

CHEMICAL BONDING

INTRODUCTION

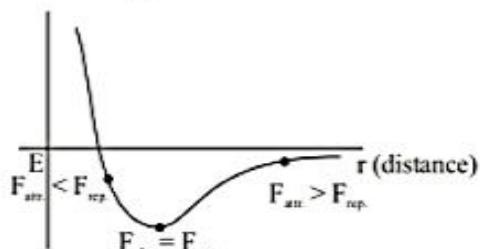
- (i) Most of the elements exist as molecules which are cluster of atoms. How do atoms combine to form molecules and why do atoms form bonds. Such doubts will be discussed in this chapter.
- (ii) A molecule will only be formed if it is more stable and has a lower energy, than the individual atoms.

CHEMICAL BOND

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

Cause of Chemical Combination

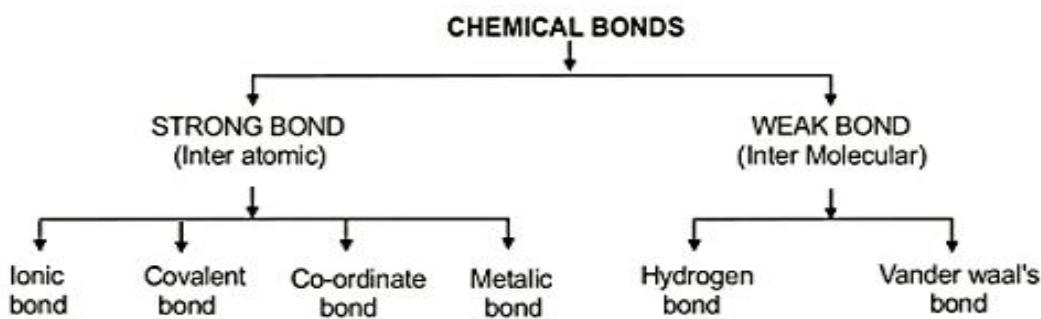
1. Tendency to acquire minimum energy :



- (i) When two atoms approaches to each other. Nucleus of one atom attracts the electron of another atom.
- (ii) According to quantum theory when two atoms of element approach each other then there will be force of attraction as well as force of repulsion between the bonded atoms. At the minimum distance where these forces becomes equal is called bond formation condition (equilibrium state) and atom of the elements get stabilized by bond formation phenomena by lowering their energy.
- (iii) If net result is attraction, the total energy of the system (molecule) decreases and a chemical bond forms.
- (iv) So, Attraction \propto 1/energy \propto Stability.
- (v) Bond formation is an exothermic process

2. Tendency to acquire noble gas configuration :

- (i) Atom combines to acquire noble gas configuration.
- (ii) Only outermost electron i.e. ns, np and (n-1)d electrons participate in bond formation.
- (iii) Inert gas elements do not participate, as they have stable electronic configuration and hence minimum energy. (Stable electronic configuration : 1s² or ns²np⁶)



Lewis Octet Rule

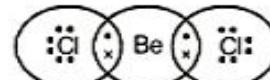
- Every atom has a tendency to complete its octet.
- Hydrogen has the tendency to complete its duplet.
- To acquire inert gas configuration atoms loose or gain electron or share electron.
- The tendency of atoms to achieve eight electrons in their outer most shell is known as Lewis octet rule.

e.g., H_2O molecule



obeys octet rule

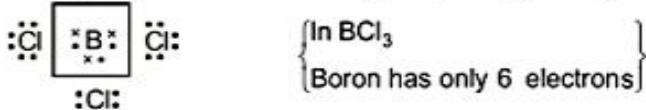
e.g., BeCl_2 Molecule



Doesn't obey octet rule

Exception of Octet Rule :

- (a) **Incomplete octet molecules : or (electron deficient molecules) or Hypovalent molecules**
Compound in which octet is not complete in outer most orbit of central atom.
Examples - Halides of IIIA groups, BF_3 , AlCl_3 , BCl_3 , hydride of III A/13th group etc.



Other examples - BeCl_2 (4 electron), ZnCl_2 (4 electron), $\text{Ga}(\text{CH}_3)_3$ (6 electron)

- (b) **Expansion of octet or (electron efficient molecules) or Hypervalent molecules**
Compound in which central atom has more than 8 electron in outermost orbits.
Example - PCl_5 , SF_6 , IF_7 , the central atom P, S and I contain 10, 12, and 14 electrons respectively.



Electron dot formula of PCl_5

- (c) **Pseudo inert gas configuration :-**
Cations of transition metals, which contains 18 electrons in outermost orbit

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

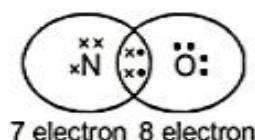
Electronic configuration of Ga - $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^1$

Electronic configuration of Ga^{+3} - $1s^2, 2s^2 2p^6, \underbrace{3s^2 3p^6 3d^{10}}_{18 \text{ electron}}$

(d) **Odd electron molecules :-**

Central atom have an unpaired electron or odd number (7 electron, 11 electron, etc) of electrons in their outer most shell.

Examples : NO, NO₂, ClO₂, ClO₃ etc.
e.g., NO molecule

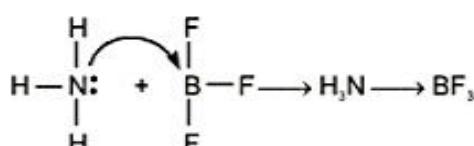


CO-ORDINATE BOND (DATIVE BOND)

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

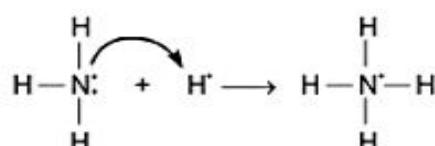


- (iii) Atom which provide electron pair for sharing is called donor.
- (iv) Other atom which accepts electron pair is called acceptor. That is why it is called donor-acceptor or dative bond

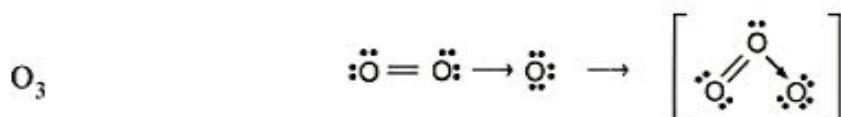
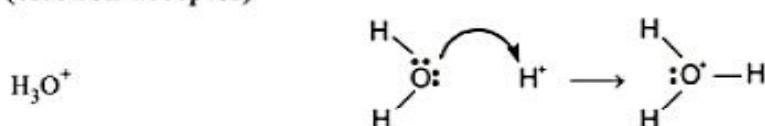


BF_3 is electron deficient compound.

Example: NH_4^+



(Bronsted - Lowry acid)
(electron acceptor)



IMPORTANT LEWIS ELECTRON DOT/CROSS STRUCTURES

	Compound	Structure	Electron dot/Cross formula
1.	Sodium Sulphide (Na_2S)	$2(\text{Na}^+)\text{S}^{--}$	$\text{Na}^+ \ddot{\text{:S}}^{\ominus} \text{Na}^+$
2.	Calcium Hydride (CaH_2)	$\text{Ca}^{++}2(\text{H}^-)$	$\text{H}: \text{Ca}^{++} \text{H}: \text{H}$
3.	Hydrogen Peroxide (H_2O_2)	$\text{H}-\text{O}-\text{O}-\text{H}$	$\text{H}: \ddot{\text{O}}: \ddot{\text{O}}: \text{H}$
4.	Phosphine (PH_3)	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{P}-\text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{H}: \ddot{\text{P}}: \text{H} \end{array}$
5.	Carbon mono-oxide(CO)	$\text{C} \equiv \text{O}$	$:\text{C} \quad \ddot{\text{:}} \quad \text{O}:$
6.	Carbon di-oxide (CO_2)	$\text{O}=\text{C}=\text{O}$	$\ddot{\text{O}} \quad \ddot{\text{:}} \quad \text{C} \quad \ddot{\text{:}} \quad \ddot{\text{O}}$
7.	Hydrogen Cyanide (HCN)	$\text{H}-\text{C}\equiv\text{N}$	$\text{H} \quad : \quad \text{C} \quad \ddot{\text{:}} \quad \text{N}:$
8.	Potassium Isocyanide (KNC)	$\text{K}^+ \text{N}\equiv\text{C}$	$\text{K}^+ [\ddot{\text{N}} \quad \ddot{\text{:}} \quad \text{C}]^-$
9.	Sodium Hydroxide (NaOH)	$\text{Na}^+\text{O}-\text{H}$	$\text{Na}^+ [\ddot{\text{O}}: \text{H}]^-$
10.	Nitrous oxide (N_2O)	$\text{N}=\text{N}\rightarrow\text{O}$	$:\text{N} \quad \ddot{\text{:}} \quad \text{N} \quad : \quad \ddot{\text{O}}:$
11.	Nitric oxide (NO or N_2O_2)	$\text{O}=\text{N}-\text{N}=\text{O}$	$\ddot{\text{O}} \quad \ddot{\text{:}} \quad \text{N} \quad \ddot{\text{:}} \quad \text{N} \quad \ddot{\text{:}} \quad \ddot{\text{O}}$
12.	Dinitrogen tri oxide (N_2O_3)	$\begin{array}{c} \text{O} \\ \\ \text{O}-\text{N}-\text{N}=\text{O} \end{array}$	$\ddot{\text{O}} \quad \ddot{\text{:}} \quad \text{N} \quad \ddot{\text{:}} \quad \text{N} \quad \ddot{\text{:}} \quad \ddot{\text{O}}$
13.	Dinitrogen tetraoxide (N_2O_4)	$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{O}-\text{N}-\text{N}=\text{O} \end{array}$	$\begin{array}{c} \ddot{\text{O}} \quad \ddot{\text{:}} \\ \\ \ddot{\text{O}}: \quad \text{N} \quad \ddot{\text{:}} \quad \text{N} \quad \ddot{\text{:}} \quad \ddot{\text{O}} \end{array}$
14.	Nitrogen Penta oxide (N_2O_5)	$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{O}-\text{N}-\text{O}-\text{N}=\text{O} \end{array}$	$\ddot{\text{O}} \quad \ddot{\text{:}} \quad \ddot{\text{O}} \quad \ddot{\text{:}} \quad \ddot{\text{O}} \quad \ddot{\text{:}} \quad \ddot{\text{O}}$
15.	Nitrous acid (HNO_2)	$\text{H}-\text{O}-\text{N}=\text{O}$	$\text{H}: \ddot{\text{O}}: \text{N} \quad \ddot{\text{:}} \quad \ddot{\text{O}}$
16.	Nitric acid (HNO_3)	$\begin{array}{c} \text{O} \\ \\ \text{H}-\text{O}-\text{N}=\text{O} \end{array}$	$\text{H}: \ddot{\text{O}}: \text{N} \quad \ddot{\text{:}} \quad \ddot{\text{O}}$

17.	Nitrate Ion (NO_3^-)	$\begin{array}{c} \text{O} \\ \\ \text{O}-\text{N}-\text{O}^- \end{array}$	$\left[\begin{array}{c} :\ddot{\text{O}}: \\ \vdots \\ :\ddot{\text{O}} : \text{N} : \ddot{\text{O}}: \\ \vdots \end{array} \right]^-$
18.	Ammonium Chloride (NH_4Cl)	$\left[\begin{array}{c} \text{H} \\ \\ \text{H}-\text{N}-\text{H} \\ \\ \text{H} \end{array} \right]^+ \text{Cl}^-$	$\left[\begin{array}{c} \text{H} \\ \\ \text{H} \cdots \text{N} \cdots \text{H} \\ \\ \text{H} \end{array} \right]^+ :\ddot{\text{Cl}}^-$
19.	Carbonate Ion (CO_3^{--})	$\begin{array}{c} \text{O} \\ \\ \text{O}-\text{C}-\text{O}^- \end{array}$	$\left[\begin{array}{c} :\ddot{\text{O}}: \\ \vdots \\ :\ddot{\text{O}} : \text{C} : \ddot{\text{O}}: \\ \vdots \end{array} \right]^{--}$
20.	Sulphur di-oxide (SO_2)	$\text{O} \leftarrow \text{S}=\text{O}$	$:\ddot{\text{O}} : \text{S} :: \ddot{\text{O}}$
21.	Sulphur Tri-oxide (SO_3)	$\begin{array}{c} \text{O} \\ \uparrow \\ \text{O} \leftarrow \text{S}=\text{O} \end{array}$	$:\ddot{\text{O}}: \\ :\ddot{\text{O}} : \text{S} :: \ddot{\text{O}}$
22.	Sulphite Ion (SO_3^{--})	$\begin{array}{c} \text{O} \\ \uparrow \\ \text{O}-\text{S}-\text{O}^- \end{array}$	$\left[\begin{array}{c} :\ddot{\text{O}}: \\ \vdots \\ :\ddot{\text{O}} : \text{S} : \ddot{\text{O}}: \\ \vdots \end{array} \right]^{--}$
23.	Sulphate Ion (SO_4^{--})	$\begin{array}{c} \text{O} \\ \uparrow \\ \text{O}-\text{S}-\text{O}^- \\ \downarrow \\ \text{O} \end{array}$	$\left[\begin{array}{c} :\ddot{\text{O}}: \\ \vdots \\ :\ddot{\text{O}} : \text{S} : \ddot{\text{O}}: \\ \vdots \\ :\ddot{\text{O}}: \end{array} \right]^{--}$
24.	Thio-sulphate Ion ($\text{S}_2\text{O}_3^{--}$)	$\begin{array}{c} \text{S} \\ \uparrow \\ \text{O}-\text{S}-\text{O}^- \\ \downarrow \\ \text{O} \end{array}$	$\left[\begin{array}{c} :\ddot{\text{S}}: \\ \vdots \\ :\ddot{\text{O}} : \text{S} : \ddot{\text{O}}: \\ \vdots \\ :\ddot{\text{O}}: \end{array} \right]^{--}$
25.	Phosphoric Acid (H_3PO_4)	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{O}-\text{P}-\text{O}-\text{H} \\ \\ \text{O} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{H} \cdots \ddot{\text{O}} \cdots \text{P} \cdots \ddot{\text{O}} \cdots \text{H} \\ \\ :\ddot{\text{O}}: \end{array}$

26.	Phosphorous acid (H_3PO_3)	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{O}-\text{P}-\text{O}-\text{H} \\ \\ \text{O} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{H}:\ddot{\text{O}}:\text{P}(\text{O}^-):\ddot{\text{O}}:\text{H} \\ \\ :\ddot{\text{O}}: \end{array}$
27.	Phosphate Ion (PO_4^{3-})	$\begin{array}{c} \text{O}^- \\ \\ \text{O}-\text{P}-\text{O}^- \\ \\ \text{O} \end{array}$	$\left[\begin{array}{c} :\ddot{\text{O}}: \\ \text{:} \\ \text{:}\ddot{\text{O}}\text{:} \text{P}(\text{O}^-)\text{:} \ddot{\text{O}}\text{:} \\ \text{:} \\ :\ddot{\text{O}}: \end{array} \right]^-$
28.	Potassium Permagnate (KMnO_4)	$\begin{array}{c} \text{O} \\ \\ \text{O}-\text{Mn}-\text{O} \\ \\ \text{O} \end{array}$	$\left[\begin{array}{c} :\ddot{\text{O}}: \\ \text{:} \\ \text{:}\ddot{\text{O}}\text{:} \text{Mn}(\text{O}^-)\text{:} \ddot{\text{O}}\text{:} \\ \text{:} \\ :\ddot{\text{O}}: \end{array} \right]^-$

Illustration

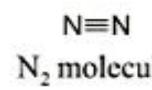
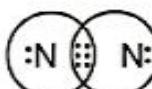
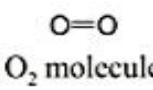
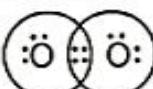
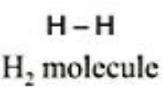
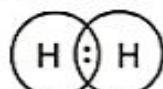
Ans. (B)

Sol. Hypervalent : Central atom of the compound having more than $8 e^-$.

Exercise

COVALENT BOND

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



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

(iii) Shairing 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 – $\begin{array}{c} \text{H}-\ddot{\text{N}}-\text{H} \\ | \\ \text{H} \end{array}$ Three single bonds (not triple bond)

$\ddot{\text{N}}=\ddot{\text{N}}$, Triple bond. (not three single bond)

$\ddot{\text{O}}=\ddot{\text{O}}$, Double bond (Not two single bond)

$\text{H}-\ddot{\text{O}}-\text{H}$, (Two single bonds.)

Orbital concept of covalent bond :

- One orbital can accomodate at the most 2 electrons with opposite spins $1\downarrow$
- Half filled orbital or unpaired electron orbital accepts one electron from another atom, to complete its orbitals.
- 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 defined as the number of electrons contributed by an atom of the element for shairing with other atoms to achieve noble gas configuration.
- If the outermost orbit has empty orbitals then covalent bonds are formed in excited state.

Variable valency in covalent bonds :

- Variable valencies are shown by those elements which have empty orbitals in outermost shell.
- Lone pair electrons gets 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) Phosphorus \rightarrow Ground state

$1\downarrow$	1	1	1
3s	3p		

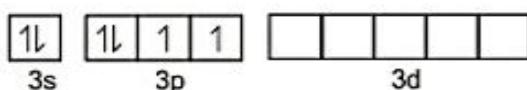
Covalency 3 (PCl_3)

Phosphorus \rightarrow Excited state

1	1	1	1	1			
3s	3p				3d		

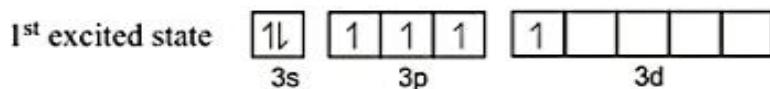
Covalency – 5 (PCl_5)

(b) Sulphur \rightarrow Ground state.

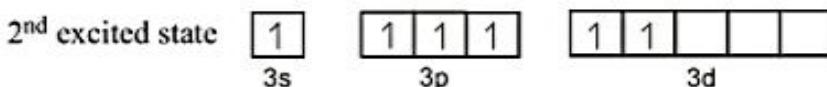


Covalency – 2 (SF_2)

Sulphur \rightarrow Excited state



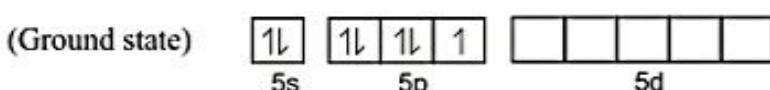
Covalency – 4 (SF_4)



Covalency – 6 (SF_6)

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

(c) Iodine has three lone pair of electrons



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

Variable Valencies are 1, 3, 5, 7

Applications of Variable Valency :

To explain existence of molecules :

NCI_3 – exists

NCI_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 exists due to presence of d-orbital, present in its valence shell.

Note : Compound in which Ionic, covalent and co-ordinate bonds are present are following

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

Wave mechanical concept of chemical bonding – (Overlapping)

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

(1) Valence bond theory (VBT)

(2) Molecular orbital theory (MOT)

VALENCE BOND THEORY

- It was presented by Heitler & London to explain how a covalent bond is formed.
It was extended by Pauling & Slater.
- The main points of theory are –
 - To form a covalent bond overlapping occurs between half filled valence shell orbitals of the two atoms.
 - Resulting bond acquires a pair of electrons with opposite spins to get stability.
 - Orbitals come closer to each other from the direction in which there is maximum overlapping
 - So covalent bond has directional character.
 - Extent of overlapping \propto strength of chemical bond.

(f) Extent of overlapping depends on two factors.

(i) Nature of orbitals – p, d and f are directional orbitals → more overlapping

s-orbitals → non directional – less overlapping

(ii) Nature of overlapping – Co-axial overlapping - extent of overlapping more.

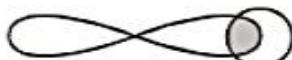
Collateral overlapping - extent of overlapping less

Order of strength of Co - axial overlapping –

$$p - p > s - p > s - s$$



p - p



p - s



s - s

(g) As the value of n increases, bond strength decreases.

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

(h) If n is same bond strength order will be following

$$2p - 2p > 2s - 2p > 2s - 2s$$

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

(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 trivalence of boron, tetravalency of carbon, penta-valency of phosphorus etc.

(k) Two types of bonds are formed on account of overlapping.

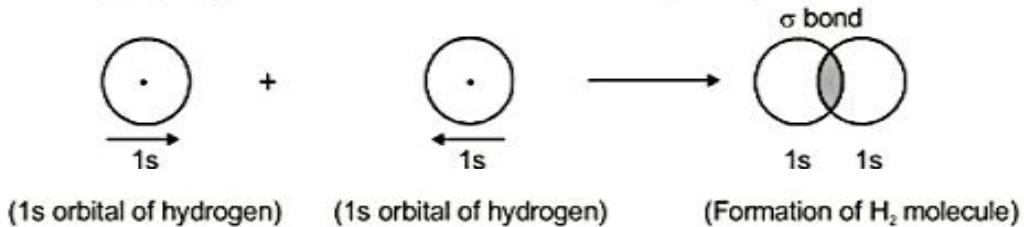
(A) Sigma (σ) bond (B) Pi (π) bond

(A) Sigma (σ) bond :

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

Sigma bond are formed by four types of overlapping

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

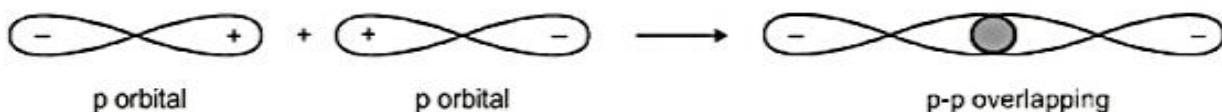


(b) s - p overlapping (Formation of HF) – When half filled s-orbital of one atom overlap with half filled p-orbital of other atom.



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

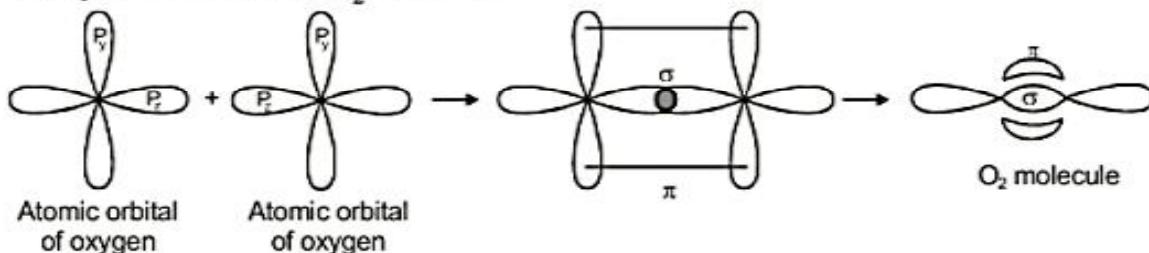
e.g. Formation of Cl_2 , F_2 , Br_2



(B) Pi (π) bond

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

Example – Formation of O₂ molecule –



Only p_x and p_z of oxygen atom have unpaired electron in each orbital for bonding.

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

- (iii) Free rotation about a π bond is not possible.
 - (iv) π bond is weaker than σ bond (Bond energy difference is 63.5 KJ or 15 K cal/mole)
 - (v) π bond takes part in resonance.
 - (vi) π bond formed by pure or unhybrid orbitals.

Illustration

- 1.** When $2s - 2s$, $2p - 2p$ and $2p - 2s$ orbitals overlap, the bond strength decreases in the order:
 (A) $p - p > s - s > p - s$ (B) $p - p > p - s > s - s$ (C) $s - s > p - p > p - s$ (D) $s - s > p - s > p - p$

Ans. (B)

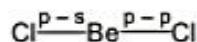
Sol. Bond strength \propto directional property of orbitals.

Exercise

HYBRIDISATION

Consider an example of Be compound :-

If it is formed without hybridisation then -



both the Be–Cl bonds should have different parameters and p-p bond strength is greater than s-p bond strength.

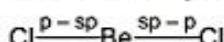
Practically bond strength and distance of both the Be-Cl bonds are same.

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

Hybridisation :

- (i) It is introduced by pauling, to explain equivalent nature of covalent bonds in a molecule.
- (ii) **Definition :** Mixing of different shapes and approximate equal energy atomic orbitals, and redistribution of energy to form new orbitals, of same shape & same energy. These new orbitals are called hybrid orbitals and the phenomenon is called hybridisation.

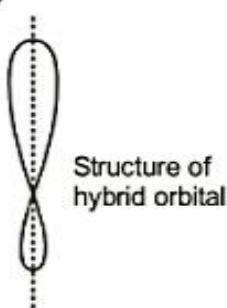
Now after considering s-p hybridisation in BeCl_2



bond strength of both the bonds will be equal.

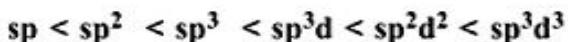
Characteristic of Hybridisation :

- (i) Hybridisation is a mixing of orbitals and not electrons. Therefore in hybridisation full filled, half filled and empty orbitals may take part.
- (ii) Number of the hybrid orbitals formed is always be equivalent to number of atomic orbital which have taken part in the process of hybridisation.



- (iii) Each hybrid orbital having two lobes, one is larger and other is smaller. Bond will be formed from large lobe.
- (iv) The number of hybrid orbitals on central atom of a molecule or ion = number of σ bonds + lone pair of electron.
 - (a) The 1st bond between two atoms will be sigma.
 - (b) The other bond between same two atoms will be π bond.
 - (c) The electron pair of an atom which do not take part in bond formation called as lone pair of electron.
- (v) One element can represent many hybridisation state depending on experimental conditions for example, Carbon showing sp , sp^2 and sp^3 hybridisation in its compounds.
- (vi) Hybrid orbitals are differentiated as sp , sp^2 , sp^3 etc.

- (vii) The order of repulsion between ℓp & bp is : $\ell p - \ell p > \ell p - bp > bp - bp$
- (viii) 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.



Difference between hybridisation & overlapping

Overlapping	Hybridisation
<ol style="list-style-type: none"> It occurs between orbitals of two atoms Only half filled orbitals takes part in overlapping It occurs during bond formation bond formed after hybridisation Orbital of different energies may participates in excited states. 	<ol style="list-style-type: none"> It occurs among orbitals of the same atom Any type of orbital can participates Process, just before overlapping. It may takes place in ground or in excited state In ground state— NH₃, NCl₃, PH₃, PCl₃,

Determination of hybridisation state :

Method (I) :

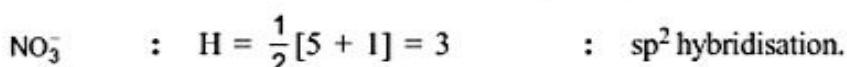
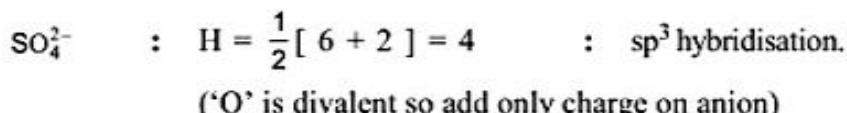
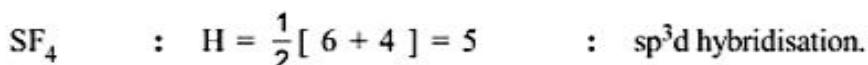
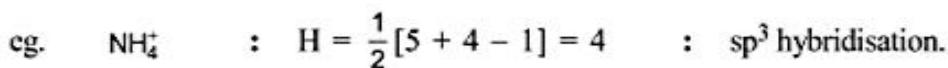
Count the following pair of electron around the central atom :

- Count all pure σ bonded electron pairs (or σ bonds)
- Count all lone pair of electron
- Count Co-ordinate bond

Method (II) :

To predict hybridisation following formula may be used :

Number of hybrid orbital = $\frac{1}{2}$ [Total number of valence electron in the central atom + total number of monovalent atoms – charge on cation + charge on anion]



Where, H is the number of hybrid orbitals.

If such type of electron pairs are –

two	–	sp	hybridisation
three	–	sp ²	hybridisation
four	–	sp ³	hybridisation
five	–	sp ³ d	hybridisation
six	–	sp ³ d ²	hybridisation
seven	–	sp ³ d ³	hybridisation

Shape of covalent molecules :

- It was given by Sidgwick & Powell.

No. of electron pair	electronic geometry	ℓ.p.	b.p.	Shape of molecule	Example
2		0	2	 linear	BeCl ₂ , CO ₂
3		0	3		BF ₃ , BCl ₃
		1	2		SnCl ₂
4		0	4		CH ₄
		1	3		NH ₃
		2	2		H ₂ O
5		0	5		PCl ₅

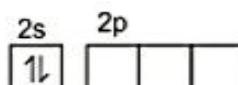
		1	4	 see-saw/distorted tetrahedron	SF ₄
		3	2	 T-shape	ClF ₃
		2	3	 linear	XeF ₂
6	 hexagonal planar	0	6	 Octahedral	SF ₆
		1	5	 square pyramidal	BrF ₅
		2	4	 square planar	XeF ₄

Types of Hybridisation :

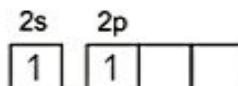
sp hybridisation :

- (i) In this hybridisation one s-orbital & 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.
- (ii) These two sp hybrid orbitals are arranged in straight line & 180° bond angle
- (iii) % s-character is 50%

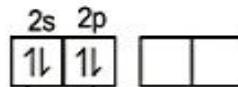
Be (ground state)



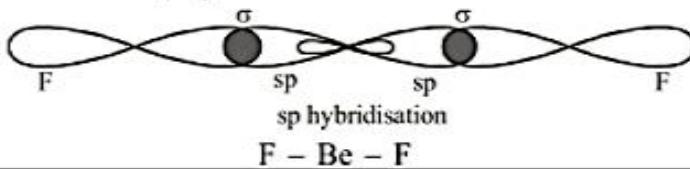
Be (excited state)



Be atom accepts two electrons
from F in BeF₂,

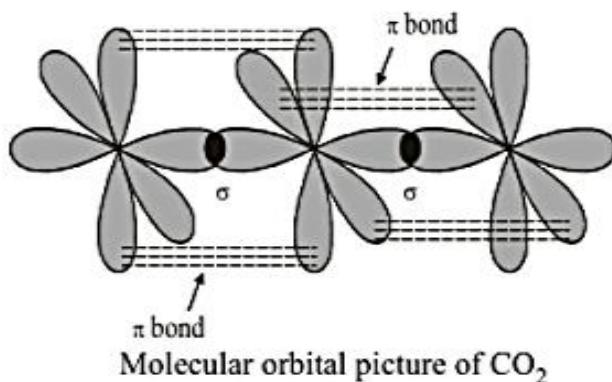


two sp hybridisation



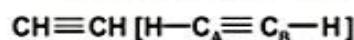
CO₂ Molecule (O = C = O) :

In CO₂ molecule, C has two sp hybrid orbitals & two unhybridised p orbitals.



Molecular orbital picture of CO₂

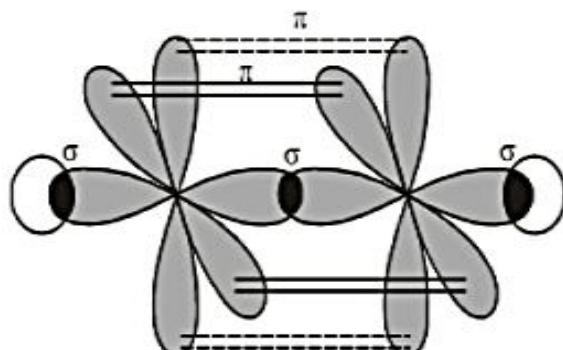
- Thus, CO₂ molecule is a linear in shape & having 180° bond angle.
- The bond length between C–O bond is reduced due to the presence of π bond.



In CH≡CH molecules, each C atom contains two sp hybrid orbitals & two unhybridised p orbitals

	2s	2p
C(ground state)	1l	1 1
C(excited state)	1	1 1 1
C atom accepts two electrons from H & C, In C ₂ H ₂	1l 1l	1 1

two sp hybridisation



Molecular orbital of C₂H₂



sp hybrid orbital of each C atom 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 $\text{H}–\text{C}_A \equiv \text{C}_B–\text{H}$

sigma bond between $C_A - C_B$ is formed 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 :

$$3\sigma + 2\pi \text{ bond} = 5 \text{ bonds}$$

Examples on sp hybridisation

Example	σ bond	Lone pair electrons	Hybridisation	Bond angle	Shape
$BeH_2, BeCl_2, CO_2NO_2^+, C_2H_2, HCN, HgCl_2, N_2O, N_3^-$	2	0	sp	180°	Linear

sp^2 Hybridisation :

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

B (ground state)

2s	2p
$1\downarrow$	$1 \quad \quad \quad$

B (excited state)

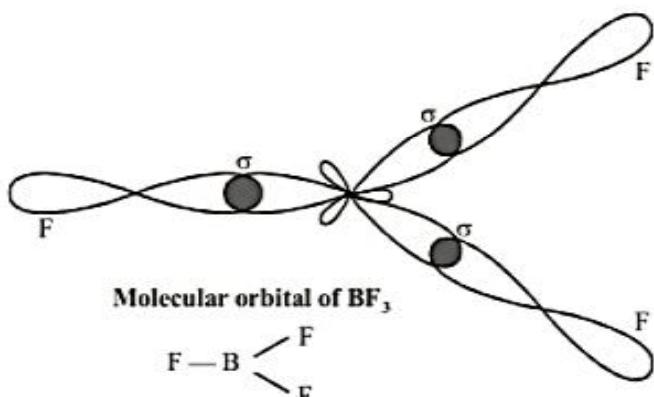
1	$1 \quad 1$
-----	-------------

B atom accepts 3 electrons

$1\downarrow$	$1\downarrow$	$1\downarrow$	\square
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three sp^2 hybrid orbitals

From 3 F atom \therefore in BF_3

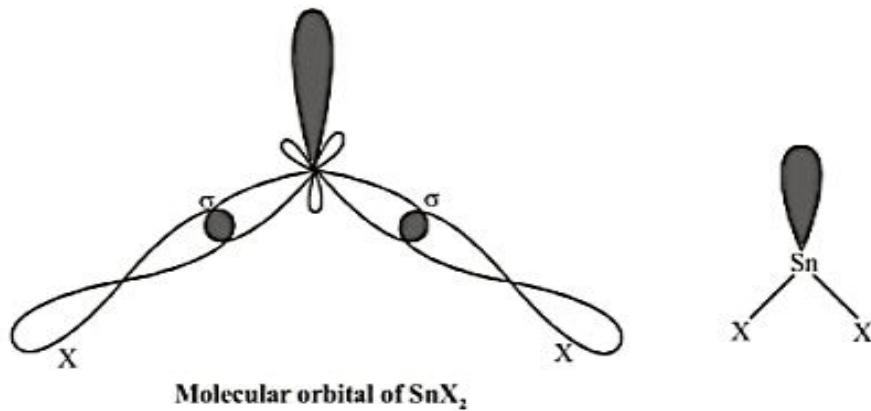
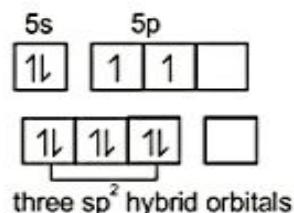


$$(iii) \% \text{ s - character} = 33.3\%$$

SnX_2 ($X = \text{F, Cl, Br, I}$)

Sn (ground state)

Sn after hybridisation shares two electron with two atom.

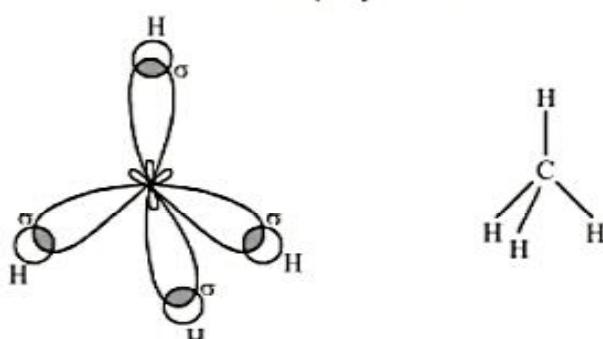
Molecular orbital of SnX_2 SnX_2 having two σ bonds & one lone pair electron, therefore, hybridisation is sp^2 The bond angle is SnX_2 will be less than 120° (due to presence of one lone pair electrons.)The shape of SnX_2 molecule is bent.**Examples on sp^2 hybridisation**

Example	σ bond	Lone pair electron	Hybridisation	Bond angle	Shape
BF_3	3	-	sp^2	120°	Trigonal planar
CH_3^+	3	-	sp^2	120°	Trigonal planar
$\text{CH}_2=\text{CH}_2$	3, 3	-	sp^2	120°	Trigonal planar
Graphite	3	-	sp^2	120°	Trigonal planar
NO_3^-	3	-	sp^2	120°	Trigonal planar
HNO_2	2	1	sp^2	$< 120^\circ$	Angular (V-shaped)
SO_2	2	1	sp^2	$< 120^\circ$	Angular (V-shaped)
SO_3	3	-	sp^2	120°	Trigonal planar
HCO_3^-	3	-	sp^2	120°	Trigonal planar
SnCl_2	2	1	sp^2	$< 120^\circ$	Angular (V-shaped)
SnI_2	2	1	sp^2	$< 120^\circ$	Angular (V-shaped)
AlCl_3	3	-	sp^2	120°	Trigonal planar

sp³ Hybridisation :

- (i) In this hybridisation one s orbital & three p orbitals of an atom of a molecule or ion, are mixed to give four new hybrid orbitals called as sp³ hybrid orbitals.
- (ii) The angle between these four hybrid orbitals will be 109°28'

C (ground state)	2s	2p
	1l	1 1
C (excited state)		1
C atom share four electrons with		1 1 1
4 hydrogen atoms		1l 1l 1l 1l
		four sp ³ hybridisation

Molecular tetrahedral orbital of CH₄

- (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 :

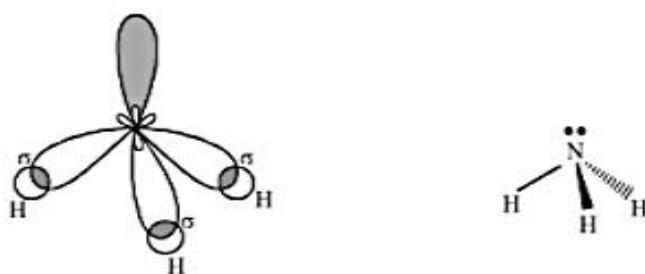
The following examples represent this condition.

CH₄, CF₄, CCl₄, CBr₄, NH₄⁺, BF₄⁻, BeF₄⁻², etc.

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

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

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

Molecular pyramidal orbital of NH₃ Molecular pyramidal orbital of NH₃

NH₃, NF₃, PF₃, NCl₃, PCl₃, H₃O⁺, ClO₃⁻ etc.

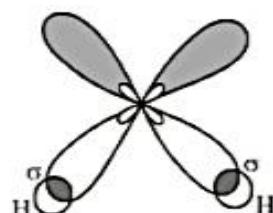
- (ii) sp³ hybridisation, pyramidal shape & bond angle will be less than 109° 28' due to the presence of the lone pair electron on nitrogen repels bond pair electron more therefore bond angle is reduced from 109°28' to 107°. The repulsion between lone pair – bond pair > bond pair – bond pair.

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

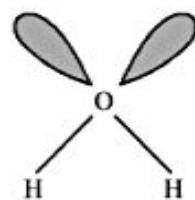
- (i) This condition is shown by following compounds and ions.

H₂O, OCl₂, OBr₂, OF₂, etc.

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



Molecular angular orbital of H_2O



Structure of H_2O
(Angular)

In H_2O the hybridisation on O atom is sp^3 , but due to presence of two lone pair electrons they repel each other and then repel their adjacent bond pair electron. These repulsion will be in following order.

$$l.p. - l.p. > l.p. - b.p. > b.p. - b.p.$$

l.p. = lone pair electron

b.p. = bond pair electron

Examples on sp^3 Hybridisation

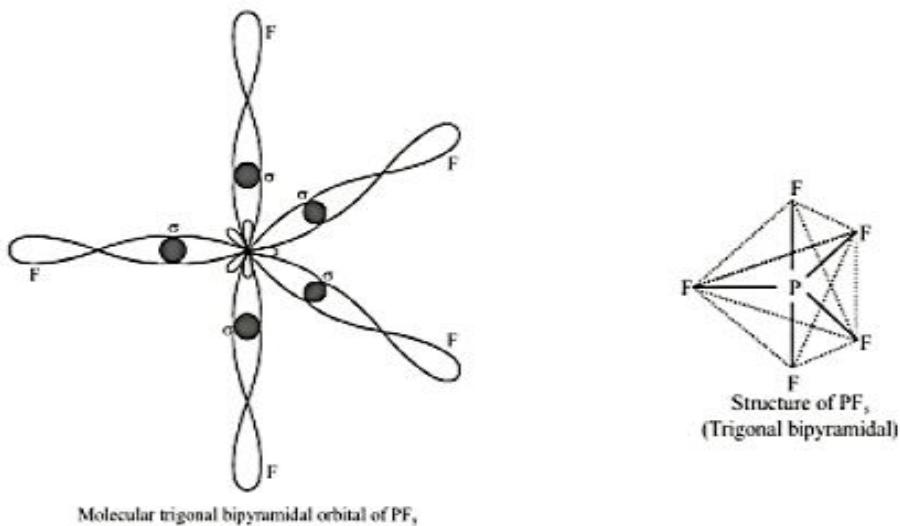
Example	σ bond	lone pair electron	Hybridisation	Shape
CH_4	4	-	sp^3	Tetrahedron
$\overset{\oplus}{PCl}_4$	4	-	sp^3	Tetrahedron
$\overset{\oplus}{NH}_4$	4	-	sp^3	Tetrahedron
$\overset{\ominus}{BF}_4$	4	-	sp^3	Tetrahedron
BeF_4^{-2}	4	-	sp^3	Tetrahedron
MgF_4^{-2}	4	-	sp^3	Tetrahedron
NF_3	3	1	sp^3	Pyramidal
$N(CH_3)_3$	3	1	sp^3	Pyramidal
$\overset{\ominus}{CH}_3$	3	1	sp^3	Pyramidal
H_3O^+	3	1	sp^3	Pyramidal
XeO_3	3	1	sp^3	Pyramidal
$\overset{\ominus}{NH}_2$	2	2	sp^3	Angular (V-shaped)
Cl_2O	2	2	sp^3	Angular (V-shaped)
SCl_2	2	2	sp^3	Angular (V-shaped)
Diamond	4	-	sp^3	Tetrahedron
SiO_2	4	-	sp^3	Tetrahedron
SiC	4	-	sp^3	Tetrahedron

sp³d Hybridisation :

- (i) In this hybridisation one s orbital, three p-orbital and one d orbital are mixed to give five new hybrid orbitals called as sp³d hybrid orbitals.
- (ii) Out of these five 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 is trigonal bipyramidal.

For example, PF₅ showing sp³d hybridisation

P (ground state)	3s	3p	3d
	1l	1 1 1	
P* (excited state)	3s	3p	3d
	1	1 1 1	1
P atom share with five e of F	1l	1l 1l 1l 1l 1l	
			five sp ³ d hybrid orbitals



- (iii) In this hybridisation d_{z²} orbital is hybridised with s and p orbitals.

In this way five sp³d hybrid orbitals form five sigma bond with five F atoms and give a molecule of PF₅, shape of this molecule is trigonal bipyramidal.

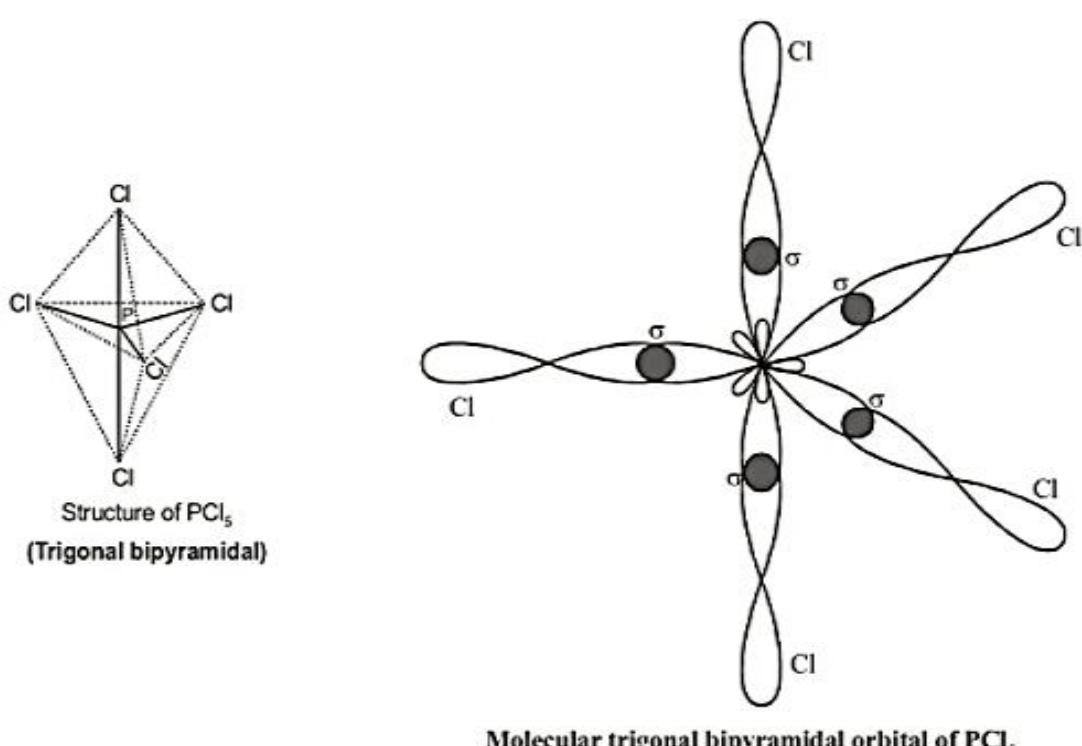
Axial two P–Cl bonds are longer than equatorial three P–Cl bond due to repulsion between 3 equatorial bond pair of electron and 2 axial bond pair of electron.

In above hybridisation there are four conditions

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

The following examples represent this conditions.

PF₅, PCl₅, PBr₅, PI₅, AsF₅, AsCl₅, SbCl₅, SbF₅ etc.



The shape of all above molecules is trigonal bipyramidal.

(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.

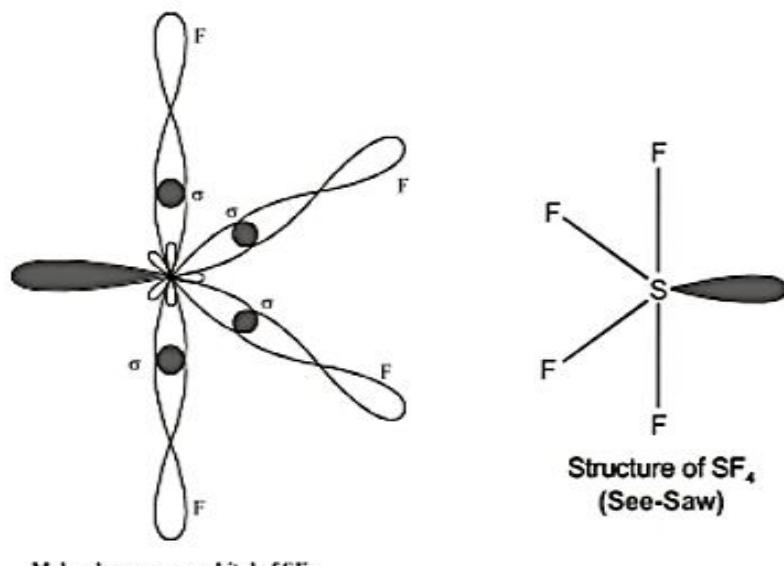
The shape of all above examples will be irregular tetrahedron/see saw.

Examples SF_4

S ground state	3s	3p	3d
	1l	1l 1 1	

S excited state	3s	3p	3d
	1l	1 1 1	1

S atom share with four electron of F	1l	1l	1l	1l	1l	1	1	1	1
five sp^3d hybrid orbitals									

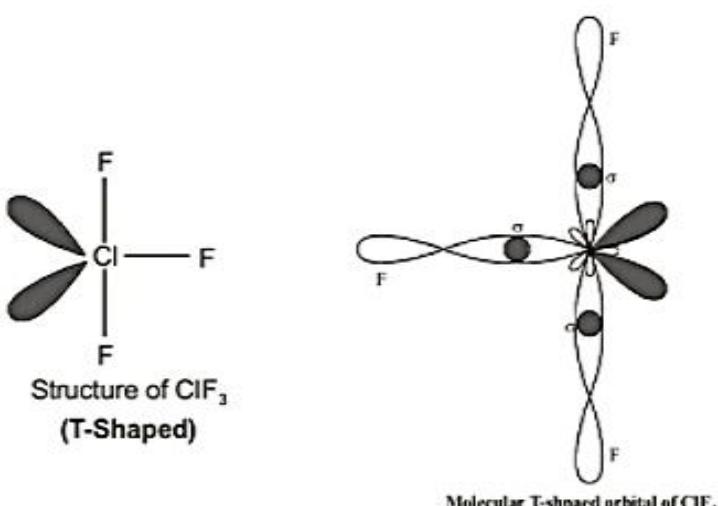


(c) Three sigma bonds & two lone pair of electrons :

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.



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

The following examples represent this condition.

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

The geometry of above examples will be linear

sp^3d^2 Hybridisation :

- In this hybridisation, one s-orbital, three p-orbitals & two d-orbitals are mixed to give six new hybrid orbitals known as sp^3d^2 hybrid orbitals.
- The shape of molecule obtained from above six hybrid orbitals will be symmetrical octahedral.
- 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^- ,

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

SF₆ :

S (ground state)

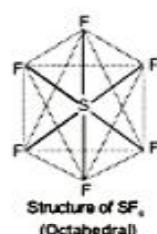
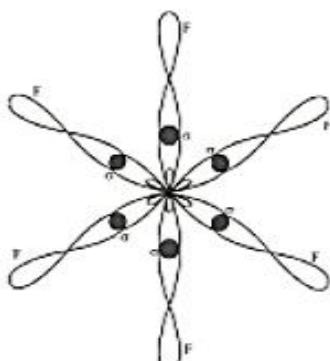
3s	3p	3d
1↑	1↑ 1 1	

S (excited state)

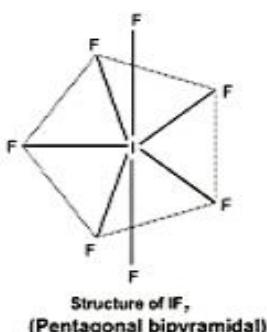
3s	3p	3d
1	1 1 1	1 1

S (after hybridisation)

1↓	1↓	1↓	1↓	1↓	1↓		
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six sp^3d^2 hybrid orbitals**sp³d³ Hybridisation :**

- In this hybridisation, one s-orbital, three p-orbitals & three d-orbitals are mixed to give seven new hybrid orbitals known as sp^3d^3 hybrid orbitals.
- In this hybridisation d-orbitals used are d_{xy} , $d_{x^2-y^2}$ & d_{z^2} orbitals.
- These seven sp^3d^3 orbitals are configurated in pentagonal bipyramidal shape.
- Five bond angles are of 72° & two hybrid orbitals are perpendicular to the plane of five hybrid orbitals that is pentagonal planar, the shape of molecule becomes pentagonal bipyramidal.
- The following examples showing sp^3d^3 hybridisation : IF₇ & XeF₆.

**Illustration**

- Which of the following statement is not correct?
 - Hybridization is the mixing of atomic orbitals
 - sp^2 – hybrid orbitals are formed from two p - atomic orbitals and one s- atomic orbitals
 - dsp^2 – hybrid orbitals are at 90° to one another
 - d^2sp^3 – hybrid orbitals are directed towards the corners of a regular octahedron

Ans. (A)**Sol.** Hybridization is the mixing of atomic orbitals having comparable energy.

2. The correct order of increasing s-character (in percentage) in the hybrid orbitals of following molecules/ ions is:

- (I) CO_3^{2-} (II) XeF_4 (III) I_3^- (IV) NCl_3 (V) BeCl_2
 (A) II < III < IV < I < V (B) II < IV < III < V < I (C) III < II < I < V < IV (D) II < IV < III < I < V
(A)
 $\text{CO}_3^{2-} \rightarrow \text{sp}^2$ % s character = 33.3%
 $\text{XeF}_4 \rightarrow \text{sp}^3\text{d}^2$ 16.6%
 $\text{I}_3^- \rightarrow \text{sp}^3\text{d}$ 20%
 $\text{NCl}_3 \rightarrow \text{sp}^3$ = 25%
 $\text{BeCl}_2 \rightarrow \text{sp}$ 50%

Exercise

1. Which of the following statement is incorrect ?
(A) NH_2^+ shows sp^2 – hybridisation whereas NH_2^- shows sp^3 – hybridisation
(B) $Al(OH)_4^-$ has a regular tetrahedral geometry
(C) sp^2 – hybridized orbitals have equal s- and p- character
(D) Usually hybridized orbitals form σ - bonds

Ans. (C)

Ans. (A)

HYBRIDISATION IN SOLID STATE / AQUEOUS STATE OF MOLECULES

Hybridization of covalent species which exist in ionic form in solid state.

Gaseous State	Hybridization	Solid State	Hybridization (Cation)	Hybridization (Anion)
PCl ₅	sp ³ d	[PCl ₄] ⁺ + [PCl ₆] ⁻	sp ³	sp ³ d ²
PBr ₅	sp ³	[PBr ₄] ⁺ + Br ⁻	sp ³	
XeF ₆	sp ³ d ³	[XeF ₅] ⁺ + F ⁻	sp ³ d ²	
N ₂ O ₅	sp ²	[NO ₂] ⁺ + [NO ₃] ⁻	sp	sp ²
N ₂ O ₄		[NO] ⁺ + [NO ₃] ⁻		sp ²
N ₂ O ₃	sp ²	[NO] ⁺ + [NO ₂] ⁻		sp ²
BrF ₃	sp ³ d	[BrF ₂] ⁺ + [BrF ₄] ⁻	sp ³	sp ³ d ²
IF ₅	sp ³ d ²	[IF ₄] ⁺ + [IF ₆] ⁻	sp ³ d	sp ³ d ³
ICl		[I ₂ Cl] ⁺ + [ICl ₂] ⁻	sp ³	sp ³ d
Cl ₂ O ₆	sp ³	[ClO ₂] ⁺ + [ClO ₄] ⁻	sp ²	sp ³
I ₄ O ₉		I ³⁺ + [IO ₃] ₃		sp ³
I ₂ Cl _{6(l)}		[ICl ₂] ⁺ + [ICl ₄] ⁻	sp ³	sp ³ d ²
I ₂		[I ₃] ⁺ + [I ₃] ⁻	sp ³	sp ³ d
ICN	sp (C)	[I ₂ CN] ⁺ + [I(CN) ₂] ⁻	sp ³ (I)	sp ³ d (I)

Illustration

1. The cationic part of solid Cl_2O_6 is having the " _____ " shape.
(A) linear (B) angular (C) Tetrahedron (D) undefined
Ans: (B)

Sol. $\text{Cl}_2\text{O}_6 \rightleftharpoons [\text{ClO}_2]^{+} + [\text{ClO}_4]^{-}$

Exercise

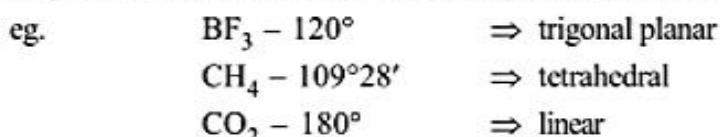
- 1.** What is the state of hybridisation of Xe in cationic part of solid XeF_6 .
(A) sp^3d^3 (B) sp^3d^2 (C) sp^3d (D) sp^3

Ans. (B)

GLASSPF AND NYHOM THEORY OR VSFPR THEORY

(Valence shell electron pair repulsion theory)

- (i) 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 & Powell



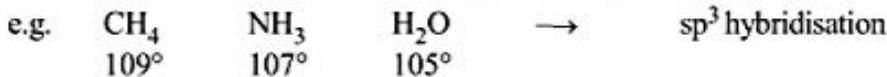
- (ii) If the central atom possess bonded pair of electrons as well as lone pair of electron, then shape of the molecule will be unsymmetrical i.e. the original bond angle will disturbed due to repulsion between lone pair of electrons.

Similarly on having different type of side atoms, molecule becomes unsymmetrical due to unequal force of repulsion between electron.

Order of repulsion is $- \ell.p > - \ell.p > \ell.p - b.p > b.p - b.p$.

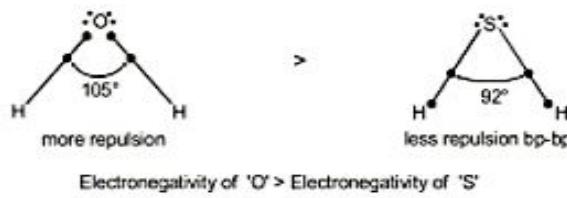
$$\text{Bond angle} \propto \frac{1}{\text{No. of lone pair of electron}}$$

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



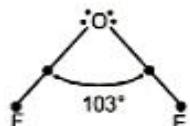
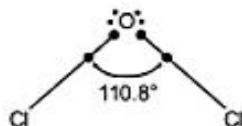
- (iv) In the different molecules if central atom have same number of lone pair of electron then bond angle will depend on electronegativities of A & B.

In AB_x type of molecules if side atoms are same Electronegativity of central atom increases, then bond angle increases.



Bond angle – $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3$

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



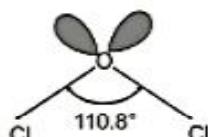
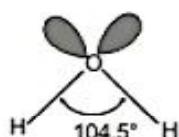
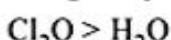
Electronegativity of Fluorine is greater than chlorine

$\text{PF}_3 < \text{PCl}_3 < \text{PBr}_3 < \text{PI}_3$ (Electronegativity of side atom decrease)

$\text{OF}_2 < \text{Cl}_2\text{O} < \text{Br}_2\text{O}$

$\text{SF}_2 < \text{SCl}_2 < \text{SBr}_2$

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



Illustration

1. Arrange the following in order of decreasing $N - O$ bond length: NO_2^+ , NO_2^- , NO_3^-
 (A) $\text{NO}_3^- > \text{NO}_2^+ > \text{NO}_2^-$ (B) $\text{NO}_3^- > \text{NO}_2^- > \text{NO}_2^+$ (C) $\text{NO}_2^+ > \text{NO}_3^- > \text{NO}_2^-$ (D) $\text{NO}_2^- > \text{NO}_3^- > \text{NO}_2^+$

Ans. (B)

Sol. Bond order $\propto \frac{1}{\text{Bond length}}$

	NO_2^+	NO_2^-	NO_3^-
Bond order	2	1.5	1.33

Exercise

1. Comment on the $\angle \text{CNC}$ and $\angle \text{HNN}$ in CH_3NCS and HN_3 respectively.
 (A) less than 120° and less than 120° (B) Greater than 120° and less than 120°
 (C) less than 120° and greater than 120° (D) Greater than 120° and greater than 120°
- Ans. (B)
2. The correct order of decreasing $X - O - X$ bond angle is ($X = H, F$ or Cl):
 (A) $\text{H}_2\text{O} > \text{Cl}_2\text{O} > \text{F}_2\text{O}$ (B) $\text{Cl}_2\text{O} > \text{H}_2\text{O} > \text{F}_2\text{O}$ (C) $\text{F}_2\text{O} > \text{Cl}_2\text{O} > \text{H}_2\text{O}$ (D) $\text{F}_2\text{O} > \text{H}_2\text{O} > \text{Cl}_2\text{O}$
- Ans. (B)

DRAGO'S RULE

According to Drago, when central atom of the compound is of 3rd period or below this of periodic table then lone pair is present in stereo chemically inactive s-orbital and bonding will take place through pure p-orbitals. But electronegativity of the surrounding atom must be less than or equal to 2.5. Then there is no hybridization and bond angle is nearly 90° .

NH_3 (107.8°), PH_3 (93.6°), AsH_3 (91.8°), SbH_3 (91.3°)

Illustration

1. Among the following, the correct statement is :
- Between NH_3 and PH_3 , NH_3 is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional
 - Between NH_3 and PH_3 , PH_3 is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional
 - Between NH_3 and PH_3 , NH_3 is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional
 - Between NH_3 and PH_3 , PH_3 is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional

Ans. (C)

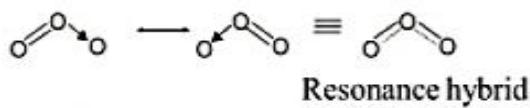
Sol. $\text{NH}_3 \rightarrow \text{sp}^3$ hybridisation (directional property),
 $\text{PH}_3 \rightarrow$ No hybridisation
So the NH_3 is a better lewis base than PH_3

Exercise

1. The bond angle in PH_3 is :
- | | |
|--|---|
| (A) Much lesser than NH_3 | (B) Equal to that in NH_3 |
| (C) Much greater than in NH_3 | (D) Slightly more than in NH_3 |

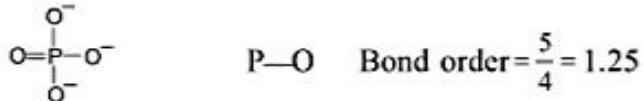
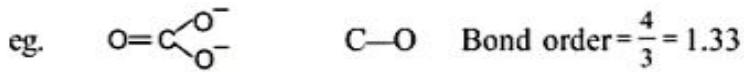
Ans. (A)**RESONANCE**

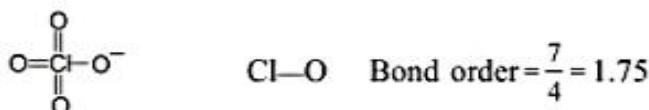
- (i) The concept of resonance was introduced by Heisenberg (1920), and later developed by Pauling and Ingold, to explain the properties of certain molecules,
- (ii) It has been found that the observed properties of certain compounds cannot be satisfactorily explained by writing a single Lewis structure. 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.
- (iii) Let us discuss resonance in ozone, according to its resonating structure it should have one single bond ($\text{O}-\text{O} = 1.48\text{\AA}$) but experiments show that both the bonds are same which can be proved by its resonance hybrid as shown below.



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

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



**Illustration**

1. (C—Cl) bond in $\text{CH}_2=\text{CH}-\text{Cl}$ (vinyl chloride) is stabilised in the same way as in:
 (A) benzyl chloride (B) ethyl chloride (C) chlorobenzene (D) allyl chloride

Ans. (C)

Sol. Both the molecule shows resonance

Exercise

1. Which of the following option is **incorrect**?

- (I) All C—O bonds in CO_3^{2-} are equal but not in H_2CO_3 .
- (II) All C—O bonds in HCO_2^- are equal but not in HCO_2H
- (III) C—O bond length in HCO_2^- is longer than C—O bond length in CO_3^{2-} .
- (IV) C—O bond length in HCO_2^- and C—O bond length in CO_3^{2-} are equal.

- (A) III & IV (B) II & III (C) II & IV (D) I & IV

Ans. (A)

2. Resonance does not occur due to the

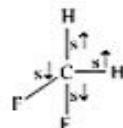
- (A) delocalization of a lone pair of electrons (B) delocalization of sigma electrons
 (C) delocalization of pi electrons (D) None of these

Ans. (B)

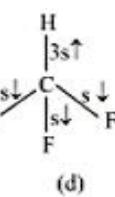
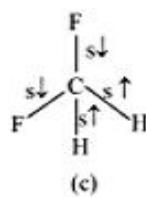
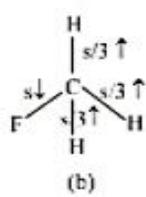
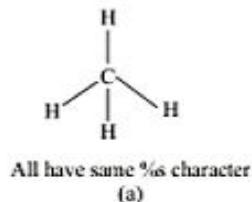
BENT RULE

When all hybrid orbitals equivalent. Ex. sp^3 , sp^2

- (1) If the more EN atom present in hybrid orbital, %s character decreases.



to compensate decrement of %s character these %s character increases on that orbital which have less EN atom bonded.

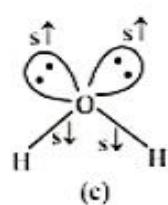
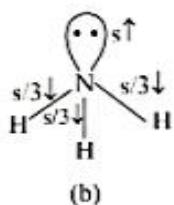
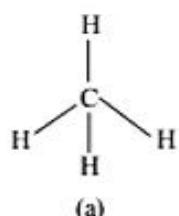
Example-1

C—H bond length a > b > c > d

HCF bond angle b < c < d

- (2) If the L.P is present in hybrid orbital, %s character increases

Example-2

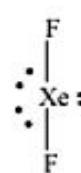
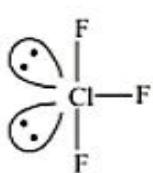
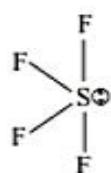
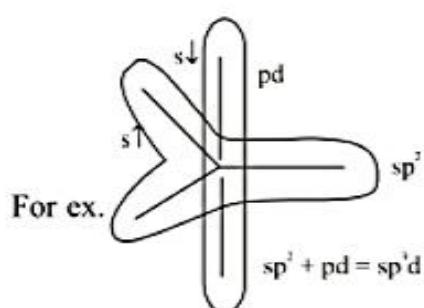


H × H bond angle a > b > c (X = Central atom)

If hybrid orbital are not equivalent

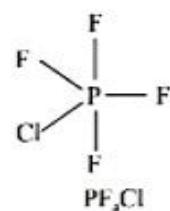
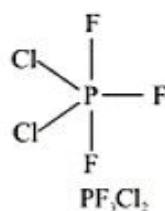
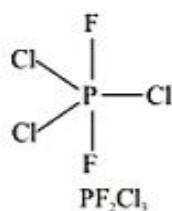
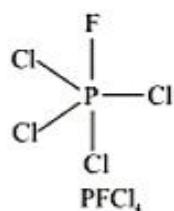
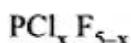
L.p. acquire place where %s character are higher

Example-3



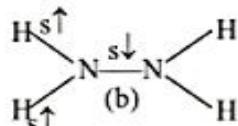
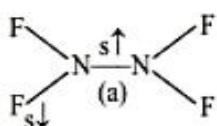
More EN atom acquire place where %s character are less

Example-4



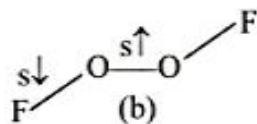
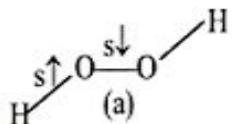
Bond length comparison

Example-5



N–N bond length a < b

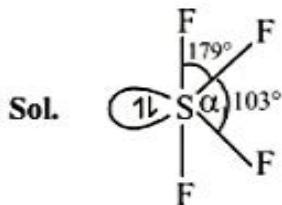
Example-6



O–O bond length a > b

Illustration

1. Comment on the effect of lone pair on axial and equatorial bond angles of SF_4 .



As expected axial bond should distort more than equatorial but actually due to lone pair has tendency to goes with more % character available bond angle decreases more than axial one.
Equatorial F—S—F angle will be 120° but it is 103°]

2. Axial B.A. in $(\text{SF}_4) > \text{CH}_2 = \text{SF}_4$. Why?

	Axial		Equatorial
	179°	178.5°	110°
	103°	170°	97°

Exercise

1. The strongest P–O bond is found in the molecule
 (A) F_3PO (B) Cl_3PO (C) Br_3PO (D) $(\text{CH}_3)_3\text{PO}$
Ans. (A)

BACK BONDING

The one sided sharing of electron pair present in the outer orbital of an atom with the empty orbital present in the adjacent atom. It leads to the formation of a π coordinate bond.

Condition for back bonding

The donor atom must have localized donatable electron pair. In general these are later half , second period P - block elements (F, O, N and C). The acceptor atom must have low energy empty orbital which generally are np or nd orbitals. Small and similar sized orbitals favour overlap.

Effects of back bonding

1. It always leads to an increase in bond order between the participating atoms.
2. It always leads to an increase in bond strength between participating atoms.
3. It always leads to a decrease in bond length between participating atoms.
4. It decreases the lewis acid character of the acceptor atom as the low energy empty orbital is now filled and not available for accepting the electron from a lewis base. This is evident in case of boron halides. Boron and fluorine are the members of the same period and hence have orbitals having similar size and energy. This allows fluorine to effectively donate the electrons from its filled p orbitals to the empty unhybridized orbital of boron. This makes BF_3 much weaker lewis acid than BCl_3 which in turn is a weaker lewis acid than BBr_3 .

Structural formula of boron trifluoride, BF_3 , showing ? bonding involving filled fluorine 2p orbitals (formally lone pairs) overlapping with the empty 2p orbital on boron and donating electron density to relieve boron's electron deficiency.

This can easily be explained by the increase in size of the halogen atom, its orbitals and decreased capacity to donate electron towards back-bonding as we move down the group. The Lewis acidity scale of boron trihalides BX_3 ($\text{X}=\text{F, Cl, Br, I}$) and character of the boron-halogen bonds have been studied by means of DV-Xm approach. Present results show that the acid strength of boron trihalides increases in the order $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$, in excellent agreement with experiments.

5. It decreases the lewis base character of the donor atom as now its electrons are not free for donation. This is evident in comparison of the lewis base character of $\text{N}(\text{SiH}_3)_3$ and $\text{N}(\text{CH}_3)_3$. In trisilyl amine the lone pair of nitrogen is involved in back bonding with empty 3d orbital of silicon. Hence it is not available for donation. This makes it much weaker base in comparison to trimethyl amine. (Another comparison could be pyrol and pyridine, aniline and methyl amine)
6. It either increases the bond angle or the bond angle remains the same but never decreases. The bond angle increases when the donation is from the peripheral atom towards the central atom as in case of PF_3 . In it the electron pair from the filled p orbital of fluorine moves into the empty 3d orbital of phosphorus. This increases the electron density in the phosphorus fluorine bond and

increases the bond pair - bond pair repulsion. This makes the F-P-F bond angle in PF₃ (98°) greater than H-P-H bond in PH₃ (94°). The bond angle increases even when the donation is from the central atom towards the peripheral atom as in the case of trisilyl amine, (SiH₃)₃N. Nitrogen donates the lone pair in its p orbital to the empty d orbital of Si. This decrease the electron density on nitrogen and with that the lone pair - bond pair repulsion also decreases. The hybridization of nitrogen changes from sp³ to sp². And so the bond angle becomes almost 120°. Same is the case with (SiH₃)₂O (144°) compared to (CH₃)₂O (110°). CH₃-NCS is bent whereas SiH₃-NCS is linear.

In some cases like BF_3 , there is no change in the bond angle due to the back bonding.

- Complex formation tendency of certain ligands which have back bonding in them is affected. $(CH_3)_2O$ readily forms complex with BF_3 but $(SiH_3)_2O$ does not as here the lone pair of O is utilized in back bonding with Si.
 - $HCCl_3$ is more acidic than HCF_3 . Although F is more electronegative than Cl and hence should make the negative charge more stable by dispersing it through inductive effect. But the observation suggests that the conjugate of $CHCl_3$, $-CCl_3$ is more stable than $-CF_3$. This can be explained by considering the transfer of electron pair from carbon to empty d orbital of Cl leading to a better dispersal of negative charge.
 - Carbenes: Dichloro and difluoro carbenes (CCl_2 and CF_2) due to back bonding from the side of halogen prefer to exist in the singlet state. Whereas for CH_2 , the triplet is the more stable state.

Illustration

Ans. (B)

Sol. Due to the presence of effective $\text{p}\pi - \text{p}\pi$ backbonding in BF_3 ; it is less acidic than BCl_3 .

Exercise

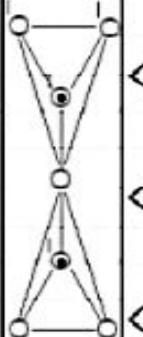
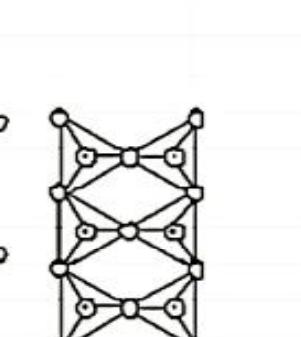
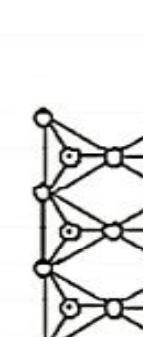
- 1.** Boron forms BX_3 type of halides. The correct decreasing order of Lewis-acid strength of these halides is
 (A) $BF_3 > BCl_3 > BBr_3 > BI_3$ (B) $BI_3 > BBr_3 > BCl_3 > BF_3$
 (C) $BF_3 > BI_3 > BCl_3 > BBr_3$ (D) $BF_3 > BCl_3 > BI_3 > BBr_3$

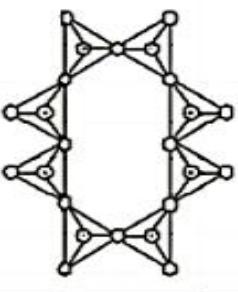
Ans. (B)

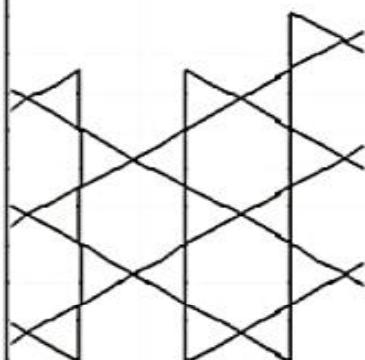
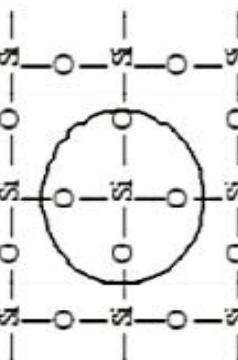
SILICATES

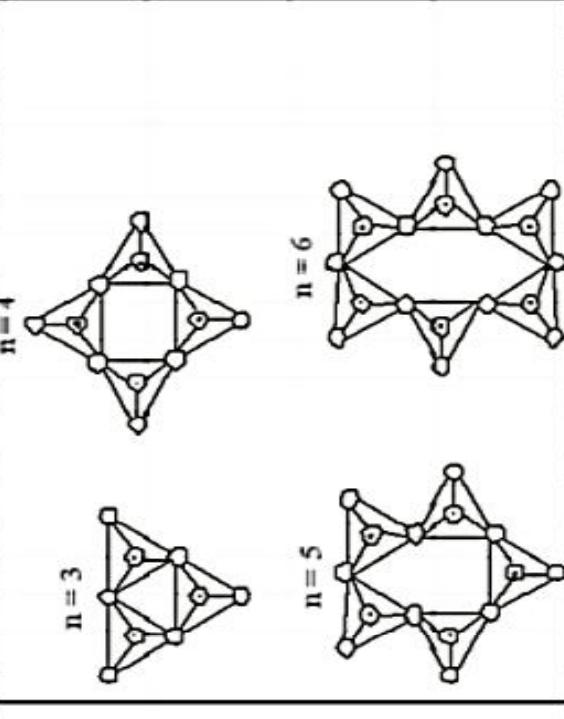
The way in which the $(\text{SiO}_4)^{4-}$ tetrahedral units are linked together provides a convenient classification of the many silicate minerals.

Classification of Silicates

Types of Silicates	No. of 'O' Shared Per molecule	General Formula	General Formula If Restricted	Structure
Ortho silicate [Neso silicate]	Zero	$[\text{SiO}_4]^{4-}$	$[\text{SiO}_4]^{4-}$	
Pyro silicate [Soro silicate]	One	$[\text{Si}_2\text{O}_7]^{6-}$	$[\text{Si}_2\text{O}_7]^{6-}$	
Single chain Silicate Pyroxene	Two 'O'	$[\text{SiO}_3]_n^{2n-} \dots$	$[(\text{SiO}_3)_n]^{2n-} + \text{O}^{2-}$	
Double chain Amphibole	$2 > \text{'O}' \leq 3$	$\text{SiO}_{4-1/2n}^{4+n}$ $n = \text{no. of 'O' shared per tetrahedron}$	$[\text{SiO}_{4-1/2n}^{4+n} + 2\text{O}^{2-}]$	
				
				

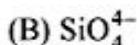
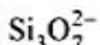
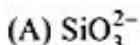
Types of Silicates	No. of 'O' Shared Per molecule	General Formula	General Formula If Restricted	Structure
	$\text{if } n=3$ $[\text{Si}_2\text{O}_5]_n^{2n-}$ $\text{if } n=7/3,$ $[\text{Si}_6\text{O}_{17}]_n^{10n-}$	$[(\text{Si}_2\text{O}_5)_n]^{2n-} + 2\text{O}^{2-}$	$[(\text{Si}_6\text{O}_{11})_n]^{6n-} + 2\text{O}^{2-}$	
		$n=9/4$ $[\text{Si}_6\text{O}_{23}]_n^{-14n}$	$[(\text{Si}_6\text{O}_{23})_n]^{-14n} + 2\text{O}^{2-}$	
		$n=11$ $[\text{Si}_{10}\text{O}_{29}]_n^{-18n}$	$[(\text{Si}_{10}\text{O}_{29})_n]^{-18n} + 2\text{O}^{2-}$	

Types of Silicates	No. of 'O' Shared Per molecule	General Formula	General Formula if Restricted	Structure
2-D sheet silicate <i>[Phyllosilicate]</i>	3 'O'	$n^1 [Si_2O_5]_n^{2n^-} \dots$	$n^1 [Si_2O_5]_n^{2n^- + O^{2-}}$ where $n = [Si_2O_5]^{2-}$ n^1 = no. of layers	
3-D Sheet silicate	4 'O'	$(SiO_2)_n$	$(SiO_2)_n$	

Types of Silicates	No. of 'O' Shared Per molecule	General Formula	General Formula if Restricted	Structure
Ring Silicate Or cyclic silicate	2 'O'	$[\text{SiO}_3]_n^{2n-}$	$[\text{SiO}_3]_n^{2n-}$	

Illustration

1. The following pictures represent various silicate anions. Their formulae are respectively:



Ans. (B)

Sol. (I) Orthosilicate is SiO_4^{4-}

(II) Ist & last are chain terminating unit. So the molecular formula is
 $\text{SiO}_{3.5}^{3-} + \text{SiO}_3^{2-} + \text{SiO}_{3.5}^{3-}$

2. $\text{Si}_2\text{O}_7^{6-}$ anion is obtained when

- (A) no oxygen of a SiO_4 tetrahedron is shared with another SiO_4 tetrahedron.
 (B) one oxygen of a SiO_4 tetrahedron is shared with another SiO_4 tetrahedron.
 (C) two oxygen of a SiO_4 tetrahedron are shared with another SiO_4 tetrahedron.
 (D) three or all four oxygens of a tetrahedron are shared with other SiO_4 tetrahedron.

Ans. (B)

Sol. Pyrosilicate \rightarrow no. of oxygen shared in each tetrahedron is 1.

Exercise

1. $\text{Si}_3\text{O}_9^{6-}$ (having three tetrahedral) is represented as:



Ans. (B)

2. The silicate anion in the mineral kinoite is a chain of three SiO_4 tetrahedra that share corners with adjacent tetrahedra. The mineral also contains Ca^{2+} ions, Cu^{2+} ions, and water molecules in a 1:1:1 ratio mineral is represented as:

- (A) $\text{CaCuSi}_3\text{O}_{10}\cdot\text{H}_2\text{O}$ (B) $\text{CaCuSi}_3\text{O}_{10}\cdot2\text{H}_2\text{O}$ (C) $\text{Ca}_2\text{Cu}_2\text{Si}_3\text{O}_{10}\cdot2\text{H}_2\text{O}$ (D) none of these

Ans. (C)

BRIDGE BOND

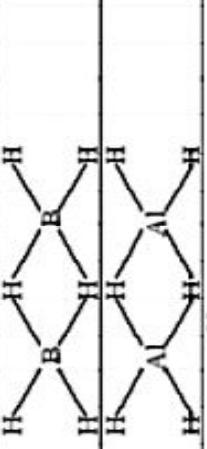
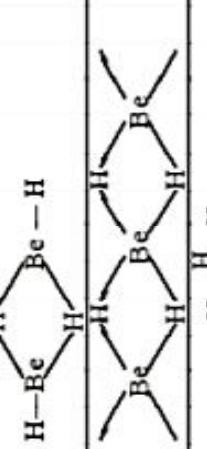
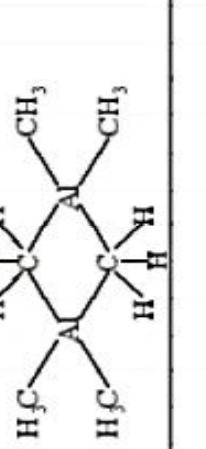
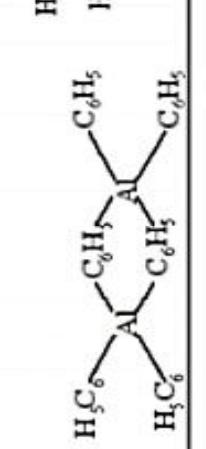
When a species seems to be exceeding its valence in a bid to join two species the bond is termed as the bridge bond.

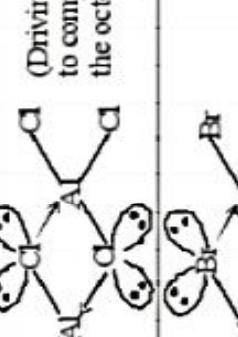
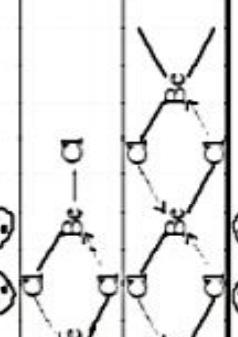
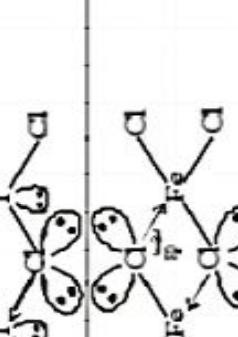
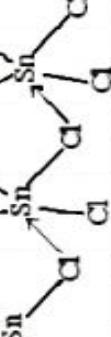
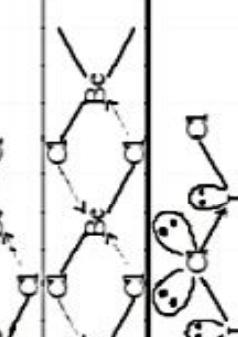
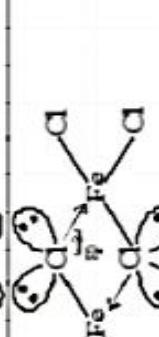
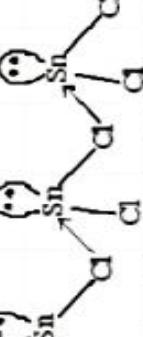
The main reason for the formation of the bridge bond is to complete the octet. This is the main but not the only reason. There could be species which have octet already exceeded and still they try to gain more electrons by the formation of the bridge bond. It seems that the reason is just the availability of low energy empty orbitals.

The first preference of every species is to satisfy the valency within the molecule. That is the back bonding. The bridge bond is formed when a species cannot satisfy the electron deficiency by back bonding.

The bridge bonds are of two types:

1. The electron deficient bridge bond. It is formed by hydrogen, alkyl or boron.
2. Coordinate bridge bonds. These are formed by the species which have an extra donatable electron pair in their valence shell. These are generally formed by halogens.

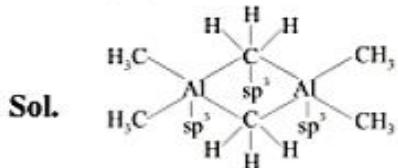
Compound	Bridge	Hybridisation	Planar / Non Planar	Structure
B_2H_6	$3\text{e}^- - 2\text{e}^-$	$\text{sp}^3-\text{s} \cdot \text{sp}^3$	Non planar	
Al_2H_6	$3\text{e}^- - 2\text{e}^-$	$\text{sp}^3-\text{s} \cdot \text{sp}^3$	Non planar	
Be_2H_4	$3\text{e}^- - 2\text{e}^-$	$\text{sp}^3-\text{s} \cdot \text{sp}^3$	Planar	
$(\text{BeH}_2)_2$	$3\text{e}^- - 2\text{e}^-$	$\text{sp}^3-\text{s} \cdot \text{sp}^3$	Non Planar	
$\text{Al}_2(\text{CH}_3)_6$	$3\text{e}^- - 2\text{e}^-$	$\text{sp}^3-\text{s} \cdot \text{sp}^3 - \text{sp}^3$	Non planar	
$\text{Al}_2(\text{C}_6\text{H}_5)_6$	$3\text{e}^- - 2\text{e}^-$	$\text{sp}^3-\text{s} \cdot \text{sp}^3$	Non planar	

<i>Compound</i>	<i>Bridge</i>	<i>Hybridisation</i>	<i>Planar / Non Planar</i>	<i>Structure</i>
Al_2Cl_6	$3\text{e} - 4\text{e}^-$	$\text{sp}^3 - \text{sp}^3 - \text{sp}^3$	Non Planar	
Al_2Br_6	$3\text{e} - 4\text{e}^-$	$\text{sp}^3 - \text{sp}^3 - \text{sp}^3$	Non Planar	
Be_2Cl_4	$3\text{e} - 4\text{e}^-$	$\text{sp}^2 - \text{sp}^3 - \text{sp}^2$	Planar	
$(\text{BeCl}_2)_n$ (solid)	$3\text{e} - 4\text{e}^-$	$\text{sp}^3 - \text{sp}^3 - \text{sp}^3$	Non Planar	
LiCl_6	$3\text{e} - 4\text{e}^-$	$\text{sp}^3\text{d}^2 - \text{sp}^3 - \text{sp}^3\text{d}^2$	Planar	
Fe_2Cl_6	$3\text{e} - 4\text{e}^-$	Not founded (we don't know)	Planar	
SnCl_6 (solid)	$3\text{e} - 4\text{e}^-$	$\text{sp}^3 - \text{sp}^3 - \text{sp}^3$	Non planar	

Illustration

1. The type of overlap in the bridge bond existing in $\text{Al}_2(\text{CH}_3)_6$ is
 (A) $\text{sp}^3 - \text{sp}^3\text{d} - \text{sp}^3$ (B) $\text{sp}^3 - \text{sp}^2 - \text{sp}^3$ (C) $\text{sp}^3 - \text{s} - \text{sp}^3$ (D) $\text{sp}^3 - \text{sp}^3 - \text{sp}^3$

Ans. (D)

**Exercise**

1. The molecular shapes of diborane is shown:

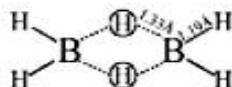
Consider the following statements for diborane:

1. Boron is approximately sp^3 hybridised
2. B–H–B angle is 180°
3. There are two terminal B–H bonds for each boron atom
4. There are only 12 bonding electrons available

Of these statements:

- | | |
|----------------------------|----------------------------|
| (A) 1, 3 and 4 are correct | (B) 1, 2 and 3 are correct |
| (C) 2, 3 and 4 are correct | (D) 1, 2 and 4 are correct |

Ans. (A)

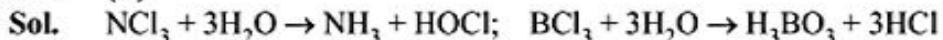
**HYDROLYSIS**

Hydrolysis is a chemical process in which a certain molecule is split into two parts by the addition of a molecule of water. One fragment of the parent molecule gains a hydrogen ion (H^+) from the additional water molecule. The other group collects the remaining hydroxyl group (OH^-).

Illustration

1. Select correct statement about hydrolysis of BCl_3 and NCl_3
- (A) NCl_3 is hydrolysed and gives HOCl but BCl_3 is not hydrolysed.
 - (B) Both NCl_3 and BCl_3 on hydrolysis gives HCl
 - (C) NCl_3 on hydrolysis gives HOCl but BCl_3 gives HCl .
 - (D) Both NCl_3 and BCl_3 on hydrolysis gives HOCl .

Ans. (C)

**Exercise**

1. Which of the following halides cannot be hydrolysed?

- | | | | |
|--------------------|--------------------|----------------------|--------------------|
| (I) TeF_6 | (II) SF_6 | (III) NCl_3 | (IV) NF_3 |
|--------------------|--------------------|----------------------|--------------------|

Choose the correct code :

- | | | | |
|--------------|-----------------|----------------|-------------|
| (A) III & IV | (B) I, II & III | (C) I, II & IV | (D) II & IV |
|--------------|-----------------|----------------|-------------|

Ans. (D)

Compound	Mechanism	Hybridisation in Intermediate	Final Product or by product	No. of Water Molecule Units	Remark (Complete hydro. partial H; Basicity (with respect to central atom)
PCl ₃	[SN ₂] _A & [SN ₂] _{AE}	sp ³ d ² , sp ³ d	H ₃ PO ₄ , HCl	4	Complete H, Basicity = 3
SF ₄	[SN ₂] _A & [SN ₂] _{AE}	sp ³ d ² , sp ³ d	H ₂ SO ₃ , HF	3	Complete H, Basicity = 2
XeF ₄	Disproportionation	--	Xe, O ₂ , XeO ₃	1	--
IF ₇	[SN ₂] _A & [SN ₂] _{AE}	sp ³ d ³	HIO ₄ , 7HF	4	Complete H, Basicity = 1
XeF ₆	[SN ₂] _A & [SN ₂] _{AE}	sp ³ d ³ , sp ³ d ²	XeO ₃ , 6HF	3	Complete H
IF ₅	[SN ₂] _A & [SN ₂] _{AE}	sp ³ d ³ , sp ³ d ²	HIO ₃ , 5HF	3	Complete H, Basicity = 1
ICl	[SN ₂] _A	sp ³ d	IOH, HCl	1	Complete H, Basicity = 1
ICl ₃	[SN ₂] _A & [SN ₂] _{AE}	sp ³ d ² , sp ³ d	HIO ₂ , 3HCl	2	Complete H, Basicity = 1
SO ₂ Cl ₂	[SN ₂] _{AE}	sp ³ d	H ₂ SO ₄ , 2HCl	2	Complete H, Basicity = 2
SOCl ₂	[SN ₂] _{AE}	sp ³ d	H ₂ SO ₃ , 2HCl	2	Complete H, Basicity = 2
POCl ₃	[SN ₂] _{AE}	sp ³ d	H ₃ PO ₄ , 3HCl	3	Complete H, Basicity = 3
SeF ₄	[SN ₂] _A & [SN ₂] _{AE}	sp ³ d ² , sp ³ d	H ₃ SeO ₃ , 4HF	3	Complete H, Basicity = 2
TeF ₆	[SN ₂] _A	sp ³ d ³	Te(OH) ₆ , 6HF	6	Complete H, Basicity = 2
PCl ₃	[SN ₂] _A	sp ³ d	P(OH) ₃ , 3HCl	3	Complete H, Basicity = 2

Compound	Mechanism	Hybridisation in Intermediate	Final Product or by product	No of Water Molecule Utilised	Remark (Complete hydro. partial H; Basicity (with respect to central atom)
BCl_3	$[\text{SN}_2]_A$	sp^3	$\text{B(OH)}_3, 3\text{HCl}$ $[\text{B(OH)}_4^-]$ in basic	3	Complete H, Basicity = 3
BeCl_2	$[\text{SN}_2]_A$	sp^2	$\text{Be(OH)}_2, 2\text{HCl}$	2	Complete H, Basicity = 2
NCl_3	$[\text{SN}_2]_A$	$\text{Cl} \rightarrow \text{sp}^3\text{d}$	$3\text{HOCl}, \text{NH}_3$	3	Complete H
XeF_2	Redox	—	$\text{Xe}, \text{HF}, \frac{1}{2}\text{O}_2$	1	—
$\text{H}_2\text{S}_2\text{O}_8$ (Marshall's acid)	$[\text{SN}_2]_{AE}$	sp^3d	$\text{H}_2\text{SO}_4, \text{H}_2\text{O}_2$	2	Complete H, Basicity = 2
P_4O_{10}	$[\text{SN}_2]_{AE}$	sp^3d	H_3PO_4	6	Complete H, Basicity = 3
$\text{H}_2\text{S}_2\text{O}_7$	$[\text{SN}_2]_{AE}$	sp^3d	$2\text{H}_2\text{SO}_4$	1	Complete H, Basicity = 2
P_4O_6	$[\text{SN}_2]_A$	sp^3d	H_2SO_4	6	Complete H, Basicity = 2
$\text{H}_4\text{P}_2\text{O}_6$	$[\text{SN}_2]_{AE}$	sp^3d	$\text{H}_3\text{PO}_4, \text{H}_2\text{O}_2$	2	Complete H, Basicity = 3
H_2SO_5	$[\text{SN}_2]_{AE}$	sp^3d	$\text{H}_2\text{SO}_4, \text{H}_2\text{O}_2$	1	Complete H, Basicity = 2
SiF_4	$[\text{SN}_2]_A$ lewis acid-base reaction	sp^3d	$\text{Si(OH)}_4, 2\text{H}_2[\text{SiF}_6]$	4	Partial H, Basicity = 4
BF_3	$[\text{SN}_2]_A$ lewis acid-base reaction	sp^3	$\text{B(OH)}_3, 3\text{H}[\text{BF}_4]$	3	Partial H, Basicity = 1

MOLECULAR ORBITAL THEORY

VBT (Valence bond theory) was unable to explain eg. Paramagnetic nature of O₂ 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:

- (i) Molecular orbital formed by overlapping of atomic orbital of same energy
- (ii) Number of molecular orbital formed = number of atomic orbital involved in overlapping
- (iii) Half of the molecular orbital have lower energy are called Bonding molecular orbital.
- (iv) Half are of higher energy is termed as Antibonding molecular orbital
- (v) Electronic configuration in various molecular orbital are governed by same three rules.
 - (a) Aufbau's rule
 - (b) Hund's rule
 - (c) Pauli's exclusion principle

Comparison of Bonding molecular orbital & Antibonding molecular orbital :

Bonding molecular orbital (BMO)	Antibonding Molecular orbital (ABMO)
Bonding MO is the result of the linear combination of AO when their wave function are added $\Psi_b = \Psi_A + \Psi_B$ Generally it does not have node. Charge density increase between two nuclei resulting attraction between two atoms Energy of BMO is less, hence stable	ABMO is result of linear combination of AO when their wave function are subtracted $\Psi_a = \Psi_A - \Psi_B$ It always have a node between two nuclei of bonded atom. Charge density decrease in between two nuclei, leads to repulsion between two atoms. Energy of ABMO is high, hence unstable

Notation of molecular orbitals:

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

For bonding molecular orbital- σ, π, δ etc.

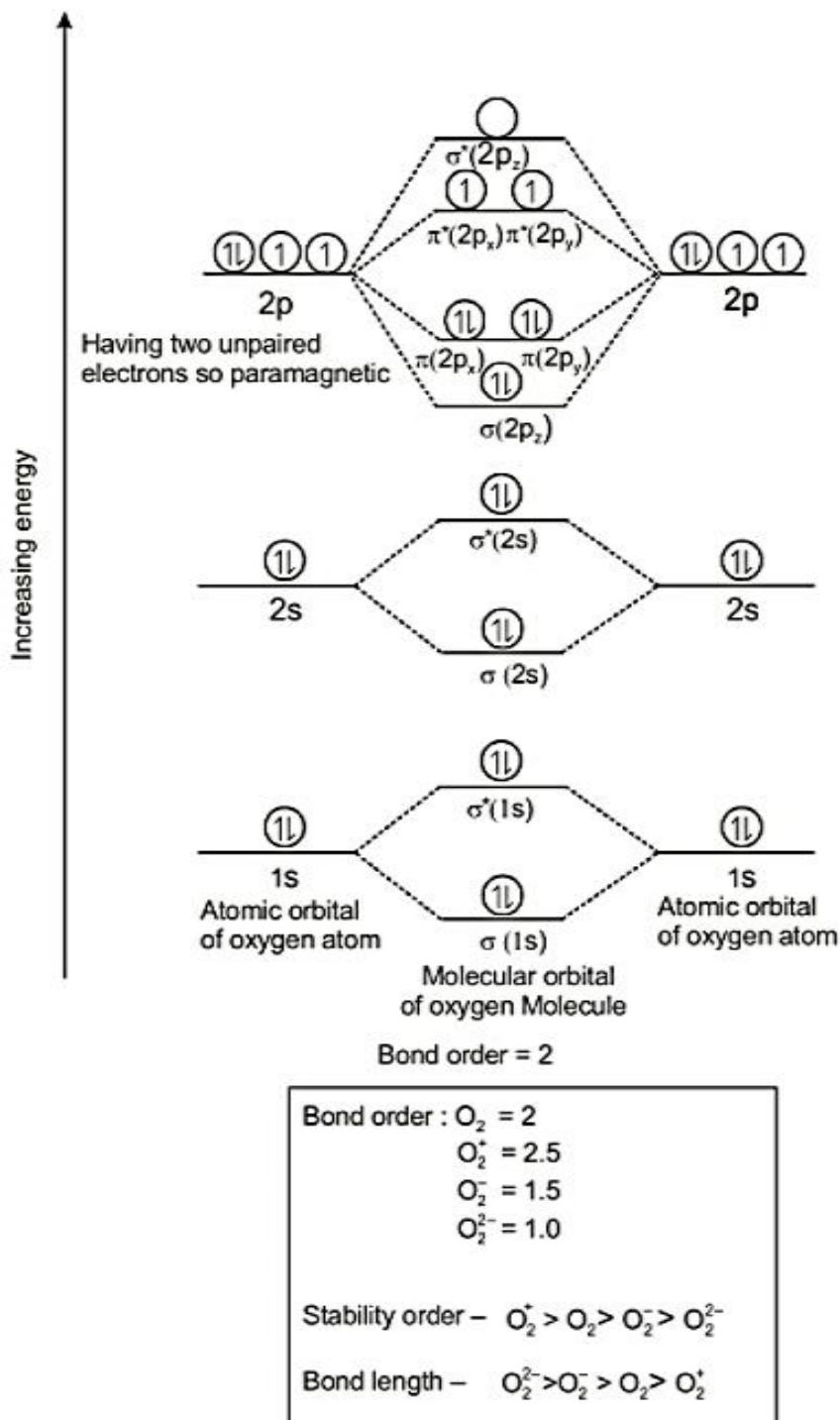
For antibonding molecular orbital- $\sigma^*, \pi^*, \delta^*$ etc.
are used for different shapes of electron cloud.

Energy Level Diagram of molecular orbital :

On the basis of Aufbau's rule - increasing order of energies of various molecular orbitals is-
 $\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \sigma(2p_z) < \pi(2p_x) = \pi(2p_y) < \pi^*(2p_x) = \pi^*(2p_y) < \sigma^*(2p_z)$

Energy level diagram for homonuclear diatomic molecules like, O₂, F₂, Ne₂

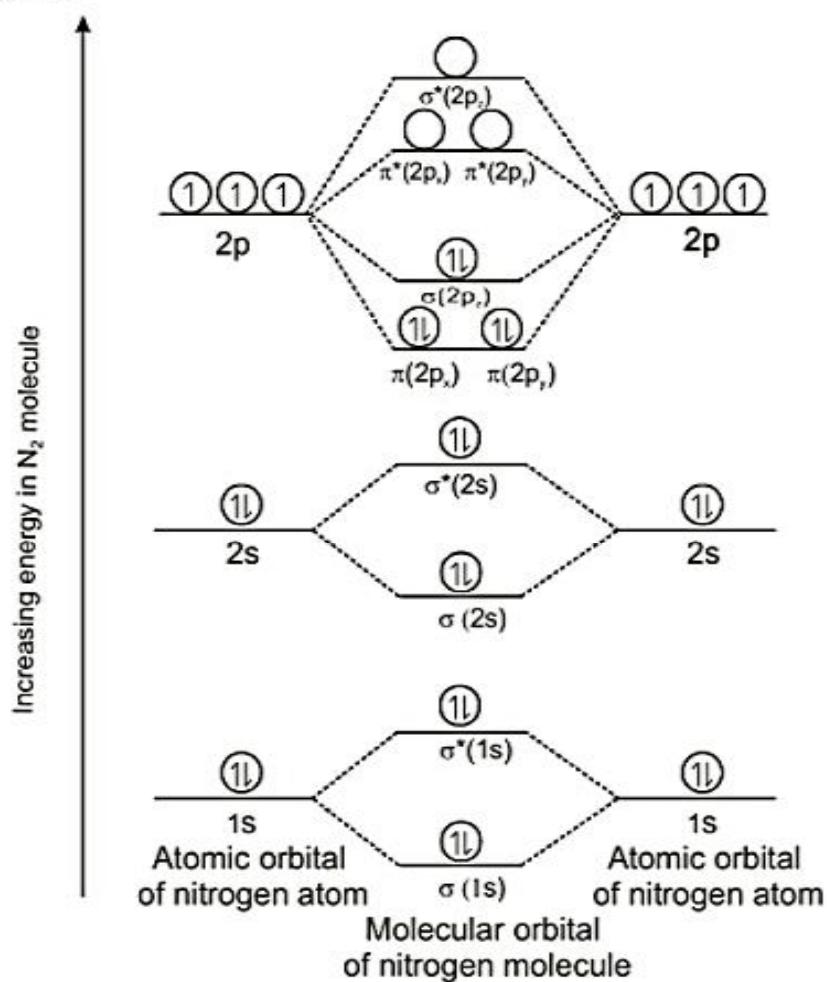
For O₂ molecule-



Energy level diagram for B_2 , C_2 and N_2 molecules -

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

For N_2 molecule



Cause of exceptional behavior of molecular orbital in B_2 , C_2 and N_2 :

Energy of 2s and 2p atomic orbitals lie fairly close

Due to small energy difference between 2s and 2p_z orbitals, the interaction between them is quite large.

This results in loss of energy by σ(2s) and σ*(2s) and thus σ(2s) and σ*(2s) becomes more stable at the cost of σ(2p_x) and σ*(2p_x) which gets destabilised (Higher energy).

Electronic configuration of molecules and their related properties :-

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

- Count the number of electrons present in two atoms and then fill in the appropriate energy level diagram according to Aufbau rule.
- The pairing in π(2p_x) and π(2p_y) or π*(2p_x) and π*(2p_y) will take place only when each molecular orbital of identical energy has one electron.
- After writing the molecular orbital diagram following parameter about molecules/ion may be predicted.

(i) Bond order :-

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

N_b – Number of electron in bonding molecular orbital

N_a – Number of electron in antibonding molecular orbital

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

If $N_b > N_a$: then molecule exist

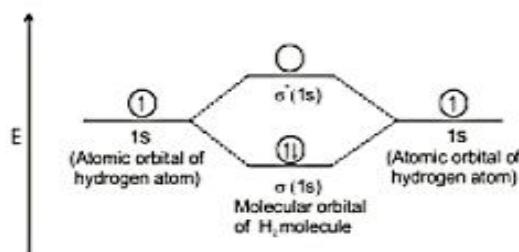
$$\left. \begin{array}{l} N_b < N_a \\ N_b = N_a \end{array} \right\} \text{Molecule does not exist}$$

(iii) Stability of molecules - stability of molecule \propto Bond order of molecule(iv) Dissociation energy - Bond dissociation energy \propto Bond order

(v) Magnetic property -

(a) When electron in Molecular orbital are paired – then the molecule is diamagnetic.

(b) When electron in Molecular orbital are unpaired – the molecule is paramagnetic.

Bonding in molecules :-(i) Hydrogen molecule- Having two H atoms with one electron each (1s)¹

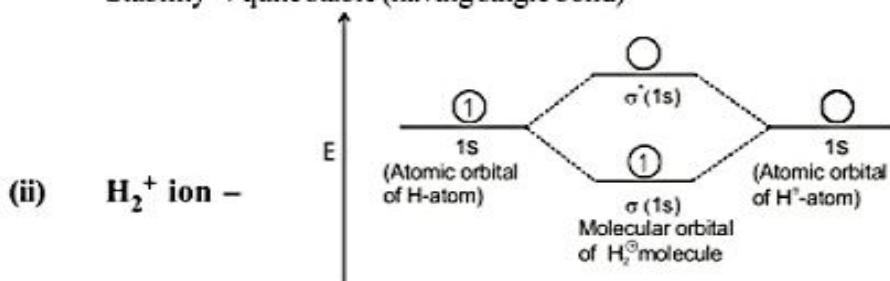
Molecular orbital (M.O.) configuration of $H_2 = \sigma(1s)^2 \sigma^*(1s)^0$

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

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

Having paired electron, so diamagnetic.

Stability → quite stable (having single bond)



Molecular orbital (M.O.) configuration of Configuration of $H_2^+ = \sigma(1s)^1 \sigma^*(1s)^0$

One electron in bonding molecular orbital.

So paramagnetic

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

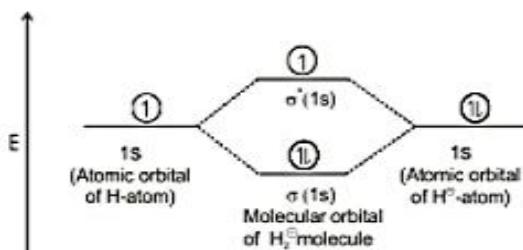
Less stable

(iii) H_2^- anion -

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

Paramagnetic

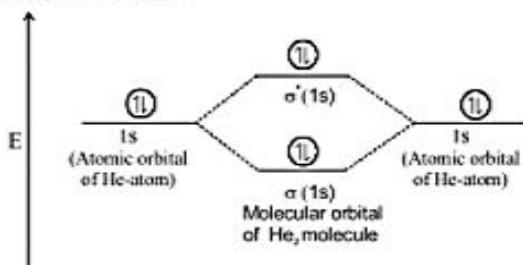
$$\text{Bond order} = \frac{1}{2} [2 - 1] = \frac{1}{2}$$



Stability is less than $[H_2^+]$ because H_2^- contain antibonding molecular orbital (ABMO) electron.

(iv) Helium molecule (He_2): Molecular orbital (M.O.) configuration $\sigma(1s)^2 \sigma^*(1s)^2$

- 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 exist
 - Stability (He_2) Highly unstable molecule



Illustration

1. Comparison of CO & CO^+ bond length on the basis of MOT.

Sol. CO is 14 electron system like N₂, have bond order three, highest energy electron in CO have slightly antibonding character due to energy difference in atomic orbital of C & O . So removing of a electron from CO decreasing in antibonding character so in CO⁺ bonding character increases therfore CO bond length in CO > CO⁺

Exercise

1. During the formation of a molecular orbital from atomic orbitals, probability of electron density is:

- (A) minimum in the nodal plane (B) maximum in the nodal plane
(C) zero in the nodal plane (D) zero on the surface of the lobe

Ans. (C)

- 2.** Pick out the incorrect statement?

- (A) N₂ has greater dissociation energy than N₂⁺ (B) O₂ has lower dissociation energy than O₂⁺
 (C) Bond length in N₂⁺ is less than N₂ (D) Bond length in NO⁺ is less than in NO.

Ans. (C)

3. Which of the following species is paramagnetic?

- (A) NO^- (B) O_2^{2-} (C) CN^- (D) CO

Ans. (A)

4. Bond order of Be_2 is:

- (A) 1 (B) 2 (C) 3 (D) 0

Ans. (D)

Characteristic of Covalent Compound :

- (i) **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

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

- (ii) **Covalent solid :** Those solids in which atoms are linked together by covalent bonds, forms infinite three dimensional giant structure. e.g. Diamond, Graphite, AfN , SiC , SiO_2 etc.

Molecular solid : Discrete (separate) molecules are formed by covalent bonds and then the molecules associated due to intermolecular force of attraction. (Vander-waal's force)

eg. Solid I_2 , dry ice (Solid CO_2) etc.

- (iii) **Conductivity :** Mostly covalent compounds are bad conductor of electricity. But few polar covalent compounds due to self ionisation can conduct electricity.e.g. H_2O , liq. NH_3 etc.



Free ions are formed which can conduct electricity.

Exceptions : Graphite, HCl in water.

- (iv) **Solubility :** Non polar compound are soluble in non polar solvents. Non polar compounds forms Vander-waal's bond with non polar solvent molecules.
- (v) **Isomerism :** Covalent bond is rigid and directional, so it shows isomerism.
 eg. Organic compounds.
- (vi) **Reaction :** Reaction between covalent compounds are slow. Because it involves breaking of old bonds and formation of new bonds

ELECTROVALENT OR IONIC BOND

- (i) 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**.

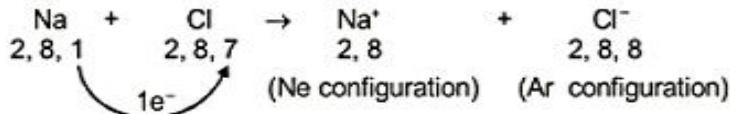
(ii) Electro positive atom loses electron (group IA to IIIA)

(iii) Electro negative atom gains electron (group VA to VIIA)

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

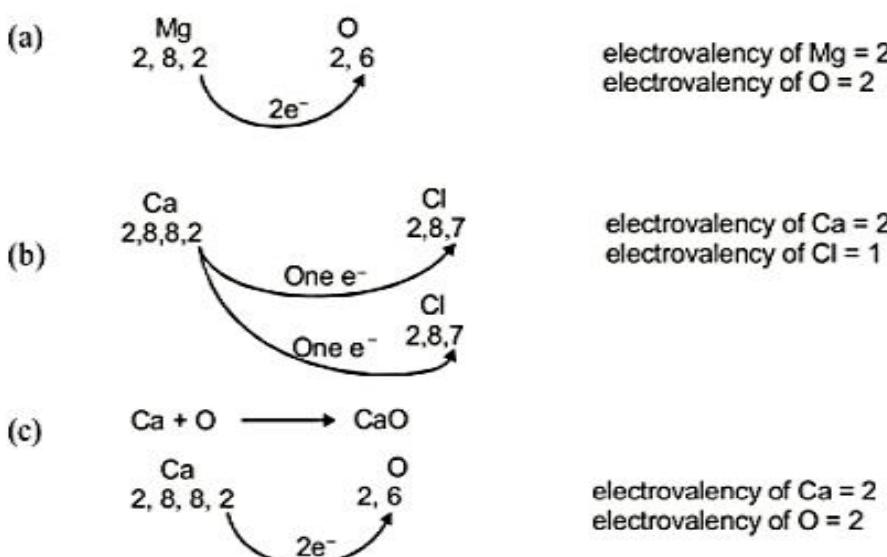
Electronegativity difference \propto nature of ionic bond.

Example IA and VIIA group elements form maximum ionic compound.



- (v) More the distance between two elements in periodic table more will be ionic character of bond.
 (vi) Total number of electron lose or gained is called electrovalency.

Example –



- (vii) The force of attraction is equal in all direction, so ionic bond is non-directional.
 (viii) Ionic compound do not have molecular formula. It has only empirical formula. e.g. NaCl is the empirical formula of sodium chloride.

Conditions for Forming Ionic Bonds :

Formation of Ionic bond depends upon these three factors :

(a) Ionization energy :

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

Lesser Ionisation energy → Greater tendency to form cation.

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

(b) Electron affinity

Amount of energy released when an electron is added to an isolated gaseous atom to form negative ion (i.e. : anion).

Higher electron affinity → Greater tendency to form anion

e.g. $\text{Cl}^- > \text{F}^- > \text{Br}^- > \text{I}^-$
 $\text{F}^- > \text{O}^{-2} > \text{N}^{-3}$

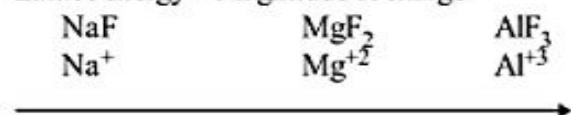
(c) Lattice energy - Amount of energy released when one mole of crystal lattice is formed. Higher lattice energy → Greater will be the stability or strength of ionic compound.

Factors affecting lattice energy :

(i) Magnitude of charge :

Lattice energy (U) $\propto z^+ z^-$ (Ionic charges of cation and anion)

Lattice energy \propto Magnitude of charge



- Lattice energy increases
- Size of cation decreases.

(ii) Size of Cation :

$$\text{Lattice energy} \propto \frac{1}{r^+ + r^-}$$



- Size of cation increasing
- Size of anion is constant
- Lattice energy decreases

Representation of formula of compounds :

- Write the symbols of the ions side by side in such a way that positive ion is at the left and negative ion is at the right as A⁺B⁻
- Write their electrovalencies in figure at the top of each symbol as A^xB^y
- Now apply criss cross rule as $A\overset{x}{\cancel{\times}}\cancel{B}^y$, i.e formula A_yB_x.

Examples : Calcium chloride $Ca\overset{2}{\cancel{\times}}\cancel{Cl}^1 = CaCl_2$

Inert Pair Configuration

The heavy elements of IIIA, IV A and V A groups form cations having charge equal to group number and two less than group number, e.g. Ti⁺³, In⁺¹, Sn⁺², Pb⁺². In these elements due to more penetration power of s orbitals, the atom generally does not lose e⁻ present in ns orbital, so only np electrons are lost by the atom. This effect is called "inert pair effect".

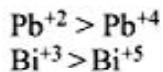
Illustration

- Among the following, the element which show inert-pair effect are :

- | | | | |
|------------|-------------|-------------|-----------------|
| (I) Bi | (II) Sn | (III) Pb | (IV) C |
| (A) I & II | (B) I & III | (C) II & IV | (D) I, II & III |

Ans. (B)

Sol. In a behaviour p-block elements lower oxidation becomes more & more stable due to the inert pair effect. So the stability of



Exercise

- Which of following stability order is incorrect due to inert pair effect.

- | | | | |
|--|---|---|---|
| (A) Hg ⁰ > Hg ²⁺ | (B) Bi ³⁺ > Bi ⁵⁺ | (C) Pb ²⁺ > Pb ⁴⁺ | (D) Fe ²⁺ < Fe ³⁺ |
|--|---|---|---|

Ans. (D)

POLARIZATION

(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 charged nucleus of anion.
- Due to this combined effect, cloud of anion is bulged or elongated towards the cation. This is called distortion, deformation or Polarization of the anion by the cation and anion is Polarized.

Polarization Power :

The ability of cation to polarise a nearby anion is called Polarization power of cation.



Polarizability :

- Ability of anion to get polarised by the cation.
- Polarization of anion causes some sharing of electron between the ions so ionic bond acquires certain covalent character.
- Polarisation \propto Covalent-character
- Magnitude of polarization depends upon a number of factors, suggested by Fajan and are known as Fajan's rule.

FAJAN'S RULE : (FACTORS AFFECTING POLARIZATION)

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

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

In a group -	BeCl_2	↓ - Size of cation increases - Covalent character decreases - Ionic character increases
	MgCl_2	
	CaCl_2	
	SrCl_2	
	BaCl_2	

Greatest polarizing power of Be^{2+} , shows its maximum covalent character in BeCl_2 .

In a period -

Na^+ , Mg^{+2} , Al^{+3} , Si^{+4}	$\xrightarrow{\hspace{1cm}}$
	- Size of cation decreases
	- Covalent character increases

- (b) **Size of anion**

If the size of the anion increases for a given cation, the covalent character increases
 $\text{Polarization} \propto$ size of anion.

CaF_2	↓ - Size of anion increases - Covalent character increases - Ionic character decreases
CaCl_2	
CaBr_2	
CaI_2	

(c) Charge on cation and anion :

\Rightarrow Polarisation \propto charge on cation / anion

(I) Charge on cation \propto Polarisation (covalent character)

eg. NaCl	MgCl ₂	AlCl ₃	SiCl ₄
Na ⁺	Mg ⁺⁺	Al ⁺⁺⁺	Si ⁺⁺⁺⁺

→

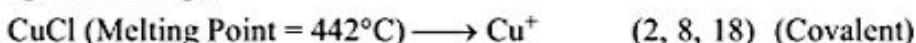
- Charge on cation increases

- Covalent character increases

- Ionic character decreases (Melting Point decreases)

$$\text{Charge on anion} \propto \text{polarisation} \propto \text{covalent nature} \propto \frac{1}{\text{Melting Point}}.$$

(d) Electronic configuration of cation : If the size of cations in different compounds are same than that of cation having inert gas configuration, polarization capacity of cation having pseudo inert gas configuration is high.



Cu⁺ and Na⁺ both the cation (Pseudo & inert) have same charge and size but polarizing power of Cu⁺ is more than Na⁺ because Z_{eff} of ns²p⁶ (inert) < Z_{eff} of ns²p⁶d¹⁰ (pseudo).



So, CuCl has more covalent character than NaCl.

Illustration

1. Amongst LiCl, RbCl, BeCl₂ and MgCl₂, the compounds with the greatest and the least ionic character, respectively are :

(A) LiCl and RbCl (B) RbCl and BeCl₂ (C) RbCl and MgCl₂ (D) MgCl₂ and BeCl₂

Sol. (B)

According to the fajans rule

$$\text{Covalent character} \propto \text{polarisation power} \propto \frac{1}{\text{size of cation}}$$

$$\propto \text{polarisability} \propto \text{size of anion}$$

Exercise

1. The melting point of AlF₃ is 1291°C and that of SiF₄ is - 77°C (it sublimes) because :
- (A) there is a very large difference in the ionic character of the Al – F and Si – F bonds
 (B) in AlF₃, Al³⁺ interacts very strongly with the neighbouring F⁻ ions to give a three dimensional structure but in SiF₄ no such interaction is possible
 (C) the silicon ion in the tetrahedral SiF₄ is not shielded effectively from the fluoride ions whereas in AlF₃, the Al³⁺ ion is shielded on all sides
 (D) the attractive forces between the SiF₄ molecules are strong whereas those between the AlF₃ molecules are weak

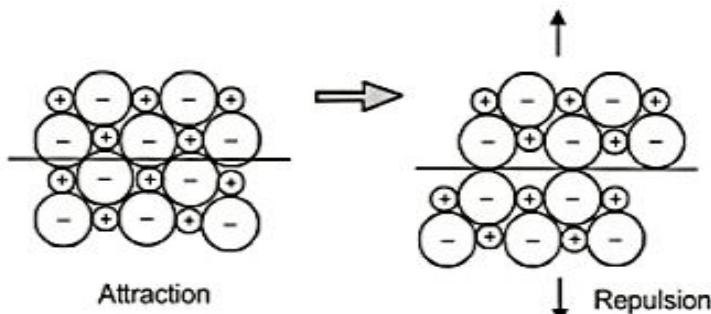
Ans. (B)

Properties of ionic compounds :

(a) Physical state :

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

Brittleness →



(Same charged ions comes nearer. So they repell each other)

(b) Isomorphism :

- (i) Two compounds are said to be isomorphous if they have similar number of electrons i.e. similar electronic configuration of their cation and anion.
- (ii) 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)

(c) Boiling point and melting point :

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

(d) Conductivity :

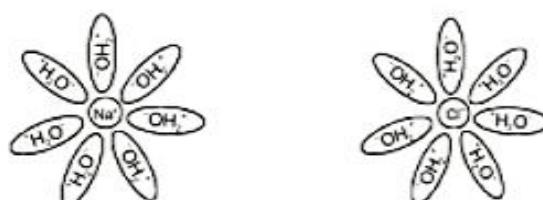
It depends on ionic mobility. In solid state - No free ions - Bad conductor of electricity.

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 water (Polar solvents) Example : NaCl in water

- (i) The Na⁺ ions get associates with negatively charged 'O' of water
- (ii) And Cl⁻ ions associates with positively charged 'H' of water.



- (iii) Thus charge on Na^+ and Cl^- decreases and electrostatics force of attraction also decreases which leads to free ion.
- (iv) The energy released due to interaction between solvent and solute is called solvation energy. If water is used as solvent it is called hydration energy.
- (v) For an ionic compound to be soluble in water
Hydration energy > Lattice energy

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

Hydration energy \propto Solubility.

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

- (vi) Hydration energy mainly depends on the cation radius because the value $\frac{1}{r_-}$ is negligible in comparison to $\frac{1}{r_+}$.
- (vii) Down the group both the lattice energy & hydration energy decreases, if decreases in lattice is greater than hydration energy, solubility increases down the group and vice versa.

Illustration

- The hydration of ionic compounds involves :

(A) Evolution of heat	(B) Weakening of attractive forces
(C) Dissociation into ions	(D) All of these
- Sol.** (D) Theory Based

Exercise

- The correct order of hydration energy is

(A) $\text{Be}^{+2} < \text{Li}^+$	(B) $\text{Na}^+ > \text{Mg}^{+2}$	(C) $\text{Na}^+ < \text{Mg}^{+2}$	(D) $\text{Al}^{+3} < \text{Na}^+$
------------------------------------	------------------------------------	------------------------------------	------------------------------------
- Ans.** (B)

Factor affecting solubility :

(i) Dielectric constant :

The capacity of solvent to neutralise the charge of ionic compounds is called Dielectric constant. It is represented by " ϵ "

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

$(\text{CH}_3\text{OH}, \epsilon = 35)$,	$(\text{Acetone}, \epsilon = 21)$
$(\text{C}_2\text{H}_5\text{OH}, \epsilon = 27)$,	$(\text{Ether}, \epsilon = 4.1)$
$(\text{Benzene}, \epsilon = 2.3)$		

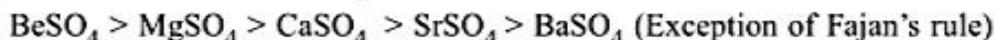
$$\text{H}_2\text{O} > \text{CH}_3\text{OH} > \text{CH}_3\text{CH}_2\text{OH} > \text{CH}_3\text{COCH}_3 > \text{CH}_3\text{OCH}_3 > \text{C}_6\text{H}_6$$
- Ionic compounds are more soluble in the solvents, having high dielectric constant.
- H_2SO_4 and H_2O_2 have high dielectric constant but these are not a good solvent due to oxidising nature.

(ii) Size of Ion :

- (a) Keeping size of cation constant, the lattice energy decreases with the increases of anionic radius. Hence, order of solubility of LiX in water is $\text{LiF} < \text{LiCl} < \text{LiBr} < \text{LiI}$

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

- (b) In LiI covalent nature is more according to Fajan's rule but Hydration Energy > Lattice Energy, therefore Li is more soluble in water.
- (c) Keeping size of anion constant, the hydration energy decreases with the increase of cationic radius. Hence order of solubility of MSO_4 will be –



- (d) If size of cation and anion is very large, solubility decreases from top to bottom.
- (e) Solubility decreases in a period (as ionic nature decreases and covalent nature increases)

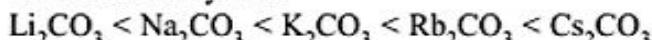
***Illustration***

1. Which of the following is/are incorrect about solubility trend in group I & II?

	Least soluble in water	Most soluble in water
(A) Hydroxides	:	LiOH
(B) Carbonates	:	Cs_2CO_3
(C) Nitrate	:	$\text{Ba}(\text{NO}_3)_2$
(D) Sulphates	:	BaSO_4

Sol. (B)

Correct solubility order

***Exercise***

1. Choose the correct code for the following statements.

- I. The (-)ve value of ΔH for the dissolution of ionic compound is enough to predict the compound is soluble in water at any temperature.
- II. For the alkali metals carbonate, solubility order decreases down the group.
- III. For the alkali metals ozonide, the thermal stability order increases down the group.
- IV. For the alkaline earth metals nitride, the thermal stability order increases down the group.

(A) T T F F (B) T F F T (C) T F T F (D) F T T F

Ans. (C)

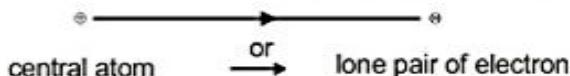
DIPOLE MOMENT**(Ionic Nature in Covalent Bond)**

- (i) Polarity of any polar covalent bond or molecule is measured in terms of dipole moment.
- (ii) For measurement of extent of polarity, Pauling introduced the concept of dipole moment (μ).

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

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

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



- (v) Unit of dipole moment is Debye

$$\begin{aligned} 1 \text{ Debye} &= 1 \times 10^{-18} \text{ esu cm.} \\ &= 3.33 \times 10^{-30} \text{ coulomb metre} \end{aligned}$$

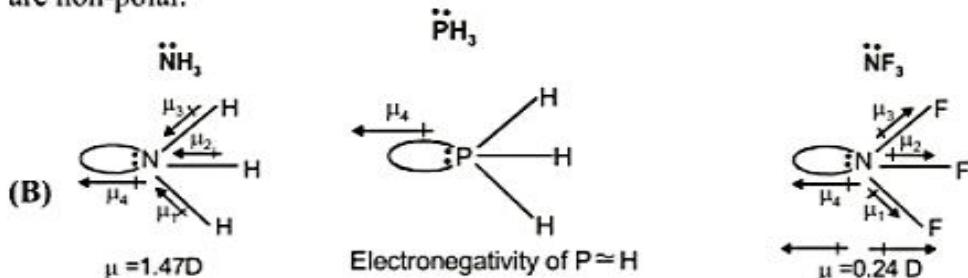
- (vi) In the diatomic molecule dipole moment (μ) depends upon difference of Electronegativity i.e. dipole moment (μ) \propto Electronegativity difference
order of dipole moment (μ) : H-F > H-Cl > H-Br > H-I

dipole moment (μ) = 0 for H-H, F-F, Cl-Cl, Br-Br, O=O

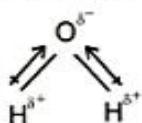
- (vii) For polyatomic molecules dipole moments (μ) depends on the vector sum of dipole moments of all the covalent bonds.
- (viii) For PCl_5 and SF_6 , etc. dipole moment (μ) = 0 due to their regular geometry.
- (ix) Benzene, naphthalene, biphenyl have dipole moments (μ) = 0 due to planar structure.
- (x) If the vector sum is zero, than compound is non-polar compound or symmetrical compound (and it is not essential that individual dipole moments (μ) of every bond should be zero).

Example : (A) 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.



- (xi) Dipole moment of H_2O is 1.85 D which is resultant dipole moment (μ) of two O-H bonds.



dipole moment (μ) of H_2O is more than dipole moment (μ) of H_2S because electronegativity of oxygen is higher than sulphur.

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

Application of dipole moment :

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

If dipole moment (μ) = 0 compound is non polar and symmetrical
eg. CO_2 , BF_3 , CCl_4 , CH_4 , BeF_2 etc.

If dipole moment (μ) $\neq 0$ compound will be polar and unsymmetrical.

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

(ii) **To calculate % ionic character :**

$$\boxed{\% \text{ Ionic character} = \frac{\text{Experimental value of dipole moment}(\mu)}{\text{Theoretical value of dipole moment}(\mu)} \times 100}$$

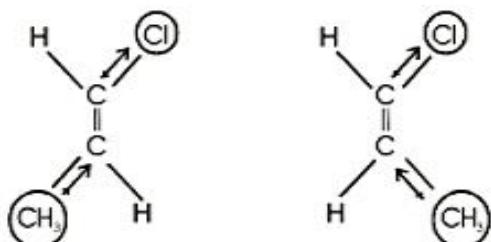
(iii) **To distinguish cis form or trans form:-**

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

eg. -



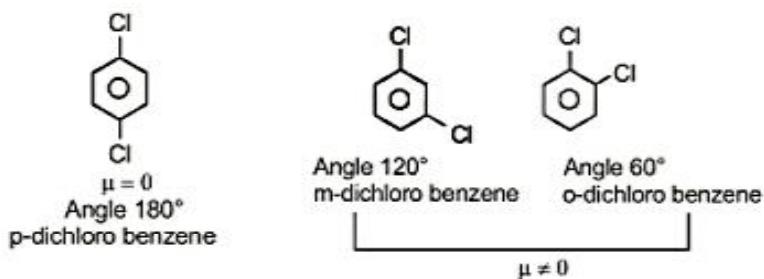
(b) If two groups have opposite inductive effect than trans-isomer will have greater dipole moment-
eg.



(iv) **To locate position of substituents in aromatic compounds.**

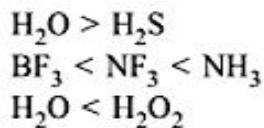
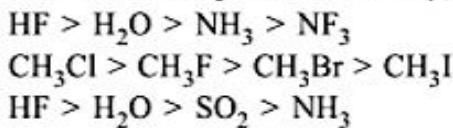
$$\text{Dipole moment } (\mu) \propto \frac{1}{\text{Bond angle}}$$

(a) If same substituents are present in the symmetrical position dipole moment (m) of benzene ring compounds will be zero.



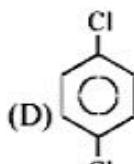
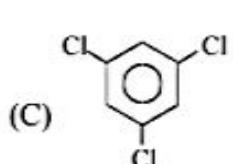
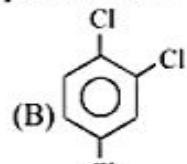
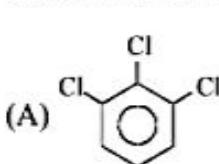
(b) As angle between substituents decrease value of dipole moment (μ) increase

Some important orders of dipole moments (μ)



Illustration

1. Which has maximum dipole moment?



Sol. (A)

Due to the symmetrical structure dipole moment of (C) & (D) are zero & (A) having maximum dipole moment.

Exercise

1. Which of the following has been arranged in order of decreasing dipole moment ?

- (A) $\text{CH}_3\text{Cl} > \text{CH}_3\text{F} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$ (B) $\text{CH}_3\text{F} > \text{CH}_3\text{Cl} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$
 (C) $\text{CH}_3\text{Cl} > \text{CH}_3\text{Br} > \text{CH}_3\text{I} > \text{CH}_3\text{F}$ (D) $\text{CH}_3\text{F} > \text{CH}_3\text{Cl} > \text{CH}_3\text{I} > \text{CH}_3\text{Br}$

Ans. (A)

2. The experimental value of the dipole moment of HCl is 1.03 D . The length of the $H - Cl$ bond is 1.275 \AA . The percentage of ionic character in HCl is :

- (A) 43 (B) 21 (C) 17 (D) 7

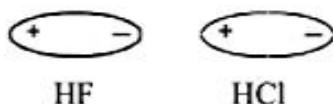
Ans. (C)

VANDER WAAL'S FORCES

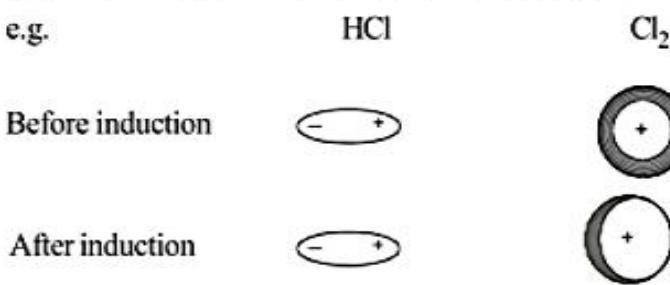
- (a) This type of attractive forces occurs in case of non-polar molecules such as H_2 , O_2 , Cl_2 , CH_4 , CO_2 etc.
- (b) The existence of weak attractive forces among the non-polar molecule was first proposed by dutch scientist J.D. Vander Waal
- (c) Vander waal's force \propto molecular weight
 \propto Atomic weight
 \propto Boiling point

Types of Vander Waal's force :-

- (i) **Dipole-Dipole attraction or Keason force** - It is attraction in between two polar molecules such as HF and HCl

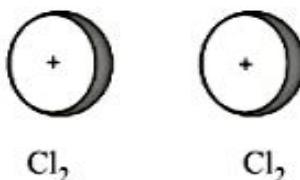


- (ii) **Dipole - Induced dipole attraction or Debye force** : In this case a neutral molecule is induced as a dipole by another dipole as shown in fig.



(iii) Induced dipole - induced dipole attraction or London or dispersion force

between two non polar molecules as in Cl_2 , He etc.



Illustration

Sol. (B)

For ion-dipole interaction

$$E \propto \frac{1}{r^2}$$

2. Select the correct statement :

 - (A) Boiling point of NF_3 is greater than NMe_3 .
 - (B) Greater the dipole moments in molecule, greater will be the dipole-dipole interaction between the molecules.
 - (C) London dispersion force increases with decreasing number of electrons.
 - (D) Boiling point of hydrides of carbon family decreases down the group.

Sol. (B)

Surface area & molecular weight of NMe_3 is greater than NF_3 , so the boiling point of $\text{NMe}_3 > \text{NF}_3$.

Exercise

1. Xe can be liquified due to " _____ " with in molecules :
(A) ion-dipole interaction
(B) dipole - dipole interaction
(C) dipole - induced dipole interaction
(D) instantaneous dipole - induced dipole interaction

Ans. (D)

HYDROGEN BOND

Definition :

- (i) It is an electrostatic attractive force between covalently bonded hydrogen atom of one molecule and an electronegative atom (F, O, N)
 - (ii) It is not formed in ionic compounds
 - (iii) Hydrogen bond forms in polar covalent compounds, (not in non-polar)
 - (iv) It is also known as dipole-dipole attraction or ion-dipole interaction.

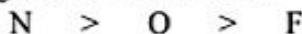


Main condition for Hydrogen bonding :

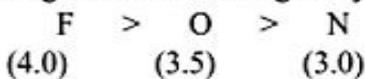
(i) Hydrogen should be covalently bonded with high electronegative element like F, O, N

(ii) Atomic size of electronegative element should be small.

Decreasing order of atomic size is –

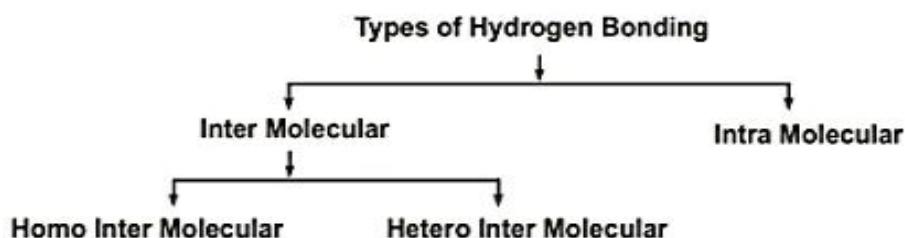


Decreasing order of electronegativity is –



(iii) Strength of Hydrogen bond \propto Electronegativity of element $\propto \frac{1}{\text{atomic size of element}}$

(iv) Hydrogen bonding occurs in HCN, due to ($\text{C} \equiv \text{N}$) triple bond (sp hybridisation), electronegativities of carbon and nitrogen increases.



(A) Intermolecular Hydrogen bond

Hydrogen bond formation between two or more molecules of either the same or different compounds known as **Inter molecular Hydrogen bonding**

These are two types.

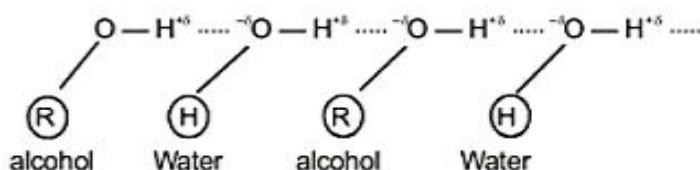
(i) **Homointermolecular** :- Hydrogen bond between molecules of same compounds.

eg.



(ii) **Heterointermolecular** :- Hydrogen bond between molecules of different compounds.

eg. alcohol, water



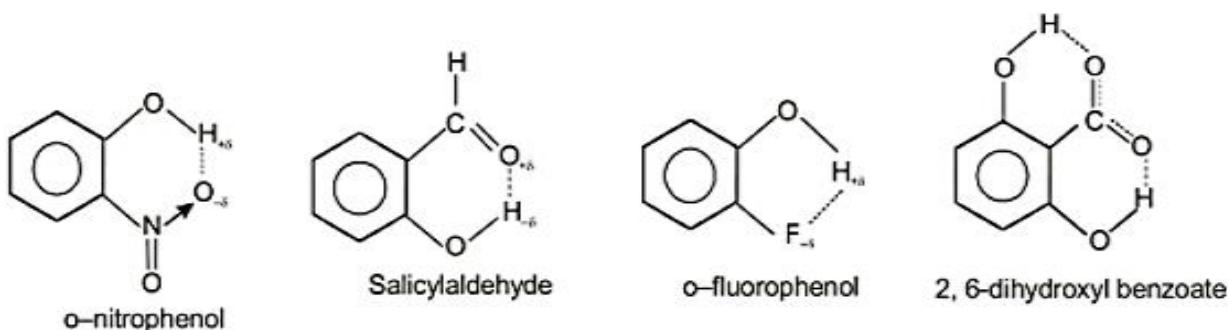
(B) Intra molecular Hydrogen bond :- It takes place within the molecule.

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

(ii) This type of Hydrogen bond is mostly occurred in organic compounds.

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

eg.

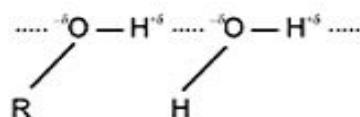


Effect of Hydrogen bond on physical properties :

(i) Solubility :

(A) Inter molecular Hydrogen bonding

- (a) Few organic compounds (Non-polar) are soluble in water (Polar solvent) due to Hydrogen bonding. e.g. alcohol, acetic acid etc. are soluble in water.



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

- (b) Ketone, ether, alkane etc. are insoluble (no Hydrogen bond)

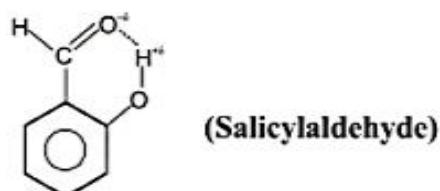
- (c) Solubility order— $\text{CH}_3\text{OCH}_3 < \text{CH}_3\text{OH}$

Primary amine > secondary amine > tertiary amine

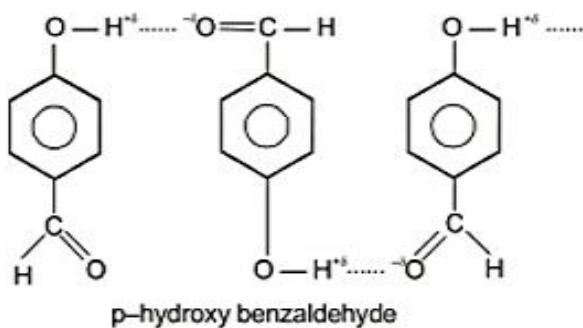
(B) Intra molecular Hydrogen bonding:

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

- (b) It can not form H-bond with water molecule so can not dissolves.



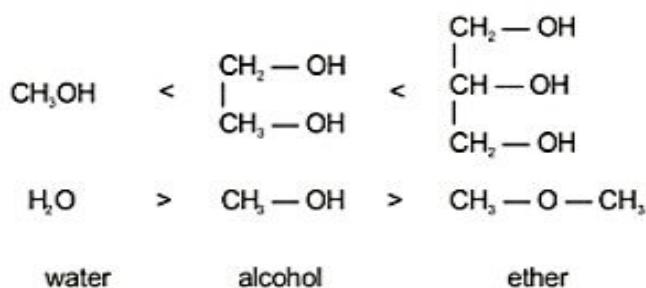
(C) Inter molecular Hydrogen bond



It can form Hydrogen bond with water molecule so it can dissolved

(ii) **Viscosity:**

Hydrogen bond associates molecules together, so viscosity increases

(iii) **Melting point and boiling point**

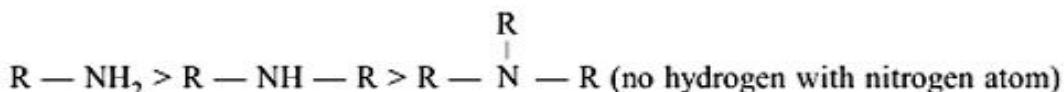
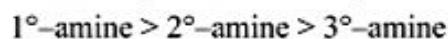
(a) Due to intermolecular Hydrogen bond Melting Point & Boiling Point of compounds increases.



(b) Trihydric alcohol > dihydric alcohol > monohydric alcohol

Monocarboxylic acid form stronger Hydrogen bond than alcohol of comparable molecular weight. Therefore Boiling Point of carboxylic acid is higher than alcohol.

(c) Decreasing order of Melting Point & Boiling Point isomer amines-



(d) Boiling points of VA, VIA, VIIA hydrides decreases on decreasing molecular weights.

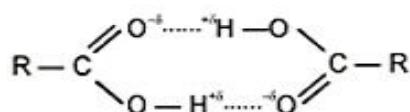
VA	VIA	VIIA	
NH_3	H_2O	HF	boiling point
PH_3	H_2S	HCl	$\text{H}_2\text{O} > \text{TeH}_2 > \text{SeH}_2 > \text{H}_2\text{S}$
AsH_3	SeH_2	HBr	$\text{NH}_3 > \text{SbH}_3 > \text{AsH}_3 > \text{PH}_3$
SbH_3	TeH_2	HI	

(e) But sudden increase in boiling point of NH_3 , H_2O and HF is due to Hydrogen bonding



Intramolecular Hydrogen bonding gives rise to ring formation, so the force of attraction among these molecules are vander waal's force. So, Melting Point and Boiling Point are low.

(iv) **Molecular weight :** Molecular weight of CH_3COOH is double of its molecular formula, due to dimer formation occur by Hydrogen bonding

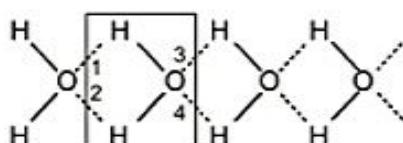


(v) **Physical state :** H_2O is liquid while H_2S is gas.

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

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

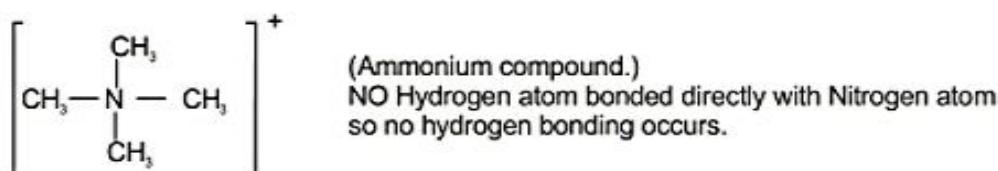
H_2O becomes solid (Ice) due to four hydrogen bond among water molecule are formed in tetrahedral manner.



(vi) Base strength

CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$, $(\text{CH}_3)_3\text{N}$, form Hydrogen bond with water. So, less hydrolysis i.e. it gives OH^- ions.

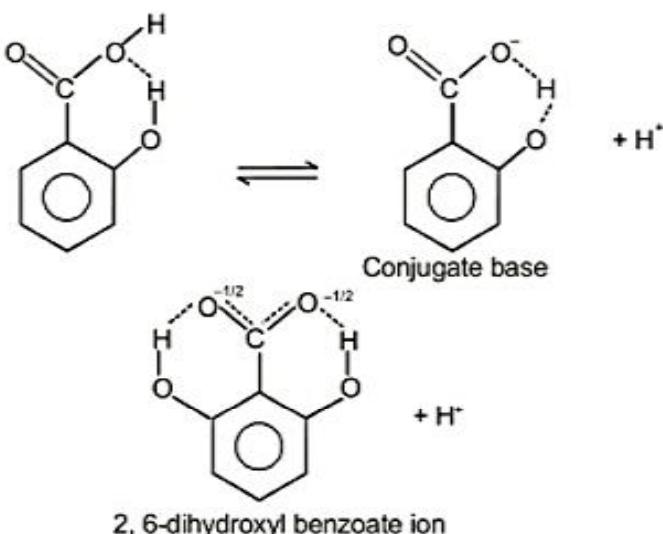
While $(\text{CH}_3)_4\text{N}^+ \text{OH}^-$ (ammonium compound) will give OH^- ion in large amount due to no Hydrogen bonding.



Effect of intramolecular H-bonding

(i) Strength of acid

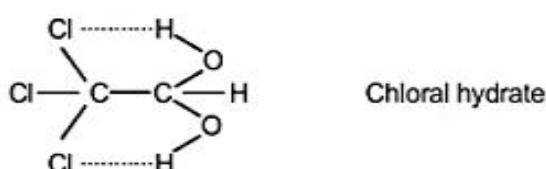
(a) The formation of intramolecular H-bonding in the conjugate base of an acid gives extra stability to conjugate base and hence acid strength increases eg. Salicylic acid is stronger than benzoic acid and 2, 6 – dihydroxy benzoic acid > salicylic acid.



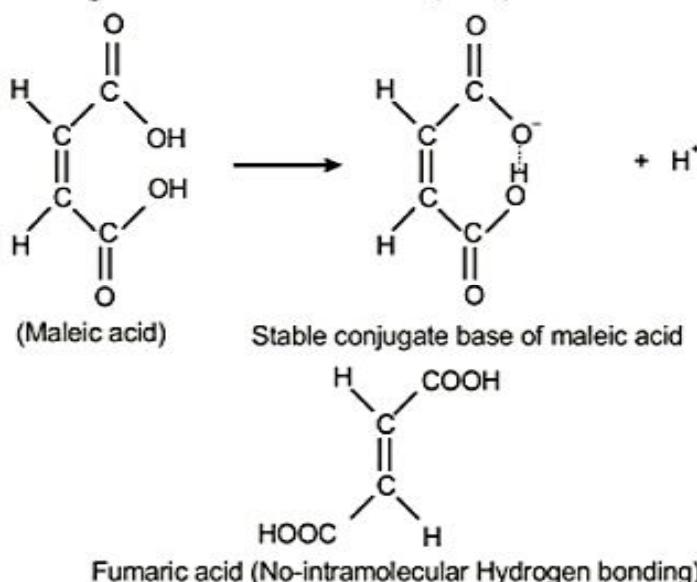
- (b) $\text{C}_2\text{H}_5\text{SH}$ is more acidic than $\text{C}_2\text{H}_5\text{OH}$. In $\text{C}_2\text{H}_5\text{OH}$, Hydrogen bond forms, so H^+ is not free
(c) HF is weaker acid than HI, due to Hydrogen bond in $\text{H} - \text{F}$, H^+ is not free

(ii) 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 Hydrogen bonding).



(iii) Maleic acid (cis) is stronger acid than fumaric acid (trans).



Note: The relative strength of various bonds is as follows

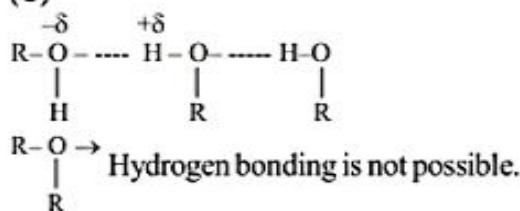
Ionic bond > Covalent bond > Metallic bond > Hydrogen bond > Vander waal's bond

Illustration

1. Ethanol has a higher boiling point than dimethyl ether though they have the same molecular weight. This is due to :

(A) resonance (B) coordinate bonding (C) hydrogen bonding (D) ionic bonding

Sol. (C)



Exercise

1. Arrange the following in order of decreasing boiling point :
 (I) *n*-Butane (II) *n*-Butanol (III) *n*-Butyl chloride (IV) Isobutane
 (A) *IV > III > II > I* (B) *IV > II > III > I* (C) *I > II > III > IV* (D) *II > III > I > IV*

Ans. (D)

METALLIC BOND

- (a) The constituent particles of metallic solids are metal atoms which are held together by metallic bond.
- (b) In order to explain the nature of metallic bond Lorentz proposed a simple theory known as electron gas model or electron sea model.
- (c) A metal atom is supposed to consist of two parts, valence electrons and the remaining part (the nucleus and the inner shells) called kernel.
- (d) The kernels of metal atoms occupy the lattice sites while the space between the kernel is occupied by valence electrons.
- (e) Due to small ionization energy the valence electrons of 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.
- (f) The simultaneous attraction between the kernels and the mobile electrons which hold the kernel together is known as metallic bond.

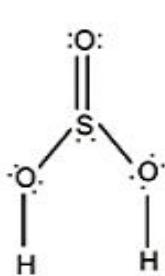
Properties of metals and their explanation by electron sea model :

1. **Metallic lusture :**
 - (a) It is due to presence of delocalised mobile electrons
 - (b) These loosely bonded electrons vibrate due to energy photon of incident light and radiates energy immediately.
2. **Electrical conductivity :**
 - (a) It is due to mobile electrons.
 - (b) These electrons flow equally in all direction.
 - (c) While applying a potential difference across a metal, there will be a directed flow of electrons towards the positive electrode.
 - (d) The directed flow of electrons carries the electric current from one point to another and therefore, the metals are known to be good conductors.
3. **Thermal conductivity :**
 - (a) It can also be explained on the basis of electron gas model.
 - (b) While heating a metal kinetic energy of electron increases and propagates through collisions.
4. **Malleability and ductility :**
 - (a) This property is due to non directional nature of metallic bond.
 - (b) Basically the kernels can slip over each other when a deforming force is applied.
5. **High tensile strength :**

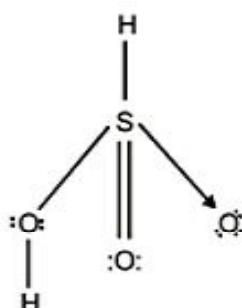
It is due to positively charged kernels and the mobile valence electrons.

POINTS TO REMEMBER

- (a) Bond energy of a diatomic molecule is enthalpy change to dissociate one mole of the diatomic gaseous molecule to form the respective gaseous atoms.
- (b) Strong metallic bonding is favoured by smaller size of kernel.
- (c) Band theory is related with metallic nature
- (d) The resonance structure do not have independent existence.
- (e) The hydration of ionic compounds involves evolution of heat, weakening of attractive forces and dissociation into ions
- (f) The maximum covalency is equal to the actual number of s-electron and p-electrons in the outermost shell
- (g) Many ionic crystals dissolve in water because water decreases the interionic attraction in the crystal lattice due to solvation.
- (h) Hydrogen bond stabilizes the secondary structure of proteins.
- (i) Isoelectronic molecular species have similar molecular orbitals and similar structure according to isoelectric principle
- (j) The amount of energy required to break one mole of the bonded atom and separate the bonded atoms in the gaseous state is known as bond dissociation energy
- (k) The average angle between the bonded orbitals is known as bond angle (θ).
- (l) Bond length may be defined as the average distance between the centres of nuclei of two bonded atoms.
- (m) Polymorphism (Allotropy) is a term used when one and the same substance can crystallise in more than one forms.
- (n) In SO_2 , there is $p\pi - p\pi$ bonding as well as $p\pi - d\pi$ bonding due to overlap of filled $p\pi$ orbitals of oxygen with the vacant 3d orbitals of sulphur.
- (o) H_2SO_3 exists in two forms which are always in equilibrium with one another



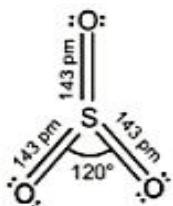
(Symmetrical sulphurous acid)



(Unsymmetrical sulphurous acid)

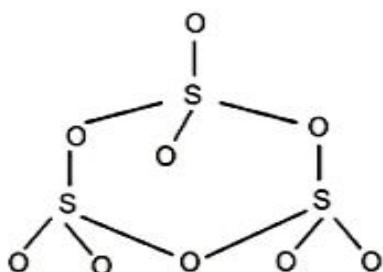
The unsymmetrical form containing S – H bond explains the reducing character of H_2SO_3 .

- (p) The anion of H_2SO_3 i.e. SO_3^{2-} has a pyramidal structure with S atom in sp^3 hybridization and all the S – O bonds are of equal bond length (134 pm)
- (q) In the gaseous phase, SO_3 is a planar triangular molecule with sulphur atom in sp^2 hybridization state

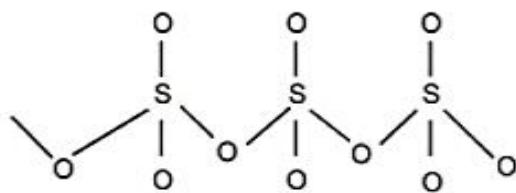


In order to account for the equivalency of all the S – O bonds and short S – O distance of 143 pm, SO_3 may be considered as a resonance hybrid involving $\text{p}\pi\text{-p}\pi$ S – O bonding along with additional $\text{p}\pi\text{-p}\pi$ bonding.

- (r) In the solid phase, SO_3 polymerizes to puckered rings or the more stable layer structure as shown.



Ring Structure



Layer Structure

SOLVED EXAMPLES

Q.1 An atom of element A has three electrons in its outer shell and B has six electrons in its outermost shell. The formula of the compound formed between these will be-

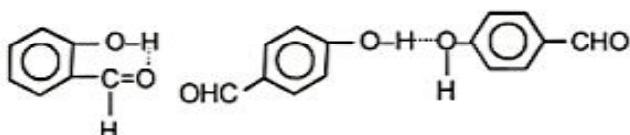
- (A) A_6B_6 (B) A_2B_3 (C) A_3B_2 (D) A_2B

Ans. (B)

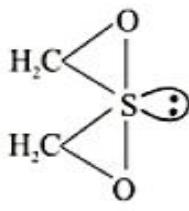
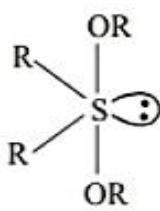
Sol. In this case the valence electron in the atom A is three and hence its valency is generally 3. In the atom B the number of valence electron is six. Hence its valency is usually 2. Hence the formula of the molecule formed from A and B could be A_2B_3 . An example of two such elements are Al and O and the formula of Aluminium oxide is Al_2O_3 .

Q.2 o-Hydroxy benzaldehyde is a liquid at room temperature while p-hydroxy benzaldehyde is a high melting solid

Sol. o-Hydroxy benzaldehyde show intramolecular H-bonding or chelation, which are weaker than intermolecular H-bonding in p-hydroxy benzaldehyde.



Q.3 Compare the bond angle in (axial bond angle)



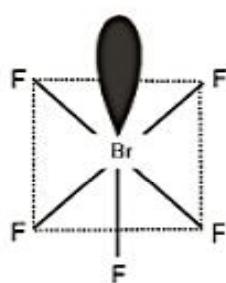
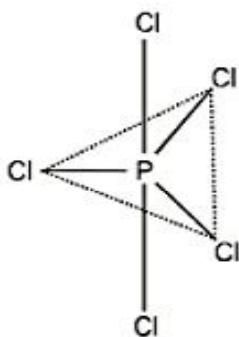
(I)

(II)

Sol. due to ring strain B.A. in second will be more than (I)

Q.4 Using VSEPR theory, draw the shape of PCl_5 and BrF_5 .

Sol.



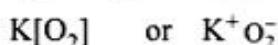
Q.5 Indicate the type of hybridization of each carbon atom in the following compounds

- (A) CH_3CN (B) $CH_3CH=CH_2$ (C) $H_3C-C\equiv C-CH_3$ (D) $HC\equiv C-CH=CH_2$

Sol. (A) sp^3 and sp (B) sp^3 , sp^2 , sp^2 (C) sp^3 , sp , sp , sp^3 (D) sp , sp , sp^2 , sp^2

Q.6 Among the following compounds/species write the order O–O bond length in O_2 , $O_2[AsF_4]$, $K[O_2]$

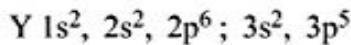
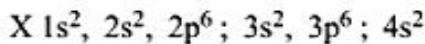
Sol. O_2



The bond length decreases with increasing bond order

Species	O_2	O_2^+	O_2^-
Bond order	2.0	2.5	1.5
Bond length	O_2^+	< O_2	< O_2^-

Q.7 Two elements X and Y have following electronic configuration-

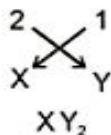


The expected compound formed by combination of X and Y will be expressed as-

- (A) XY_2 (B) X_5Y_2 (C) X_2Y_5 (D) XY_5

Ans. (A)

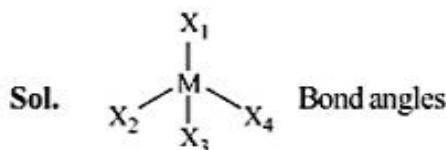
Sol. Valency of element X is 2(2 electrons in the outermost shell) while that of element Y is 1(1 electron required in the outermost shell to complete octet) So the formula of the compound between X and Y is XY_2



Q.8 The compound MX_4 is tetrahedral. The number of $\angle XMX$ angles in the compound is

- (A) Three (B) Four (C) Five (D) Six

Ans. (D)



Total angles are six [$X_1MX_2, X_1MX_3, X_1MX_4, X_2MX_3, X_2MX_4, X_3MX_4$]

Q.9 The electronegativity of H and Cl are 2.1 and 3.0 respectively. The correct statement (s) about the nature of HCl is/are

- (A) 17% ionic (B) 83% ionic (C) 50% ionic (D) 100% ionic

Ans. (A)

Sol. % ionic character = $16(X_A - X_B) + 3.5(X_A - X_B)^2$
 $= 16(3.0 - 2.1) + 3.5(3.0 - 2.1)^2$
 $= 14.4 + 2.83 = 17.235 \approx 17\%$

Q.10 The electronegativity of O, F, N, Cl and H are 3.5, 4.0, 3.0, 3.0 and 2.1 respectively. The strongest bond will be :

- (A) F – O (B) O – Cl (C) N – H (D) O – H

Ans. (D)

Sol. Bond strength \propto Difference in electronegativity of atoms

Q.11 In which solvent NaCl has maximum solubility

- (A) H_2O ($\epsilon=80$) (B) $\text{C}_2\text{H}_5\text{OH}$ ($\epsilon=27$) (C) CH_3COCH_3 ($\epsilon=21$) (D) $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ ($\epsilon=4.1$)

Ans. (A)

Sol. Solubility \propto dielectric constant (ϵ)

Q.12 Which has maximum covalent character ?

- (A) NaCl (B) SiCl_4 (C) AlCl_3 (D) MgCl_2

Ans. (B)

Sol. Polarisation in the molecule increases with increase of charge and decreases in size of the cation when the anion is same.

Q.13 The dipole moment of HBr is 2.6×10^{-30} Cm and the interatomic spacing is 1.41 \AA . The percentage of ionic character in HBr is-

- (A) 10.5 (B) 11.5 (C) 12.5 (D) 13.5

Ans. (B)

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

Theoretical dipole moment of a 100% ionic character

$$= e \times d = (1.6 \times 10^{-19} \text{ C}) \times (1.41 \times 10^{-10} \text{ m})$$

$$= 2.256 \times 10^{-29} \text{ Cm}$$

$$\text{\% ionic character} = \frac{2.6 \times 10^{-30}}{2.256 \times 10^{-29}} \times 100 = 11.5$$

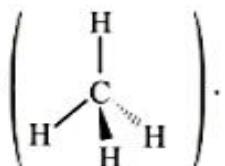
Q.14 CO_2 is isostructural with

- (A) CH_4 (B) SnCl_2 (C) HgCl_2 (D) NO_2

Ans. (C)

Sol. The structure of CO_2 is linear O=C=O, similarly the structures of HgCl_2 is linear (Cl–Hg–Cl). SnCl_2

and NO_2 have angular structures and CH_4 has tetrahedral structure

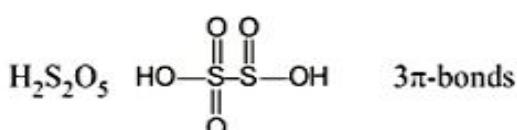
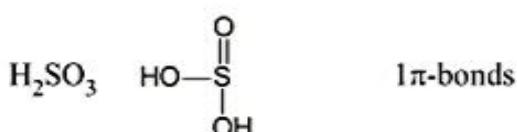
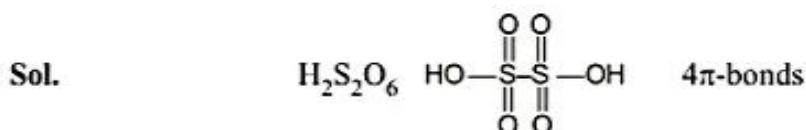


Q.15 Identify the correct sequence of increasing number of π -bonds in the structures of the following molecules:

- (I) $\text{H}_2\text{S}_2\text{O}_6$ (II) H_2SO_3 (III) $\text{H}_2\text{S}_2\text{O}_5$

- (A) I, II, III (B) II, III, I (C) II, I, III (D) I, III, II

Ans. (B)

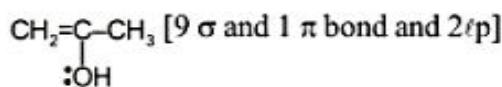


Q.16 Enol form of acetone contains the following:

- (A) 9σ -bond, 1π -bond and two lone pair of electrons
- (B) 8σ -bond, 2π -bond and two lone pair of electrons
- (C) 10σ -bond, 1π -bond and one lone pair of electrons
- (D) 9σ -bond, 2π -bond and one lone pair of electrons

Ans. (A)

Sol. Enol form of acetone is



Q.17 The decreasing order of solubility of silver halide is

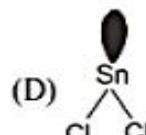
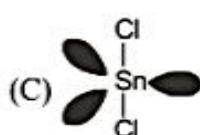
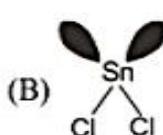
- | | |
|---|---|
| (A) $\text{AgI} > \text{AgBr} > \text{AgCl} > \text{AgF}$ | (B) $\text{AgF} > \text{AgCl} > \text{AgBr} > \text{AgI}$ |
| (C) $\text{AgCl} > \text{AgF} > \text{AgBr} > \text{AgI}$ | (D) $\text{AgBr} > \text{AgF} > \text{AgI} > \text{AgCl}$ |

Ans. (B)

Sol. AgI has maximum covalent character [$\because \text{I}^-$ is a large anion], while AgF has minimum covalent character, Therefore, it has more solubility

Q.18 The atomic number of Sn is 50. The shape of gaseous SnCl_2 molecule is :

(A) $\text{Cl}-\text{Sn}-\text{Cl}$



Ans. (D)

Sol. $\text{Sn}[Z=50], [\text{Kr}] \quad \begin{array}{|c|c|c|c|} \hline 5s & & 5p & \\ \hline \uparrow\downarrow & & \uparrow & \uparrow \\ \hline \end{array}$

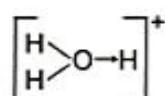
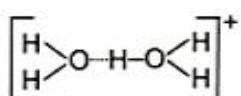
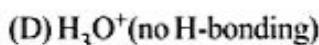
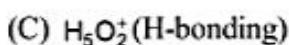
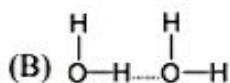
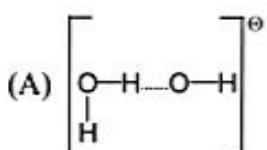
sp^2 -hybridisation :

Q.19 In which case hydrogen bond will not be observed

- (A) H_3O^- (B) H_2O (C) H_5O_2^+ (D) H_3O^+

Ans. (D)

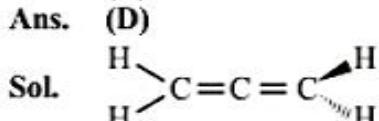
Sol. H_3O_2^- species



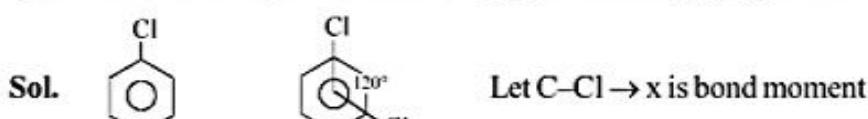
Q.20 Which of the following statements is correct in the context of the allene molecule, C_3H_4 ?

- (A) The central carbon is sp hybridized
 (B) The terminal carbon atoms are sp^2 hybridized
 (C) The planes containing the CH_2 groups are mutually perpendicular to permit the formation of two separate π -bonds.
 (D) All correct

Ans. (D)



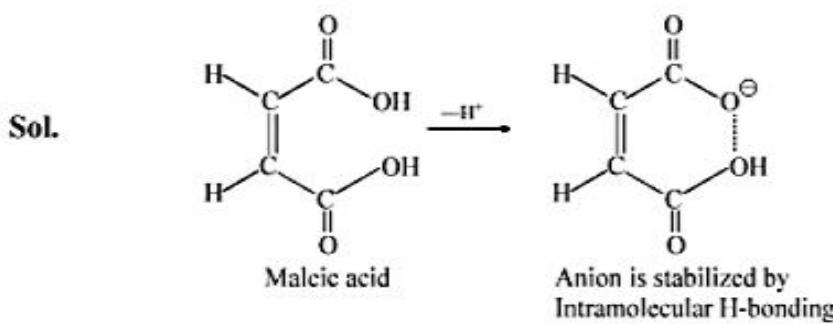
Q.21 Prove that dipole moment of $\text{C}_6\text{H}_5\text{Cl}$ and m- $\text{C}_6\text{H}_4\text{Cl}_2$ are same.



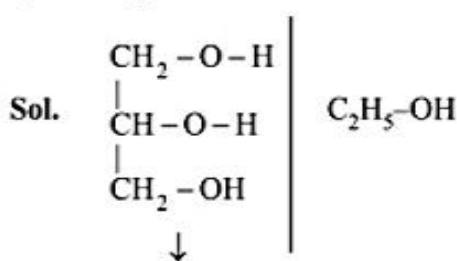
$$\begin{aligned}\mu_R &= x & \mu_R &= 2 \mu \cos \theta / 2 \\ && \mu_R &= 2 x \cos 60 \\ && &= 2 x \cdot 0.5 \\ && &= x\end{aligned}$$

Thus both have $\mu_R = x$

Q.22 Maleic acid is more acidic than fumaric acid. Why?



Q.23 Glycerol is more viscous than ethanol. Explain.



Due to presence of 3-OH groups higher no. of H-bonding, Glycerol is more viscous than ethanol.

Q.24 It has been observed that % 's' character in Sb–H bond in SbH_3 is 0.5%. Predict the % 's' character in the orbital occupied by the lone pair is.

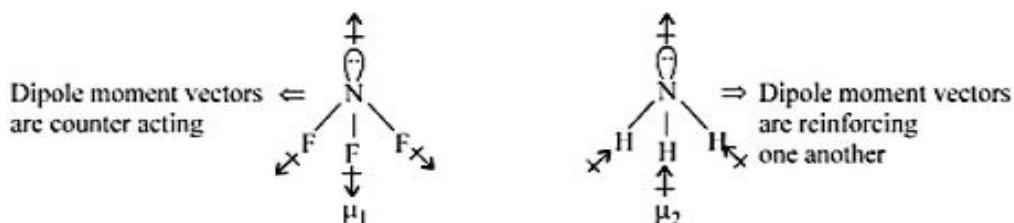
- (A) 99.5 % (B) 99.0 % (C) 98.5 % (D) 98.0 %

Ans. (C)

Sol. Total % s-character in three Sb–H bond pairs = $0.5 + 0.5 + 0.5 = 1.5\%$
 hence % s-character in $\ell.p.$ = $100 - 1.5 = 98.5\%$

Q.25 The dipole moment of NH_3 is more than that of NF_3 .

Sol.



$\therefore \mu_1 < \mu_2$
 Also Polarity of N—F bond > Polarity of N—H bond
 (E.N = 3.0) (E.N = 4.0) (E.N = 3.0) (E.N = 2.1)