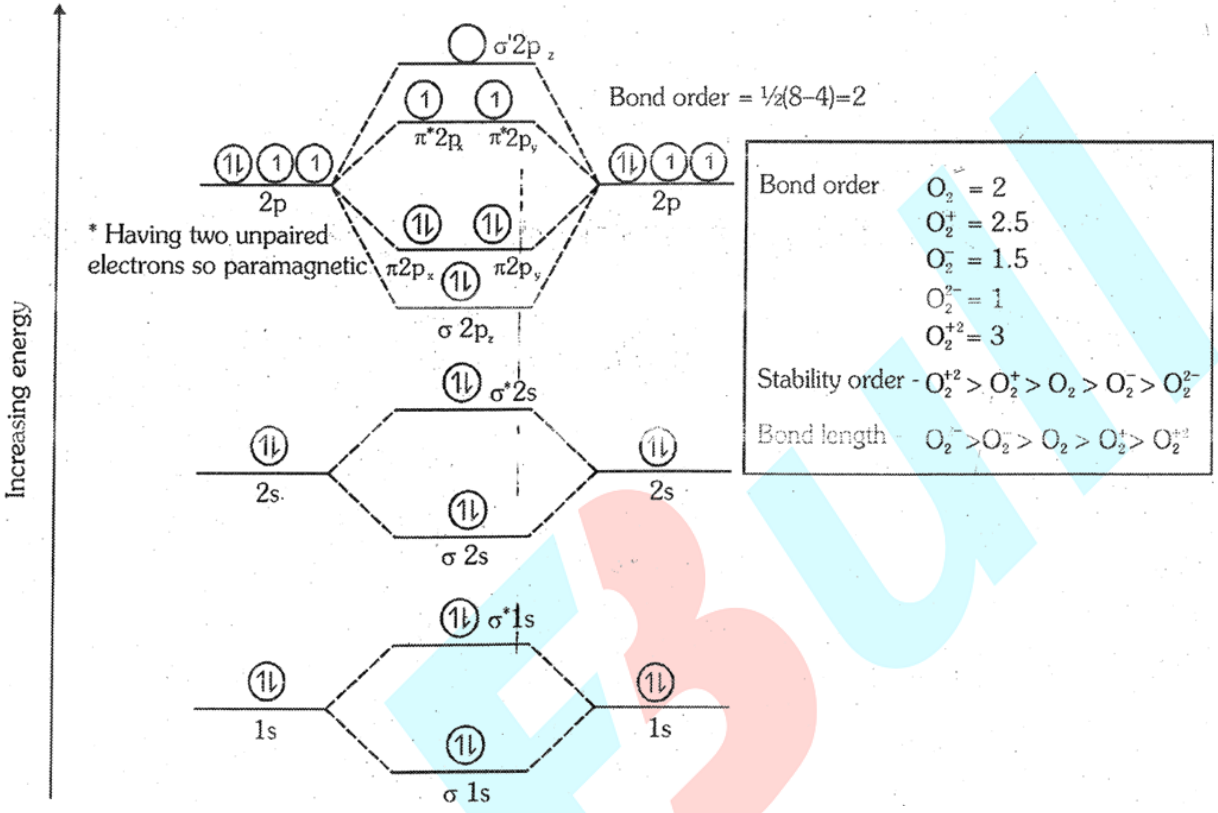
ENERGY LEVEL DIAGRAM OF MOLECULAR ORBITAL

(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 -

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

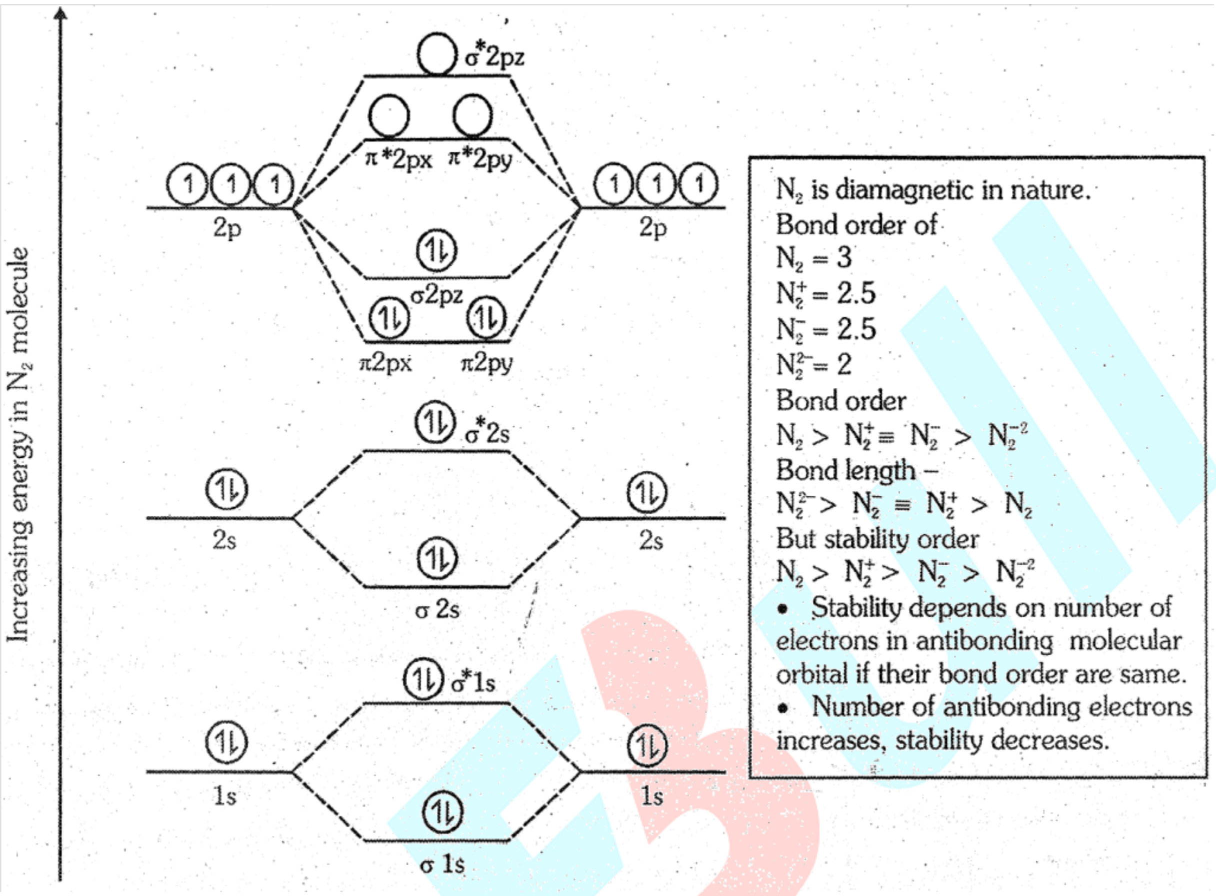
For O_2 molecule



(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



N_2 is diamagnetic in nature.
Bond order of
$N_2 = 3$
$N_2^+ = 2.5$
$N_2^- = 2.5$
$N_2^{2-} = 2$
Bond order
$N_2 > N_2^+ \equiv N_2^- > N_2^{-2}$
Bond length –
$N_2^{2-} > N_2^- \equiv N_2^+ > N_2$
But stability order
$N_2 > N_2^+ > N_2^- > N_2^{-2}$

- Stability depends on number of electrons in antibonding molecular orbital if their bond order are same.
- Number of antibonding electrons increases, stability decreases.

Electronic configuration of molecules and their related properties :-

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

(a) Count the number of electrons present in two atoms and then fill in the appropriate energy level diagram according to Aufbau rule.

(b) The pairing in π2px and π 2py or π* 2px and π* 2py will take place only when each molecular orbital of identical energy has one electron.

GOLDEN KEY POINTS

- Bond order :- $\frac{1}{2}[N_b - N_a]$ N_b = Total number of bonding electron

  N_a = Total number of antibonding electron

Application of bond order :

(i) Bond length :- (distance between two nuclei) Bond length $\propto \dfrac{1}{\text{Bond order}}$

If $N_b > N_a$ Molecule exists

$$\left.\begin{array}{l} N_b < N_a \\ N_b = N_a \end{array}\right\} \text{Molecule do not exists}$$

(ii) Stability of molecule :- stability oc Bond order of molecule

(iii) Dissociation energy :- Borid dissociation energy oc Bond order.

(iv) Magnetic property :-

(a) When electron in MO are paired -diamagnetic
(b) When electron in MO are unpaired –paramagnetic

Bonding in molecules

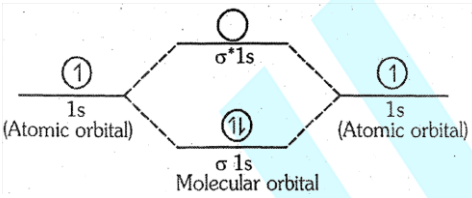
(a) Hydrogen molecule

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

M.O. configuration of H_2 = (σ 1s)2 (σ* 1s)^0

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

$= \frac{1}{2}[2 - 0] = 1$ i.e. single bond.



Having paired electron so diamagnetic.

Stability → quite stable (having single bond)

(b) H_2^+ ion -

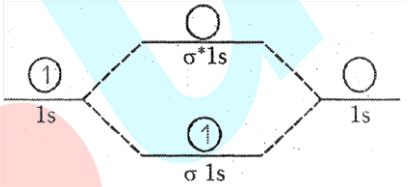
Configuration of H_2^+ = (σ*1s)1 (σ* 1s)^0

One electron in bonding molecular orbital.

So paramagnetic

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

Less stable (Incomparision to H_2)



(c) H_2^- anion -

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

Paramagnetic

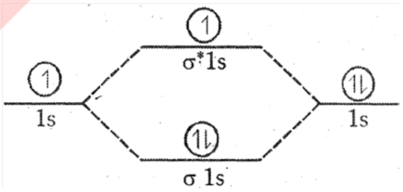
Bond order of = $\frac{1}{2}[2 - 1] = \frac{1}{2}$

Stability is less than H_2^+ because H_2^-

Cation an ABMO electron

Stability order $H_2 > H_2^+ > H_2^-$

Bond order 1.0 0.5 0.5

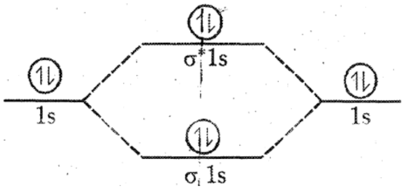


(d) Helium molecule (He_2)

M.O. configuration – (s1s)2(s*1s)2

Diamagnetic

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



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

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 nucleus
2. Identity of atom is retained	2. Identity of atom lost.
3. According to VBT O_2 is diamagnetic	3. According to MOT O_2 is paramagnetic

BEGINNER'S BOX-6

1. Which of the following is incorrect regarding the MO theory ?

(1) The number of molecular orbitals formed is always equal to the number of atomic orbitals combined.

(2) The more stable the bonding molecular orbital, the less stable the corresponding antibonding molecular orbital.

(3) In a stable molecule, the number of electrons in bonding molecular orbitals is always equal to that in antibonding molecular orbitals.

(4) Like an atomic orbital, each molecular orbital can accommodate up to two electrons with opposite spins in accordance with the Pauli exclusion principle.

2. If the z-axis is the molecular axis, then π MOs are formed by the overlap of-

(i) p_z and p_z
(ii) p_y and p_y
(iii) s_z and pz
(iv) p_x and p_x

(1) (ii), (iv)
(2) (ii), (iii)
(3) (i), (ii)
(4) (i), (iii)

3. If the z-axis is taken as the internuclear axis, then which of the following combinations of atomic orbitals is a nonbonding combination ?

(1) s and p_y
(2) p_x and d_{yz}
(3) p_x and p_y
(4) All of these

4. Which of the following is the correct order of stability?

(1) $H_2 > H_2^+ > He_2 > He_2^+$
(2) $H_2 > He_2^+ > H_2^+ > He_2$
(3) $H_2 > H_2^+ > He_2^+ > He_2$
(4) $H_2 > He_2 > He_2^+ > H_2^+$

5. Bond order in C_2^+ is:-

(1) $\frac{1}{2}$
(2) $\frac{2}{3}$
(3) $\frac{3}{2}$
(4) 1

6. In which of the following set, the value of bond order will be 2.5:-

(1) O_2^+, NO, NO^{+2}, CN
(2) CN, NO^{+2}, CN^-, F_2
(3) O_2^+, NO^{+2}, O_2^{+2}, CN^-
(4) O_2^{-2}, O_2^-, O_2^+, O_2

7. Of the following species which has the highest bond order and shortest bond length :
NO, NO^+, NO_2^+, NO^-

(1) NO only
(2) Bond order of NO is highest and bond length of NO^{2+} is shortest
(3) NO^+ only
(4) NO_2^+ only

8. The diamagnetic molecule is

(1) Super oxide ion
(2) Oxygen molecule
(3) Carbon molecule
(4) Unpositive ion of nitrogen molecule

9. On the basis of molecular orbital theory which molecules does not exist

(1) H_2
(2) He_2
(3) HeH
(4) Li_2

10. Maximum bond energy will be shown by the species

(1) O_2^+ (2) O_2 (3) O_2^- (4) O_2^{-2}

2.11 CO-ORDINATE BOND

(1) It is a covalent bond in which the shared e-pair come from one atom is called coordinate bond.

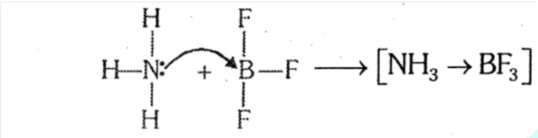
(2) Necessary conditions for the formation of coordinate bond are -

(a) Octet of donor atom should be complete and should have atleast one lone pair of electron.

(b) Acceptor atom should have defficiency of at least one pair of electron.

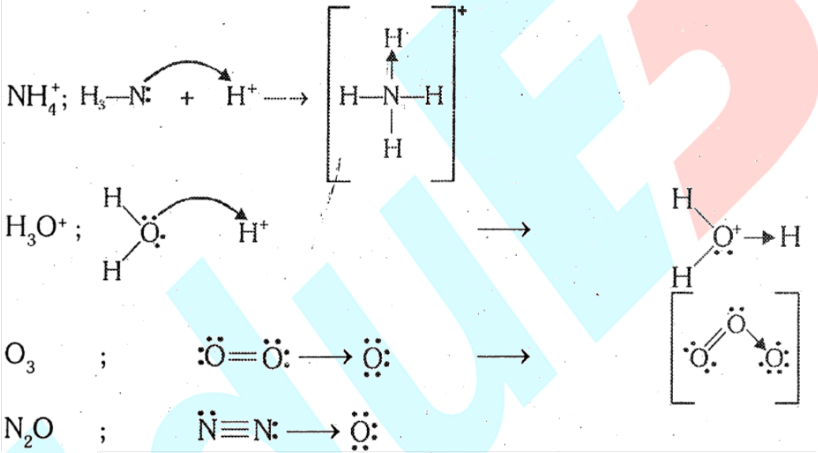
(3) Atom which provide electron pair for sharing is called donor.

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



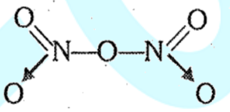
BF_3 is electron defficient compound.

Example :

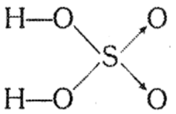


Metal co-ordinate compounds -

N_2O_5



H_2SO_4



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

NH_4Cl, $CuSO_4$, $K_4[Fe(CN)_6]$, Na_3PO_4, KNO_3 etc.

2.12 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:

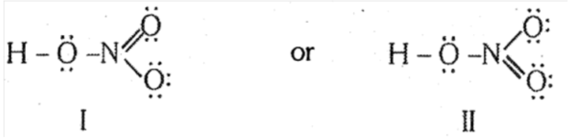
Formal charge on a atom in a Lewis structure

= (total number of valence electrons in the isolated atom) – (Total number of nonbonding electrons) – $\frac{1}{2}$(total number of bonding electrons) ……..(i)

Or FC = Valence electrons) – (Non bonding electrons) – $\frac{1}{2}$(bonding electrons)

= (Valence electrons or group number) – [(Number of unshared e^-s) + (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 (HN03) molecule which has been described by the following Lewis structures:



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

Substituting in Eq. (i), we write 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).

Hence, we write 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).

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

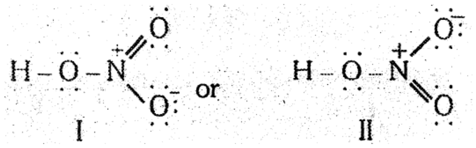
The end O atom in N = O: It has six valence electrons in the free state but in the Lewis structure (I or II), it has two lone pairs (or four non bonding electrons) and forms two bonds (or has four bonding electrons).

Thus, we can write 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 .o r six non bonding electrons and forms one bond (or has two bonding electrons).

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

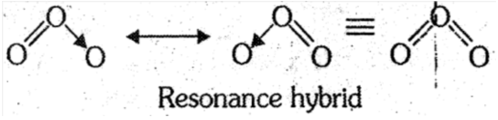
We can now write the Lewis structures (I and II) for nitric acid molecule including the formal charges as



2.13 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.

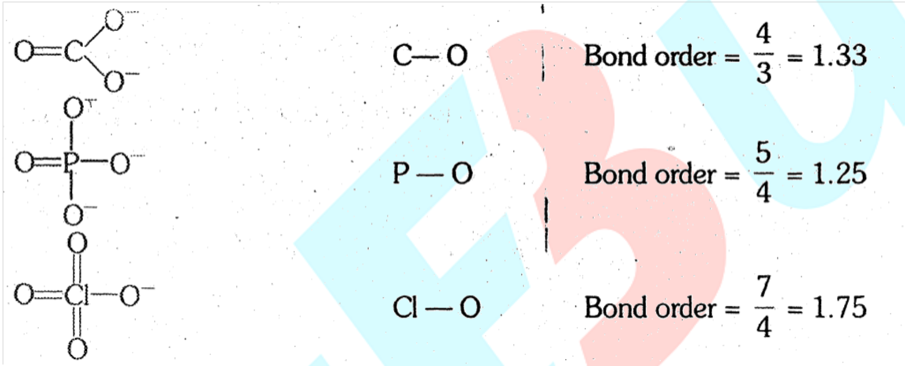
(b) Let us discuss resonance in ozone, according to its resonance structure it should have one single bond (O–O = 1:48Å) but experiments show that both the bonds are same which can be proved by its resonance hybrid as shown below.



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

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

Ex.



C — O Bond order = $\frac{4}{3}$ = 1.33

P — O Bond order = $\frac{5}{4}$ = 1.25

Cl — O Bond order = $\frac{7}{4}$ = 1.75

BEGINNER'S BOX-7

1. Which of the following ions has resonating structures ?

(1) so_4^{2-} (2) PO_4^{3-} (3) SO_3^{2-} (4) All of these

2. How many resonating structures can be drawn for NO_2?

(1) Six (2) Four (3) Five (4)Two

3. Which of the following is true for nitrate anion

(1) Formal charge on N is zero (2) Bond order of NO bond is $\frac{4}{3}$

(3) Average formal charge on oxygen is $\frac{-1}{3}$ (4) There are 2 π-bonds in the ion

4. Which of the following contains Co-ordinate and covalent bonds:-

(a) $N_2H_5^+$ (b) H_3O^+ (c) HCl (d) H_2O

Correct answer is:-

(1) a & d (2) a & b (3) c & d (4) Only a

5. The correct statement for the reaction -

$NH_3 + H^+ \rightarrow NH_4^+$:-

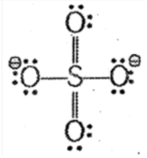
(1) Hybridisation state is changed (2) Bond angle increases

(3) NH_3 act as a Lewis acid (4) Regular geometry is changed

6. The number of coordinate bonds presents in SO_3 molecule are

(1) 1 (2) 2 (3) 3 (4) 4

7. One of the resonating structure of SO_4^{-2} is



Which set of formal charge on oxygen and bond order is correct

(1) 0.5 and 1.5 (2) 1.5 and 3

(3) 2 and 3 (4) 1.5 and 1.5

8. Resonance is not shown by -

(1) C_6H_6 (2) CO_2 (3) CO_3^{2-} (4) SiO_2

9. Bond length of C–O is minimum in -

(1) CO (2) CO_2 (3) CO_3^{-2} (4) $HCOO^-$

Subjective Type Questions

10. Discuss resonance and formal charge in N_3^- and N_2O?

11. Give the average formal charge and average bond order of XO bond in the following oxy compounds?

(a) $S04_2^-$ (b) SO_3^{2-} (c) NO_2^- (d) ClO_2^- (e) ClO_3^-

(f) ClO_4^- (g) HCO_3^- (h) CO_3^{-2} (i) HSO_3^- (j) PO_4^{3-}

2.14 METHALLIC BOND

(1) The constituent particles of metallic 5olids 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

2.15 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.

[van der Waal's force $\propto$ size of atom or molecule $\propto$ 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 orientaation effect. Example - HCl, H_2O, NH_3 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 NH_3, 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.

2.16 HYDROGEN BONDING

Definition

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

$$X\text{——}H\text{——}Y$$

X = F, O, N & sp carbon Y= F, O, N & Cl

(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 (strength 8-42 KJ/mol) but stronger than vander waal's force.

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

$$H^{\delta+}\text{—}F^{\delta-}.......H^{\delta+}\text{—}F^{\delta-}$$

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 -

N > O > F

Order of electronegativity is -

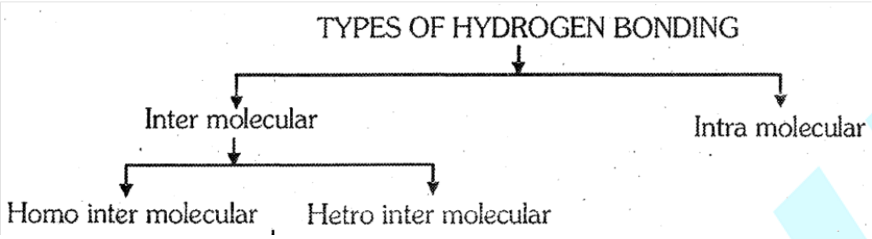
F > O > N

(4.0) (3.5) (3.0)

(c) Strength of H–bond $\propto$ Electronegativity of Z (element) $\alpha \dfrac{1}{\text{atomic size of Z}}$

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

H–C≡N **...** H–C≡N **...** H–C≡N



Intermolecular H-Bond

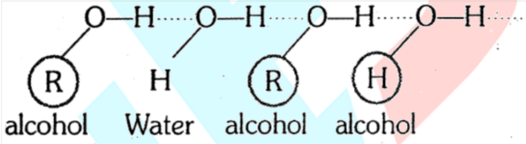
H-bond formation between two or more molecules of either the same or different compounds known as Inter molecular H-bonding.

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

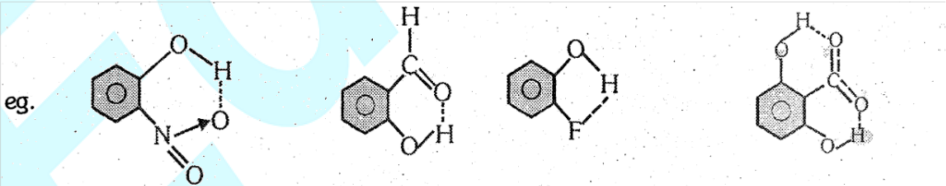
It takes place within the molecule.

(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).

eg.



O–nitrophenol Salicylaldehyde O–fluorophenol 2–6 dihydroxyl benzoate

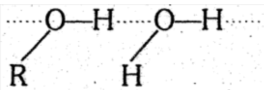
Effect of H-bond on Physical Properties

(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

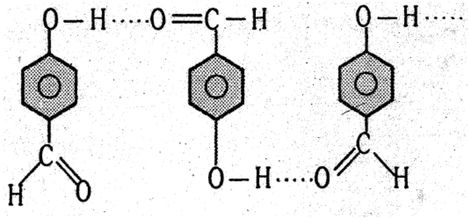


Other examples -Glucose, Fructose etc. dissolve in water:

(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- $CH_3OCH_3 < CH_3OH$

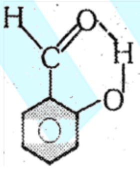
(IV)



p-hydroxy benzaldehyde.

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

(b) Intra molecular H-bonding

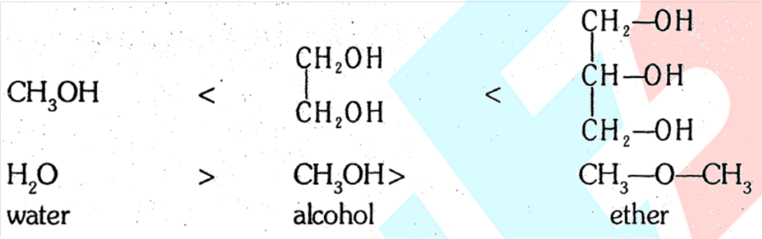


(I) It decreases solubility as it form chelate by H-bonding, so H- is not free for other molecule.

(II) It cannot form H-bond with water molecule so it cannot dissolve.

(B) Viscosity

H-bond associates molecules together so viscosity increases.



$$CH_3OH < \begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix} < \begin{matrix}CH_2{-}OH\\|\\CH{-}OH\\|\\CH_2{-}OH\end{matrix}$$

H_2O > CH_3OH> $CH_3{-}O{-}CH_3$

water alcohol ether

(C) Surface Tension

Surface tension of a liquid oc extent of H-bonding.

(D) Melting point and boiling point

(I) Due to intermolecular H-bond M.P. & B.P. of compounds increases.
$H_2O > CH_3OH > CH_3{-}O{-}CH_3$

(II) Boiling points of VA, VIA, VIIA hydrides are as shown below :

(Group 15 Hydrides)	$SbH_3 > NH_3 > AsH_3 > PH_3$
(Group 16 hydrides)	$H_2O > TeH_2 > SeH_2 > H_2S$
(Group 17 hydrides)	HF > HI > HBr > HCl

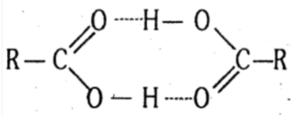
(III) But sudden increase in boiling point of NH_3, H_2O and HF is due to H-bonding.

(IV) $H_2O > HF > NH_3$ (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.



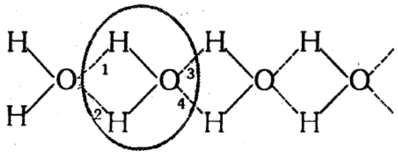
(F) Physical states

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.

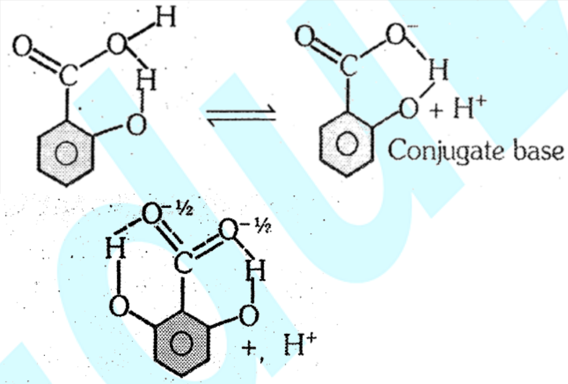


GOLDEN KEY POINTS

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.



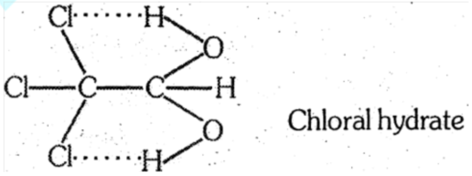
2, 6–dihydroxy benzoate ion.

(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).



BEGINNER'S BOX-8

1. Two ice cubes are pressed over each other until they unite to form one block. The force mainly responsible for holding them together is-

(1) van der Waals force (2) dipole-dipole interaction
(3) H bonding (4) covalent bonding

2. The vapor pressure of o-nitrophenol at any given temperature is predicted to be-

(1) higher than that of p-nitrophenol
(2) lower than that of p-nitrophenol
(3) same as that of p-nitrophenol
(4) higher or lower depending upon the size of the vessel

3. The hydrogen bond is strongest in:-

(1) O–H- - -S (2) S–H- - -O (3) F–H- - -F (4) O–H- - -O

4. H_2O boils at higher temperature than H_2S, because it is capable of forming:-

(1) Ionic bonds (2) Covalent bonds (3) Hydrogen bonds (4) Metallic bonds

5. Maximum number of H-bonding is shown by

(1) H_2O (2) H_2Se (3) H_2S (4) HF

6. Which is the weakest among the following types of bonds ?

(1) Debye force (2) Metallic bond
(3) Dipole-dipole bond (4) Hydrogen bond

7. The boiling point of p-nitrophenol is higher than that of o-nitrophenol because :

(1) NO_2 group at p-position behaves in a different way from that at a-position
(2) intramolecular hydrogen bonding exists in p-nitrophenol
(3) there is intermolecular hydrogen bonding in p-nitrophenol
(4) p-nitrophenol has a higher molecular weight than o-nitrophenol

8. In which molecule the 'Vander Waals force (dispersion force) is likely to be the most important in determining the m.pt. and b.pt.

(1) Br_2 (2) CO (3)H_2S (4) HCl

9. Covalent-molecules are usually held in a crystal structure by

(1) Dipole-dipole attraction (2) Electrostatic attraction
(3) Hydrogen bond (4) Van-der waal's attraction

10. In solid argon the atoms are held together

(1) By ionic bonds (2) By hydrogen bonds
(3) By vander-waals forces (4) By hydrophobic bonds

2.17 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.

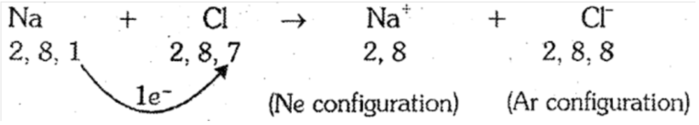
Electro +ve atom loses electron (group IA to IIIA)

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

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

Electronegativity difference α nature of ionic bond.

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

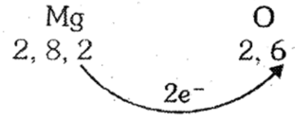


More the distance between two elements in periodic table more will be ionic character of bond.

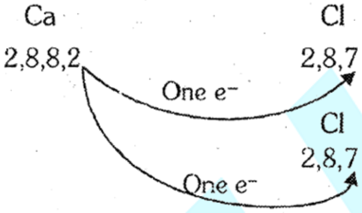
Total number of electron lose or gained is called electrovalency.

Example-

(1)



(2)



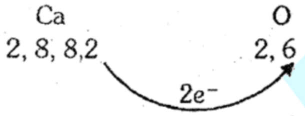
electrovalency of Mg = 2

electrovalency of O = 2

electrovalency of Ca = 2

electrovalency of Cl = 1

(3) $Ca + O \rightarrow CaO$



electrovalency of Ca = 2

electrovalency of O = 2

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 Ionisatoin energy → Greater tendency to form cation.

e.g. $Na^+ > Mg^{+2} > Al^{+3}$
$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$
} 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

$Cl^- > F^- > Br^- > I^-$
$F^- > O^{-2} > N^{-3}$
} 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 -

(i) $A_{(g)} \xrightarrow{IE} A^{+}_{(g)} + e^{-}$ (ii) $B_{(g)} + e^{-} \longrightarrow B^{-}_{(g)} + EA$

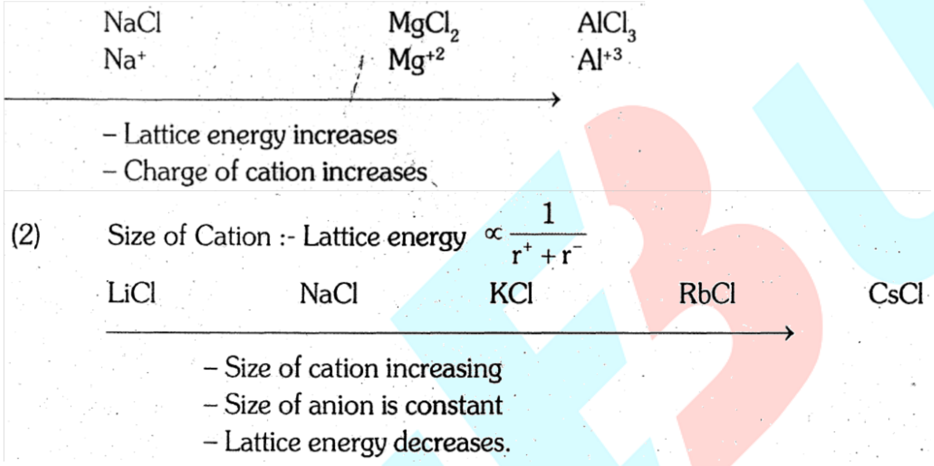
(iii) $A^{+}_{(g)} + B^{-}_{(g)} \longrightarrow 4AB(s) + LE$

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.

GOLDEN KEY POINTS

- **Factors affecting lattice energy**

(1) Magnitude of charge → α $z^{+}z^{-}$ (Ionic charge)



NaCl MgCl$_2$ AlCl$_3$

Na$^+$ Mg^{+2} Al^{+3}

– Lattice energy increases

– Charge of cation increases

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

LiCl NaCl KCl RbCl CsCl

– Size of cation increasing

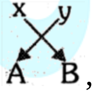
– Size of anion is constant

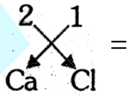
– Lattice energy decreases.

- **Representation of formula of compounds :**

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

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

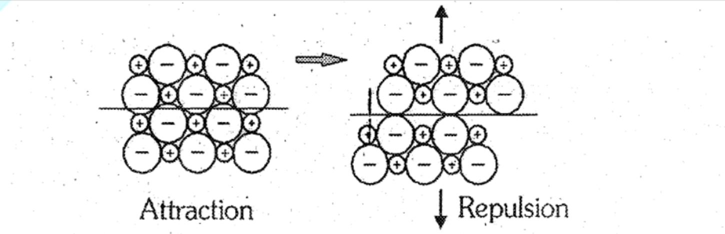
(3) Now apply cris cross rule as  i.e. formula AyBx.

Examples: Calcium chloride  = $CaCl_2$

Properties of Ionic Compound

(a) Physical state -

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

Brittleness → 

{ Same charged ions comes nearer. So they repell 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 $AgNO_3$ solution, white ppt of AgCl is formed at once.

$$Ag^+ NO_3^- + Na^+Cl^- \rightleftharpoons Na^+ NO_3^- + AgCl\downarrow$$

white ppt.

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

2.18 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.

Polarizability

Ability of an anion tq 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 number 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.

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

eg. In a group

$BeCl_2$
$MgCl_2$ - Size of cation increases
$CaCl_2$ - Covalent character decreases
$SrCl_2$ - Ionic character increases
$BaCl_2$

Greatest polarizing power of Be^{2+}, shows its maximum covalent character

In a period — Na^{+}, Mg^{+2}, Al^{+3}, Si^{+4} $\longrightarrow$

- Cation size decreases
- Covalent character increases

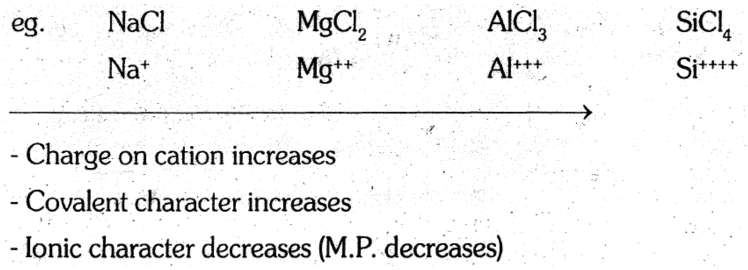
(b) **Size of anion :-** If the size of the anion increases for a given cation, the covalent character increases. Polorisation $\propto$ size of anion.

CaF_2
$CaCl_2$ - size of anion increases
$CaBr_2$ - Covalent character increases
CaI_2 - Ionic character decreases

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

Polarisation oc charge on cation or anion

(i) **Charge on cation $\propto$ Pplarisation (covalent character)**



eg. NaCl $MgCl_2$ $AlCl_3$ $SiCl_4$

Na^+ Mg^{++} Al^{+++} Si^{++++}

$\longrightarrow$

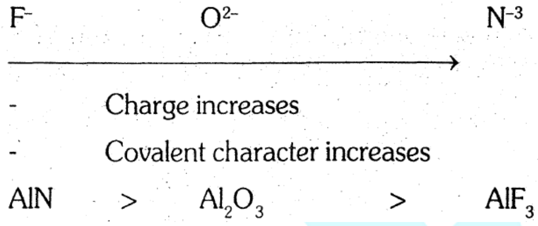
- Charge on cation increases
- Covalent character increases
- Ionic character decreases (M.P. decreases)

Ex. Write the increasing order of M.P. & B.P. of following compounds.

	(1) $SnCl_4$, $SnCl_2$	(2) $FeSO_4$, $Fe_2(SO_4)_3$	(3) $PbCl_4$, $PbCl_2$
Ans.	(1) $Sn^{+4} < Sn^{+2}$	(2) $Fe^{+3} < Fe^{+2}$	(3) $Pb^{+4} < Pb^{+2}$

(Charge on cation $\propto$ polarization power $\propto$ covalent character $\alpha \frac{1}{\text{M.P.}}$)

(ii) Charge of anion $\propto$ Polarisation



F^- O^{2-} N^{-3}

$\longrightarrow$

- Charge increases
- Covalent character increases

AlN > Al_2O_3 > AlF_3

Ex. Write increasing order of M.P. & B.P. of-

$CaSO_4$, $Ca_3(PO_4)_2$ and ClO_4^-, SO_4^{-2} , PO_4^{-3}

Ans. CaSO4 > $Ca_3(PO_4)_2$ $ClO_4^- > SO_4^{-2} > PO_4^{-3}$

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

(d) Electronic configuration of cation : -

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

CuCl → Cu^+	2, 8, 18	(Covalent)
NaCl → Na^+	2, 8	(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-

z_{eff} of ns^2p^6 (inert)	<	z_{eff} of $ns^2p^6d^{10}$ (pseudo inert)
Na^+	<	Cu^+
(Ionic		Covalent

So CuCl has more covalent character than NaCl.

Order of covalent character

- LiF < LiCl < LiBr < LiI
- $CaCl_2 < FeCl_2 < FeCl_3$
- $SrCl_2 < SnCl_2 < CdCl_2$
- $SF_2 < SF_4 < SF_6$
- $Hg_2Cl2 < HgCl_2$
- $ZnCl_2 < CdCl_2 < HgCl_2$

Note:

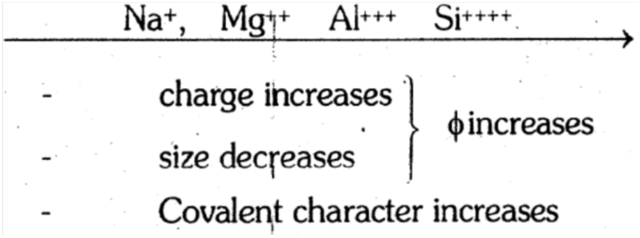
Polarisation power of a cation is usually called ionic potential or charge density.

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

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 ~ increases so covalent character increases.



Na^+, Mg^{++} Al^{+++} Si^{++++}

- charge increases
- size decreases

} ϕ increases

- Covalent character increases

From top to bottom in a group ϕ decreases so covalent, character decreases.

Li+	
Na^+	Size increases {charge is fix)
K^+	ϕ decreases
Rb^+	Hence covalent character decreases
Cs^+	

BEGINNER'S BOX-9

1. The electrovalency of the element is equal to the-

(l) number of electrons lost

(2) number of electrons gained

(3) number of electrons transferred

(4) number of electrons lost or gained by the atom of the element during the formation of ions of ionic compound

2. Which of the following polar solvents has. the highest dielectric constant?

(1) H_2O (2) D_2O (3) CH_3OH (4) C_2H_5OH

3. Which of the following cations posses neither noble gas nor pseudo noble gas configurations?

(i) Bi^{3+} (ii) Pb^{2+} (iii) Sn^{2+} (4) Tl^+

(1) (ii), (iii) (2) (i), (iv) (3) (i), (ii) (iii) (4) (i), (ii), (iii), (iv)

4. Ionic bond formation involves :

(1) Elimination of protons (2) Sharing of electrons

(3) Overlapping of orbitals (4) Formation of octets

5. The hydration of ionic compounds involves-

(l) Evolution of heat (2) Weakning of attractive forces

(3) Dissociation into ions (4) All

6. The hydration energy of Mg^{+2} is greater than the hydration energy of

(1) Al^{+3} (2) Mg^{+3} (3)Na^+ (4) Be^{+2}

7. Among the following which compounds with show the highest lattice energy?

(1) KF (2) NaF (3) CsF (4) RbF

8. The lattice energy of the lithium is in the following order : .

(1) LiF > LiCl > LiBr > LiI
(2) LiCl > LiF > LiBr > LiI
(3) LiBr > LiCl > LiF > LiI
(4) LiI > LiBr > LiCl > LiF

9. Among LiCl, $BeCl_2$, BCl_3 and CCl_4, the covalent bond character follows the order :

(l) LiCl < $BeCl_2$ > BCl_3 > CCl_4
(2) LiCl > $BeCl_2$ < BCl_3 < CCl_4
(3) LiCl < $BeCl_2$ < BCl_3 < CCl_4
(4) LiCl > $BeCl_2$ > BCl_3 > CCl_4

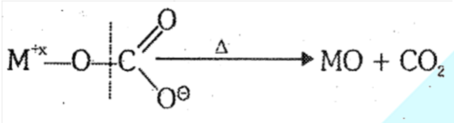
2.19 THERMAL DECOMPOSITION

Thermal stability of metal carbonates

Thermal stability of compound having poly atomic anion

CO_3^{-2}, SO_4^{-2}, OH^-, O_2^{-2}, O_2^- etc 3

$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

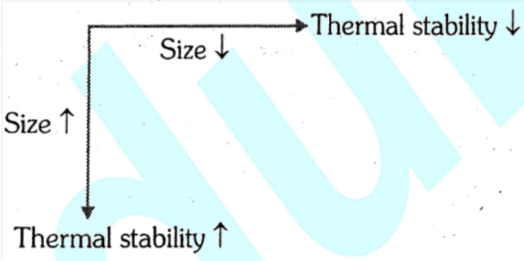


(x is +ve charge)

Polarising Power (↑) Thermal Stability (↓)

$$\text{Thermal stability} \propto \frac{1}{\text{Pol. power}} \propto \frac{\text{size of cation}}{\text{charge of cation}}$$

Compounds having poly atomic anions :



For fluoride, hydride & normal oxide

$$\left[\text{Thermal stability} \propto \frac{1}{\text{size}}\right] \text{ for a group}$$

[Thermal stability ∝ ΔEN] for a period

Thermal Stability order

For Example

$BeSO_4 < MgSO_4 < CaSO_4 < SrSO_4 < BaSO_4$
$LiNO_3 < NaNO_3 < KNO_3 < RbNO_3$
$LiHCO_3 < NaHCO_3 < KHCO_3 < RbHCO_3 < CsHCO_3$

Note:

(i) $LiHCO_3$ and IIA group bicarbonate does not exist in solid state.

(ii) Carbonate, Sulphates & hydroxide of Na, K, Rb & Cs do not decompose at high temperature only melt.

(iii) $BeCO_3$ is kept in CO_2 atmosphere due to less thermal stability.

$$BeCO_3 \rightleftharpoons BeO + CO_2$$

Heating Effect

(a) Metal Carbonate $\xrightarrow{\Delta}$ metal oxide + CO_2

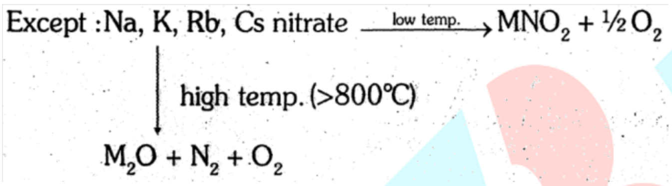
(b) Metal hydroxide $\xrightarrow{\Delta}$ metal oxide + H_2O

(c) Metal bicarbonate $\overset{\Delta}{\rightleftharpoons}$ metal carbonate + CO_2 + H_2O

(d) Ammonium salts having CO_3^{-2} , PO_4^{-3}, SO_4^{-2}, X-anion (non oxidising or weak oxidising) gives NH_3 gas on decomposition.

Ammonium salt having $Cr_2O_7^{-2}$, ClO_3^{-1}, NO_2^{-1}, NO_3^{-1} (1 (strong oxidising anion) gives N_2 or N_2O gas on decomposition.

(e) Metal nitrate $\xrightarrow{\Delta}$ metal oxide + NO_2 + O_2



$$\begin{tikzcd}\text{Except :Na, K, Rb, Cs nitrate} \arrow[r, "\text{low temp.}"] \arrow[d, "\text{high temp. (>800°C)}"] & MNO_2 + \frac{1}{2}O_2 \\ M_2O + N_2 + O_2 & \end{tikzcd}$$

Note:

(i) Some less stq.ble metal oxide like Ag_2 & HgO further decompose into metal & oxygen.

(ii) Metal salts having high percentage of oxygen like $KMnO_4$, $K_2Cr_7O_7$ & $KClO_3$ give O_2 gas on decomposition.

Complete following reactions :

$PbCO_3 \xrightarrow{\Delta}$	$FeCO_3 \xrightarrow{\Delta}$
$ZnCO_3 \xrightarrow{\Delta}$	$MgCO_3.CaCO_3 \xrightarrow{\Delta}$
$CuCO_3.Cu(OH)_2 \xrightarrow{\Delta}$	$NaCO_3.10H_2O \longrightarrow X \longrightarrow \xrightarrow{\Delta}$
$2NaHCO_3 \xrightarrow{\Delta}$	$NH_4NO_2 \xrightarrow{\Delta}$
$NH_4NO_3 \xrightarrow{\Delta}$	$(NH_4)_2SO_4 \xrightarrow{\Delta}$
$(NH_4)_2CO_3 \xrightarrow{\Delta}$	$Ba(N_3)_2$ or $NaN_3 \xrightarrow{\Delta}$
$Pb(NO_3)_2 \xrightarrow{\Delta}$	$Zn(NO_3)_2 \xrightarrow{\Delta}$
$Ca(NO_3)_2 \xrightarrow{\Delta}$	$LiNO_3 \xrightarrow{\Delta}$
$NaNO_3 \xrightarrow{400°C}$	$PbCl_4 \xrightarrow{\Delta}$
$FeCl_3 \xrightarrow{\Delta}$	$AuCl_3 \xrightarrow{\Delta}$
$CuSO_4.5H_2O \xrightarrow{<200°C} A \xrightarrow{>200°C} B \xrightarrow{800°C}$	$BaCl_2.2H_2O \xrightarrow{\Delta}$
$ZnSO_4.7H_2O \xrightarrow{<200°C} A \xrightarrow{>200°C} B \xrightarrow{800°C}$	$AlCl_3.6H_2O \xrightarrow{\Delta}$
$FeSO_4.7H_2O \xrightarrow{<200°C} A \xrightarrow{>200°C} B \xrightarrow{750°C}$	$CaCl_2.6H_2O \xrightarrow{\Delta}$
$Fe_2(SO_4)_3 \xrightarrow{\Delta}$	$FeCl_3.6H_2O \xrightarrow{\Delta}$
$CaSO_4 \cdot 2H_2O \xrightarrow{<200°C} A \xrightarrow{>200°C} B \xrightarrow{\Delta}$	$MgCl_2.H_2O \xrightarrow{\Delta}$
$2KMnO_4 \xrightarrow{\Delta}$	$K_2Cr_2O_7 \xrightarrow{\Delta}$
$2KClO_3 \xrightarrow{\Delta}$	$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta}$

2.20 SOLUBIIJtY OF IONIC COMPOUNDS

(a) Solubility of ionic compounds :

Soluble in polar solvents like water which have high dielectric constant

Factors affecting solubility of Ionic compounds :

(i) Dielectric constant of the solvent increases the solubility of compound increases

HF	12.0	H_2O	81	H_2O_2	98
H_2SO_4	102	D_2O	79		

(ii) If heat of hydration of ions exceeds the lattice energy (L.E.) of ionic compounds, the ionic compounds will be soluble in water. ·

Lattice energy as well as hydration energy depend on the size of ions. Both lattice energy and hydration energy decrease with increase in ionic size.

Two general rule, regarding the solubility is that-

(a) If the anion and the cation are of comparable size, the cationic radius wili influence the lattice energy. Since lattice energy decreases much more than the hydration energy with increasing ionic size, solubility will increase as we go down the group.

$$\underrightarrow{Be(OH)_2 < Mg(OH) < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2}$$

Solubility increases

(b) If the anion is large compared to the cation, (i.e. compound contain ions with widely different radii) the lattice energy will remain almost constant i.e. change is very small within a particular group. Since the hydration energies decrease down a group, solubility will decrease.

$$\underset{\text{Solubility decreases}}{\xrightarrow{BeCO_3 > MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3}}$$

Note:

- If common ion is small like Na^+, Li^+, O^{-2}, F^-, OH^-, IIA cation then lattice energy dominates.
- If common ion is large like Cs^+, Rb^+, Br^-, I^-, polyatomic anion like CO_3^{-2}, SO_4^{-2} then hydration energy dominates.

Some important solubility orders:

Examples

- $BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$ (SO_4^{-2} larger)
- $CsF > CsCl > CsBr > CsI$ (Cs^+ (larger)]
- $BeS > MgS > CaS > SrS > BaS$ (S^{-2} larger)

***Important facts about solubility**

(i) All metal chlorides are soluble except Ag, Pb, Hg

(ii) All metal sulphides are insoluble except : lA and arrimonium

(iii) Highly insoluble sulphides are of Hg^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Bi^{3+}

(iv) All hydroxides are insoluble except IA, lower IIA and ammonium

(v) Most insoluble hydroxides are of Al^{3+}, Fe^{3+}, Cr^{3+}

(vi) All metal nitrate, Acetate, perchlorate are souble in water

(vii) Generally metal sulphates are soluble in water except Ag, Hg, Pb, Ca, Sr, Ba

(viii) All alkali metal salts are soluble in water except. LiF, Li_2CO_3, Li_3PO_4, $Li_2C_2O_4$

2.21 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

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

Melting point of ionic compound > covalent compound

Except Giant molecules

↓

Diamond, Carborundu•m (SiC)

Norbide (B_4C), Silica (SiO_2) Borazone $(BN)_x$

Order of Hardness: Diamond> Norbide > SiC > Al_2O_3

Some important melting point orders :

Examples

$BeCl_2 < MgCl_2 < CaCl_2 < SrCl_2 < BaCl_2$

$NaF < MgF_2 < AlF_3$

$NaCl > MgCl_2 > AlCl_3$

$LiCl < NaCl > KCl > RbCl > CsCl$
$BeF_2 < MgF_2 > CaF_2 > SrF_2 > BaF_2$

Melting Point and Boiling Point of non-metallic molecules

(i) $CH_3–O–CH_3 < C_2H_5OH$ (boiling point)
(ii) $CH_4 < SiH_4 < GeH_4 < SnH_4 < PbH_4$ (boiling point)
(iii) $I–Cl > Br_2$ (boiling point)
(iv) $H_2 < O_2 < H_2O$ (boiling point)
(v) $CH_3–OH < H_2O$ (surface tension)
(vi) $HCl < HNO_3 < H_2SO_4 < H_3PO_4$ (melting point)
(vii) $H_2O < D_2O$ (boiling point)
(viii) O-nitro phenol < P-nitro phenol (boiling point)
(ix) $H_2O >> H_2S < H_2Se < H_2Te$ (melting point)
(x) $NH_3 >> PH_3 < AsH_3 < SbH_3$ (melting point)
(xi) $HCl < HBr < HI < HF$ (boiling point)
(xii) $HCl < HBr <HF < HI$ (melting point)

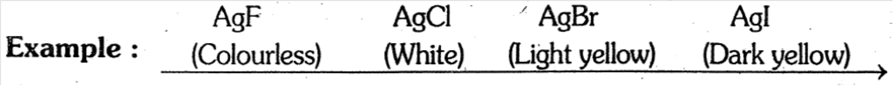
Melting point & boiling point of elements

(i) Li > Na > K > Rb > Cs (melting point)
(ii) Be > Ca > Sr > Ba > Mg (11,1elting point)
(iii) 3d series
Melting point $\propto$ number of unpaired electrons
$\therefore$ In 3d series (MP) maximum = Cr (chromium)
In 4d series (MP) maximum = Mo
In 5d series (MP) maximum = W
(iv) 3d < 4d < Sd (melting point)
(v) Zn > Cd > Hg (Melting point)
He < Ne < Ar < Kr < Xe (boiling point)
$F_2 < Cl_2 < Br_2 < I_2$ (boiling point)
$N_2 < P_4 < As_4$ (boiling point)
$O_2 < S_8 < Se_8 < Te_8$ (boiling Point)
$H_2 > He$ (melting point)

Note : Maximum melting point in Boron family → Boron
Minimum melting point in Boron family → Gallium
Maximum melting point in all elements → Carbon
Minimum melting point in all elements → Helium
Maximum melting point in Metals → Tungsten
Minimum melting point in Metals → Mercury

COLOUR OF COMPOUNDS

More the covalent character, more will be the colour intensity.
Colour intensity $\propto \phi$ (Covalent character)



Example :
AgF (Colourless)
AgCl (White)
AgBr (Light yellow)
AgI (Dark yellow)

BEGINNER'S BOX-10

Arrange in order of thermal stability :

1. $BeCO_3$, $MgCO_3$, $CaCO_3$, $SrCO_3$, $BaCO_3$
KO_2 , RbO_2 , CsO_2
NH_3 , PH_3 , AsH_3 , SbH_3 , BiH_3
H_2O, H_2S, H_2Se, H_2Te
BeO, MgO, CaO, SrO, BaO
NH_3, H_2O, HF
NaF, MgF_2 , AIF_3
Na_2SO_4, $MgSO_4$, $Al_5(CO_4)_3$
CCl_4 , $SiCl_4$, $GeCl_4$, $SnCl_4$, $PbCl_4$

2. Give solubility order for :-
(i) alkali metal hydroxide
(ii) Sodium halides
(iii) alkali metal per chlorates
(iv) alkali metal oxides
(v) alkaline earth metal carbonates
(vi) alkali metal carbonates
(vii) alkali metal bicarbonates
(viii) silver halides
(ix) lead (II) halides
(x) mercury (II) halides

3. Give the order of melting points
- Na_2O, MgO, Al_2O_3
- $CaCl_2$, $FeCl_2$, $FeCl_3$
- NaF, MgO, ScN, TiC
- $SnCl_2$, $SnCl_4$
- KCl, CuCl, $CuCl_2$

ANSWER KEY

BEGINNER'S BOX-1

1.	(3)	**2.**	(4)	**3.**	(2)	**4.**	(1)

BEGINNER'S BOX-2

1.	(3)	**2.**	(1)	**3.**	(4)	**4.**	(3)	**5.**	(1)
6.	(3)	**7.**	(1)	**8.**	(2)				

BEGINNER'S BOX-3

1.	(3)	**2.**	(1)	**3.**	(3)	**4.**	(2)	**5.**	(2)
6.	(2)	**7.**	(3)	**8.**	(4)	**9.**	(4)	**10.**	(3)
11.	(4)								

BEGINNER'S BOX-4

1.	(1)	**2.**	(3)	**3.**	(2)	**4.**	(3)	**5.**	(3)
6.	(2)	**7.**	(1)	**8.**	(2)	**9.**	(1)	**10.**	(3)

BEGINNER'S BOX-5

1.	(1)	**2.**	(2)	**3.**	(3)	**4.**	(1)	**4.**	(2)

BEGINNER'S BOX-6

1.	(3)	**2.**	(1)	**3.**	(4)	**4.**	(3)	**5.**	(3)
6.	(1)	**7.**	(3)	**8.**	(3)	**9.**	(2)	**10.**	(1)

BEGINNER'S BOX-7

1.	(4)	**2.**	(4)	**3.**	(2)	**4.**	(2)	**5.**	(2)
6.	(2)	**7.**	(1)	**8.**	(4)	**9.**	(2)		

BEGINNER'S BOX-8

1.	(3)	**2.**	(1)	**3.**	(3)	**4.**	(3)	**5.**	(1)
6.	(1)	**7.**	(3)	**8.**	(4)	**9.**	(3)		

BEGINNER'S BOX-4

1.	(4)	**2.**	(1)	**3.**	(4)	**4.**	(4)	**5.**	(4)
6.	(3)	**7.**	(2)	**8.**	(1)	**9.**	(3)		