

2

Chemical Bonding and Molecular Structure

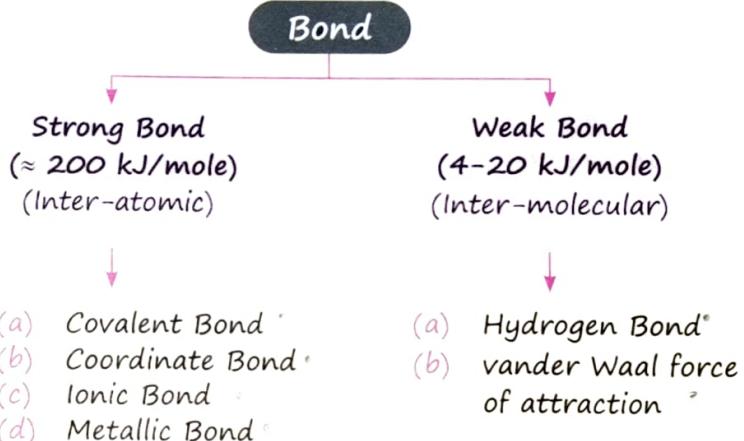
(JEE Advanced)

Syllabus

Orbital overlap and covalent bond; Hybridisation involving s, p and d orbitals only; Molecular orbital energy diagrams for homonuclear diatomic species (up to Ne_2); Hydrogen bond; Polarity in molecules, dipole moment; VSEPR model and shapes of molecules (linear, angular, triangular, square planar, pyramidal, square pyramidal, trigonal bipyramidal, tetrahedral and octahedral).

WHAT IS BOND?

- Bond = Force of attraction
- The attractive force which holds various constituents (atoms, ions, etc.) together in different chemical species is called a chemical bond.
- Bond Formation → Exothermic Process



Reason for Bond Formation

- Tendency to gain stability
- Tendency to acquire minimum energy
- Tendency to attain Inert gas configuration

VALENCE ELECTRON & LEWIS SYMBOL

Lewis Symbol → No of dots = no of valence electrons

Group No.	1	2	13	14	15	16	17	18
Valence Electron	1	2	3	4	5	6	7	8
Lewis Symbol	.Li	.Be.	.B.	.C.	:N:	:O:	:F:	:Ne:

Lewis Symbol of Cl \rightarrow $:\ddot{\text{Cl}}:$

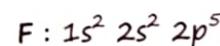
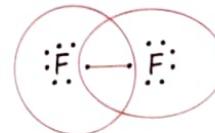
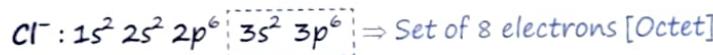
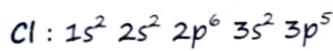
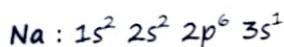
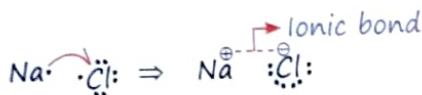
Lewis Symbol of S \rightarrow $:\ddot{\text{S}}:$

Lewis Symbol of P \rightarrow $:\ddot{\text{P}}:$

Lewis Symbol of Xe \rightarrow $:\ddot{\text{Xe}}:$

OCTET RULE

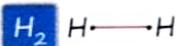
Atoms can combine either by transfer of electron from one atom to another atom or by sharing electrons in order to have an octet in their valence shell.



After bonding F attain 8 electrons in its valence shell.

M&N.11 Ionic Bond : The bond formed, as a result of the electrostatic attraction between the positive and negative ions was termed as electrovalent bond.

Covalent Bond : When two atoms share one electron pair they are said to be joined by single covalent bond.



1. NBE = Zero
2. LP = Zero
3. BP = 1

1. Non-bonding Electrons [NBE]
2. Lone Pair [LP]
3. Bond Pair [BP]



1. NBE = 8
2. LP = 4
3. BP = 2



1. LP = 2
2. BP = 3
3. NBE = 4

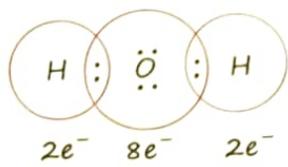
Selection of Central Atom in a Molecule

Central Atom

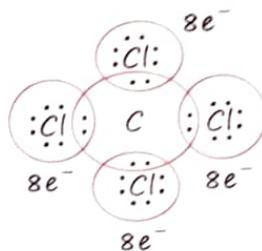
Less in number

Least electronegative

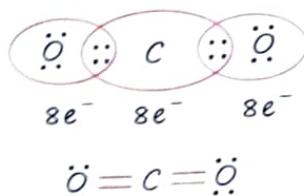
Tendency to form maximum number of bonds



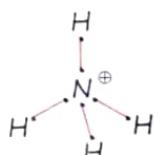
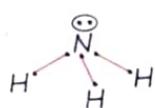
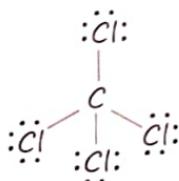
H atoms attain a duplet of electrons and O attain the octet



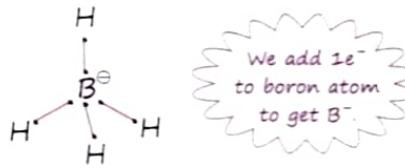
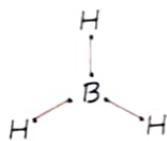
Each of the four Cl atoms along with the C atom attains octet of electrons



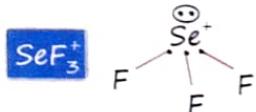
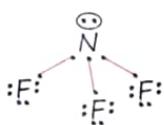
If two atoms share two pairs of electrons, the covalent bond between them is called a double bond.



We remove 1e⁻ from nitrogen atom to get N^+ . So N^+ has 4e⁻ in valence shell.

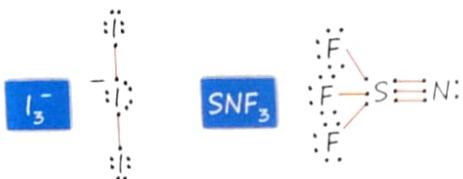
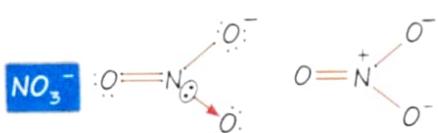
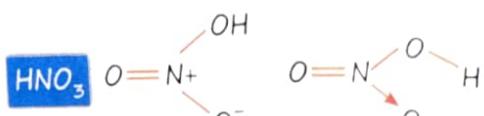
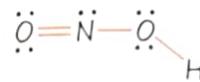
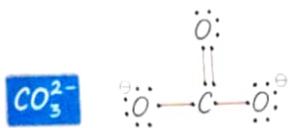
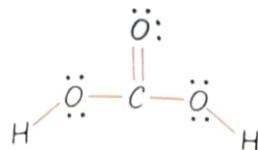


We add 1e⁻ to boron atom to get B^- .



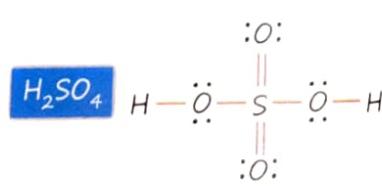
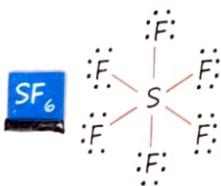
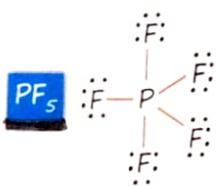
Note

F & H can never act as central atom.



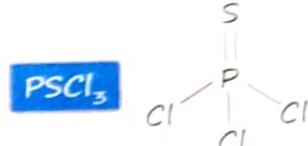
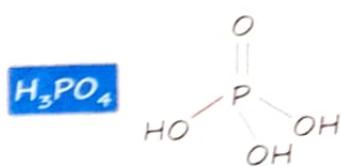
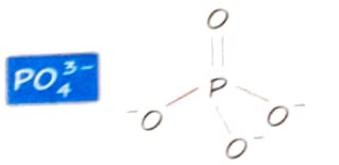
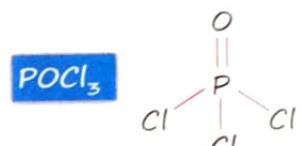
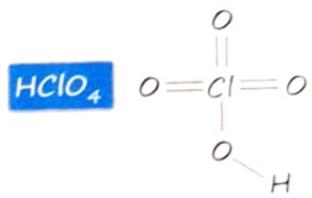
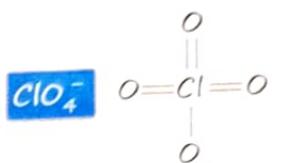
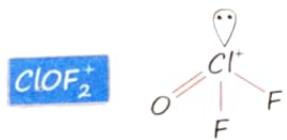
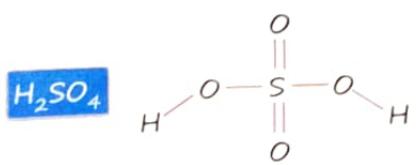
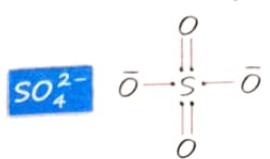
Limitations of Octet Rule

- It applies mainly to 2nd period elements.
- 2nd Period elements [B, C, N, O, F] → s + p subshell in valence shell
→ maximum no. of electrons = 2 + 6 = 8
- Expanded or Super or Hypervalent Octet: Elements in and beyond the 3rd period of periodic table have d orbitals for bonding.
- 3rd Period elements [Al, Si, P, S, Cl] → s + p + d subshell in valence shell
→ maximum no. of electrons = 2 + 6 + 10 = 18

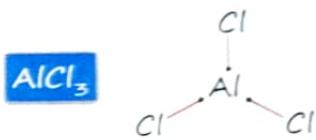
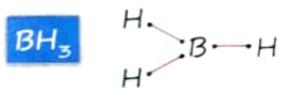


- In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet.

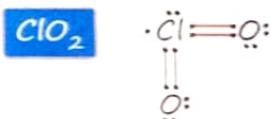
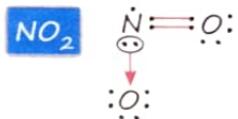
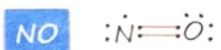
↓
More than $8e^-$



3. Incomplete Octet: In some compounds, the number of electrons surrounding the central atom is less than eight.



4. Odd Electron Molecules: Molecules with an odd number of electrons



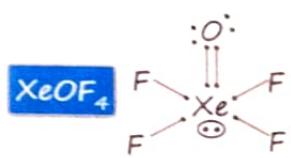
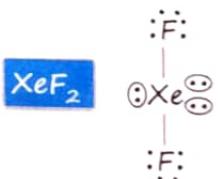
Total no. of electrons in $\text{NO} = 7 + 8 = 15$ (odd)

Total no. of electrons in $\text{NO}_2 = 7 + 8 \times 2 = 23$ (odd)

Total no. of electrons in $\text{ClO}_2 = 17 + 8 \times 2 = 33$ (odd)

5. Octet rule is based upon the chemical inertness of noble gases.

Some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like XeF_2 , KrF_2 , XeOF_4 etc.



1. The number of molecules or ions from the following, which do not have odd number of electrons are _____.

(A) NO_2 (B) ICl_4^-

(C) BrF_3 (D) ClO_2

[29 Jan, 2023 (Shift-1)]

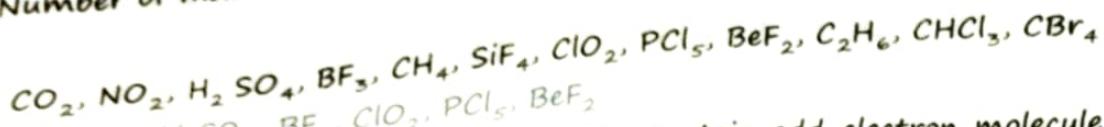
Sol. [3] ICl_4^- , BrF_3 and NO_2^+ do not have odd number of e^-

(E) NO_2^+

(F) NO

2. Number of molecules from the following which are exceptions to octet rule is _____.

[08 April, 2024 (SP)]



Sol. [6] NO_2 , H_2SO_4 , BF_3 , ClO_2 , PCl_5 , BeF_2

3. Which of the following pair of molecules contain odd electron molecule and an expanded molecule?

[29 July, 2022 (SP)]

- (a) BCl_3 and SF_6
 (c) SF_6 and H_2SO_4

Sol. (b)

BCl_3 - electron deficient molecule

SF_6 - expanded octet molecule

(b) NO and H_2SO_4

(d) BCl_3 and NO

NO - odd electron containing molecule

H_2SO_4 - expanded octet molecule

FORMAL CHARGE (FC)

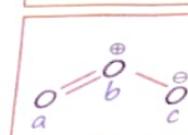
Difference between the number of valence electrons of that atom in free state and the number of electrons assigned to that atom in the Lewis structure.

V = Total number of valence electrons in the free atom

N = Number of non-bonding electrons

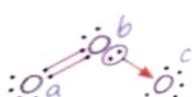
B = Number of bonding electrons

$$FC = V - N - \frac{B}{2}$$



	FC
a	zero
b	+1
c	-1

O_3



FC on "a"

$$\begin{aligned} V &= 6 \\ N &= 4 \\ B &= 4 \end{aligned} \rightarrow FC = 6 - 4 - \frac{4}{2} = 0$$

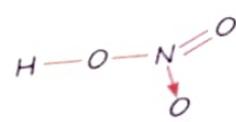
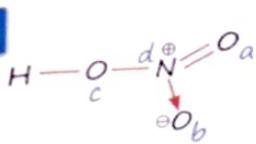
FC on "b"

$$\begin{aligned} V &= 6 \\ N &= 2 \\ B &= 6 \end{aligned} \rightarrow FC = 6 - 2 - \frac{6}{2} = +1$$

FC on "c"

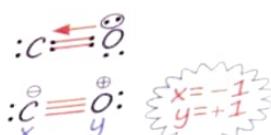
$$\begin{aligned} V &= 6 \\ N &= 6 \\ B &= 2 \end{aligned} \rightarrow FC = 6 - 6 - \frac{2}{2} = -1$$

HNO_3



$$a = 0, b = -1, c = 0, d = +1$$

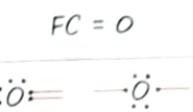
CO



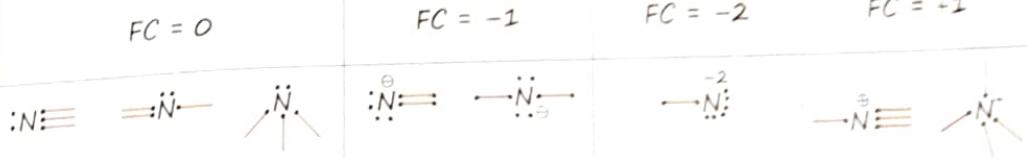
CHEMISTRY

OP* Points

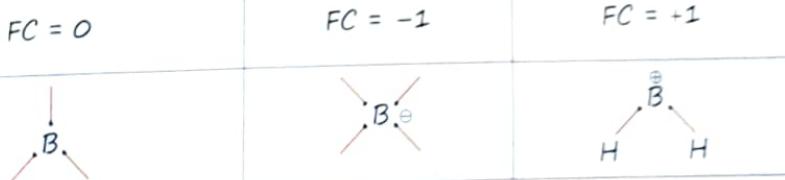
Formal charge on Oxygen



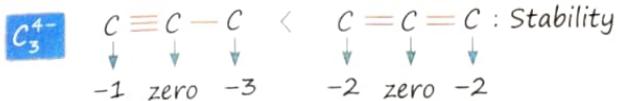
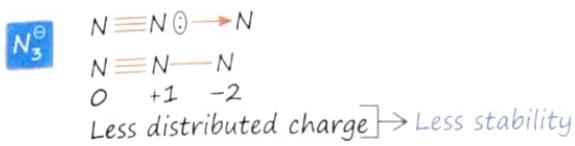
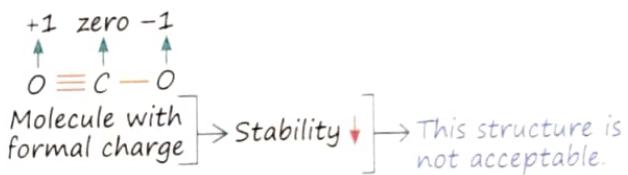
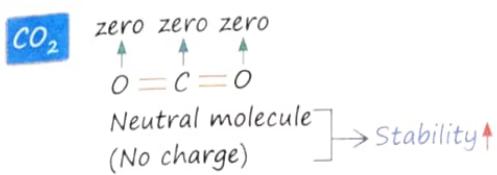
Formal charge on Nitrogen



Formal charge on Boron



- The structure of least energy (most stable) is usually the one with minimal formal charge and most distributed real charge.



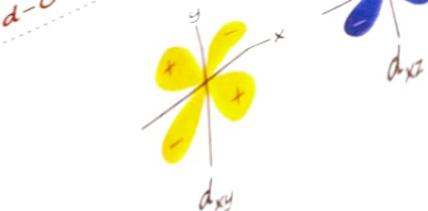
NATURE, SHAPE & PHASE OF ATOMIC ORBITAL



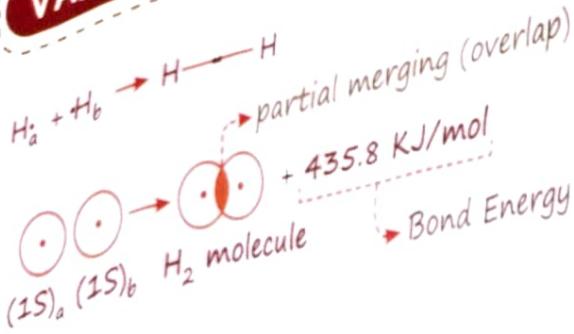
- s orbital (1 lobe)
- Non-directional nature
- + or - sign



- p orbital (2 lobes)
- Directional nature
- p_x, p_y, p_z



VALENCE BOND THEORY

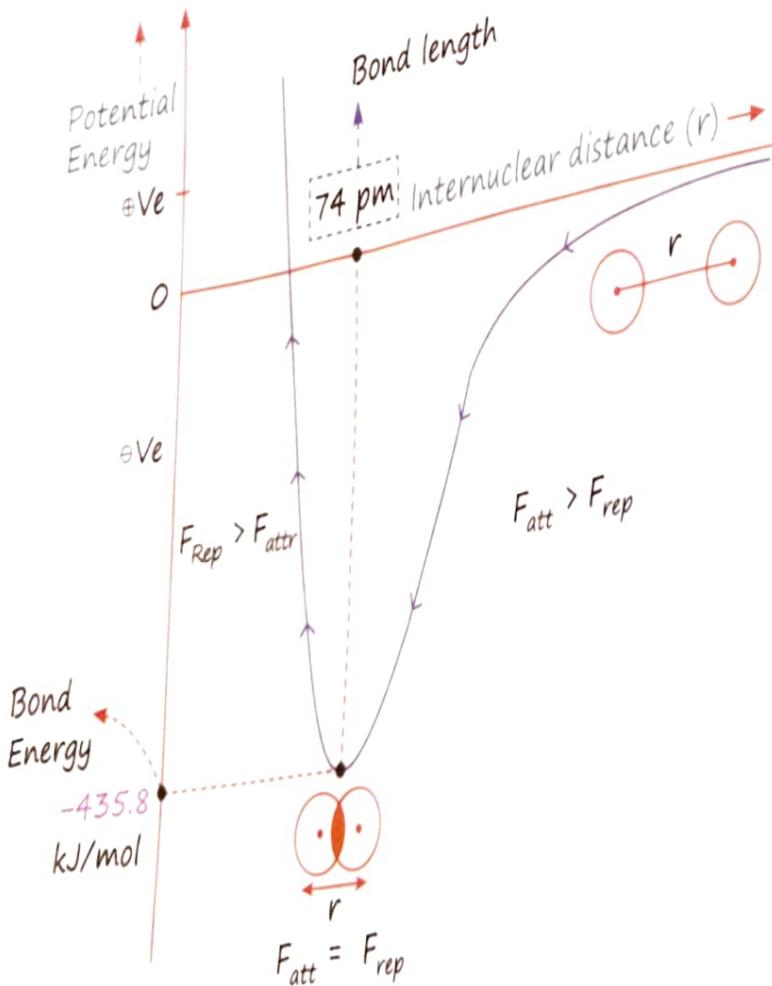


Force of attraction: (i) $(e^-)_a - (N)_b$
(ii) $(e^-)_b - (N)_a$

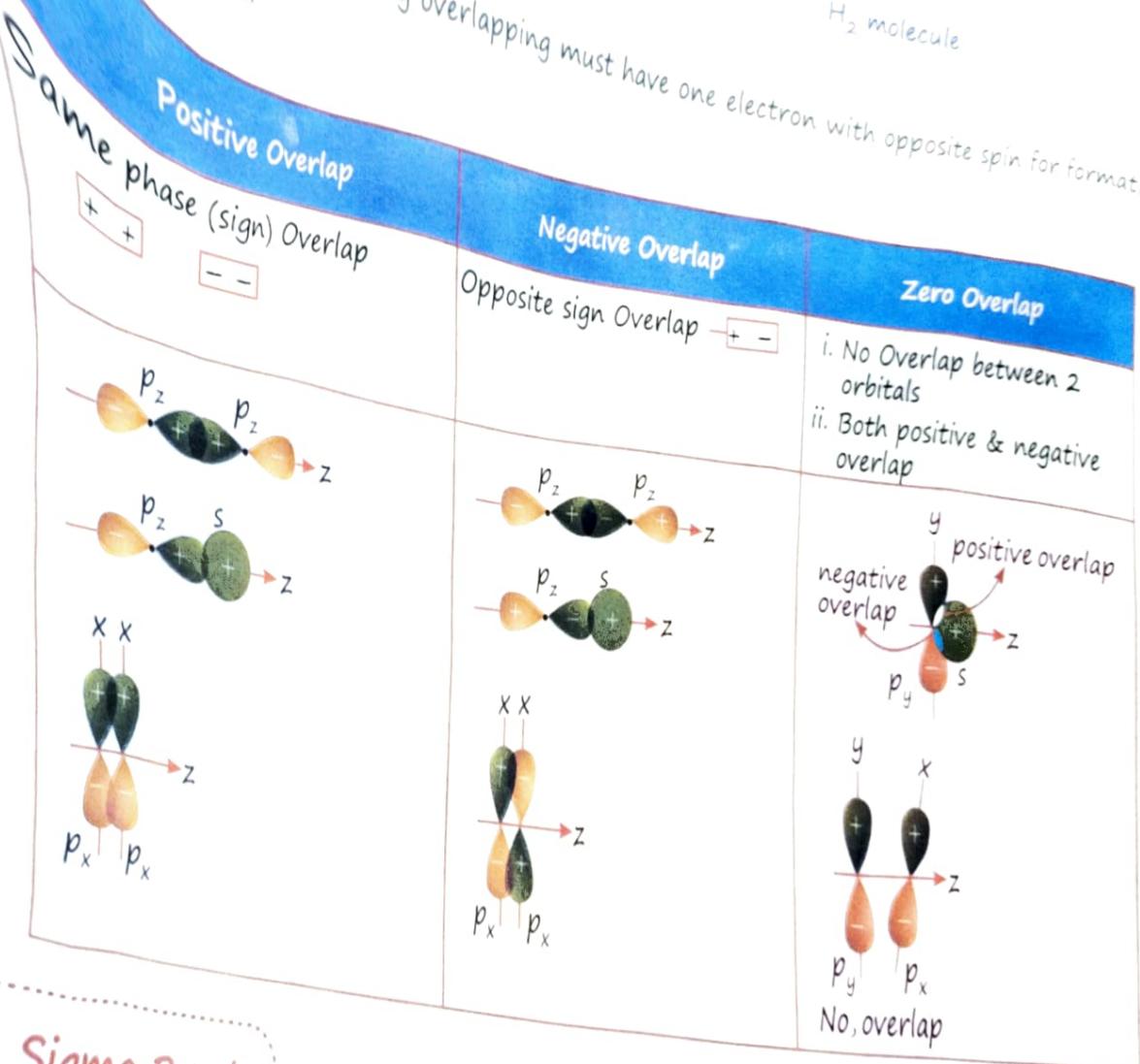
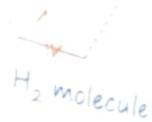
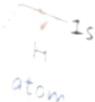


N_a → Nucleus of a
 e_a^- → Electron density of a

Force of repulsion: (i) $(e^-)_a - (e^-)_b$
(ii) $(N)_a - (N)_b$

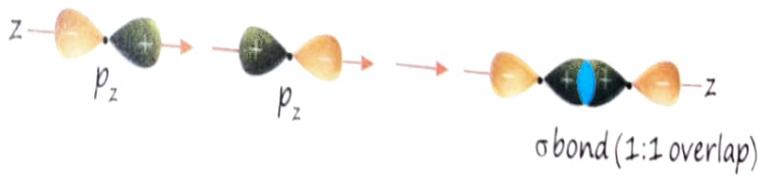


which are undergoing overlapping must have one electron with opposite spin for formation

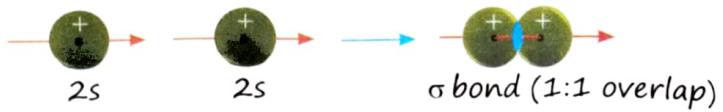


Sigma Bond

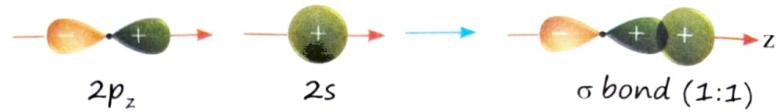
Overlapping along the molecular axis/Head on overlapping



i. s-s overlapping



ii. s-p overlapping



iii. p-p overlapping



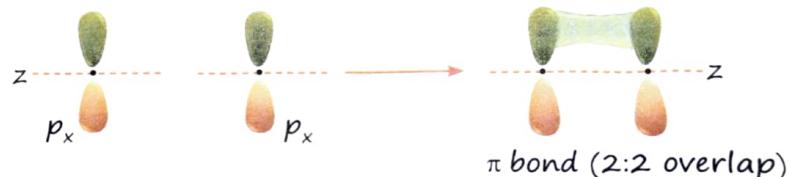
□ Extent of overlapping ↑ → Strength of bond ↑

Extent of overlapping : $2s - 2s < 2s - 2p < 2p - 2p$

Strength: $2s-2s < 2s-2p < 2p-2p$

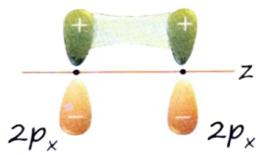
Pi Bond

Overlapping \perp to molecular axis (Side ways overlapping)

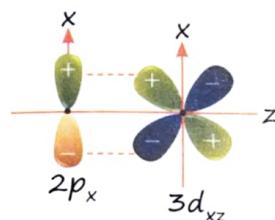


Strength : σ bond > π bond

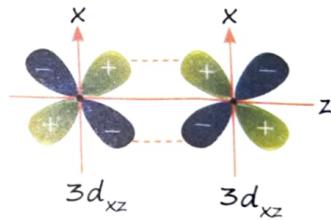
(i) $p\pi-p\pi$ bond



(ii) $p\pi-d\pi$ bond



(iii) $d\pi-d\pi$ bond



□ Extent of overlapping ↑ : $(n_1 + n_2) \downarrow$

Extent of overlapping : $2p-2p > 2p - 3d > 3d - 3d$

$n_1 + n_2$: $(2 + 2) < (2 + 3) < (3 + 3)$

Strength of π bond : $2p-2p > 2p-3d > 3d-3d$

Strength of Bond

(i) When $n_1 + n_2$ is same : $2s-2s < 2s-2p < 2p-2p$: σ bond strength

$(n_1 + n_2) \rightarrow (2 + 2) (2 + 2) (2 + 2)$

When $n_1 + n_2$ is different:

$1s - 1s > 2s - 2s > 3s - 3s$: σ bond strength

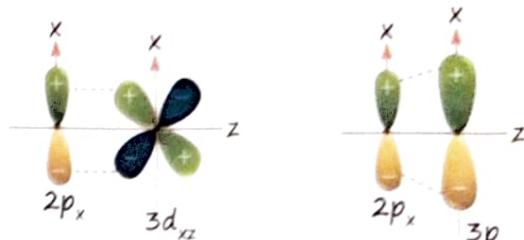
$(n_1 + n_2) \rightarrow (1+1) (2+2) (3+3)$

$2p - 2p > 2p - 3d$: π bond strength

$(n_1 + n_2) \rightarrow (2+2) (2+3)$

$2p - 3p < 2p - 3d$: π bond strength

$(n_1 + n_2) \rightarrow (2+3) (2+3)$

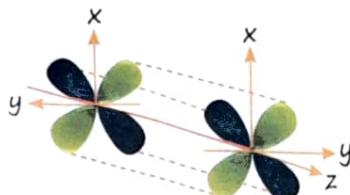


Better overlapping in $2p - 3d$ w.r.t $2p - 3p$

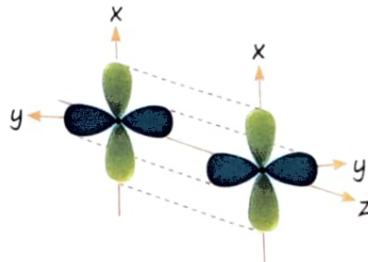
Bonding in d-Orbitals

Delta Bond $\rightarrow 4:4$ overlap

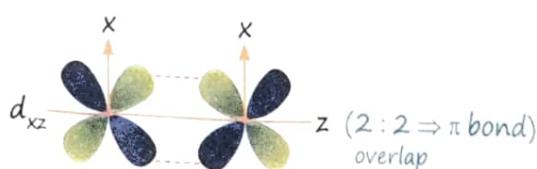
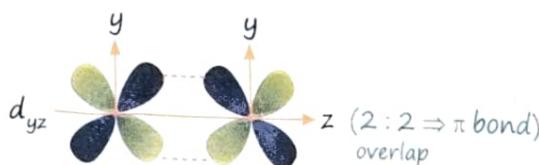
1. d_{xy} and d_{xy}



2. $d_{x^2-y^2}$ and $d_{x^2-y^2}$

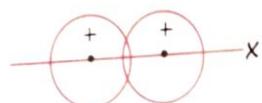


Overlapping of 2 $d_{x^2-y^2}$ or 2 d_{xy} orbitals gives a δ bond, when z axis is internuclear axis.



Bond	σ	π	δ
Orbital			
s	✓	✗	✗
p	✓	✓	✗
d	✓	✓	✓

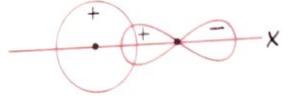
$s + s = \sigma$ bond



$p_x + p_x = \sigma$ bond

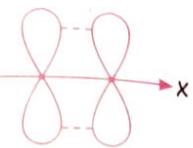


$s + p_x = \sigma$ bond

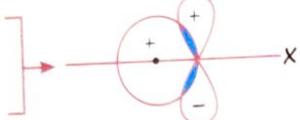


$p_y + p_y = \pi$ bond

$p_z + p_z = \pi$ bond



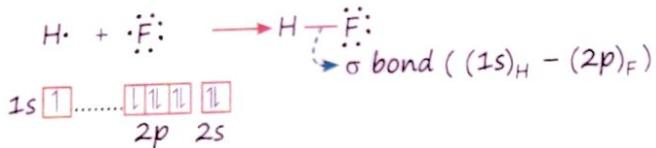
$s + p_y = \text{No bond}$



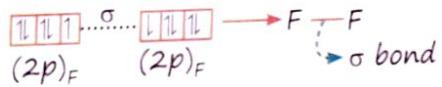
$s + p_z = \text{No bond}$

□ Overlapping of orbitals when x axis is internuclear axis.

HF Molecule



F_2 Molecule



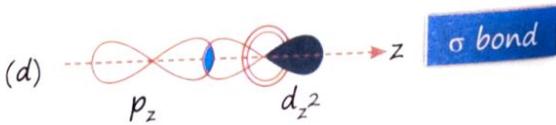
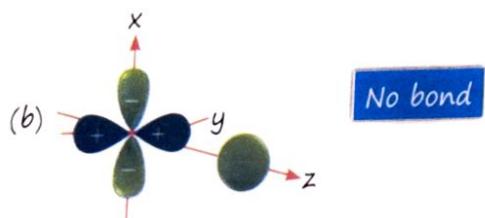
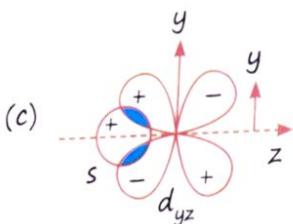
4. Draw the type of overlaps between given orbitals, Z is internuclear axis.

(a) s and d_{z^2}

(b) s and $d_{x^2-y^2}$

(c) s and d_{yz}

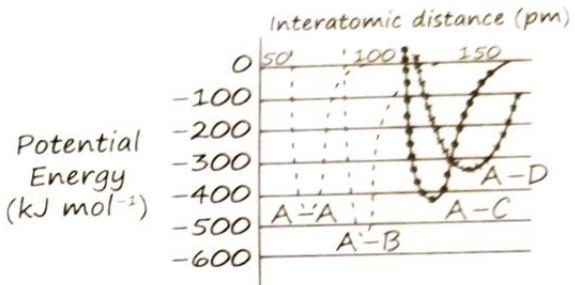
(d) p_z and d_{z^2}



No bond

σ bond

5. The intermolecular potential energy for the molecules A, B, C and D given below suggest that:
 [4 Sept, 2020 (Shift-1)]



- (a) A - A has the largest bond enthalpy (b) A - D has the shortest bond length
 (c) D is more electronegative than other atoms (d) A - B has the stiffest bond.

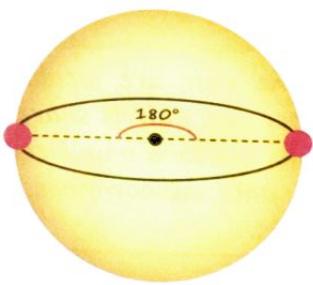
Sol. (d) Lower the potential energy, stronger will be the bond. A - B has lowest potential energy which means it has stronger bond.

VSEPR THEORY VALENCE SHELL ELECTRON PAIR REPULSION THEORY

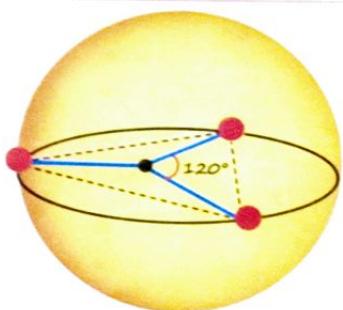
Main Postulates

- The shape of a molecule depends upon the number of valence shell electron pairs [bonded or non-bonded] around the central atom.
- The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
- Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
- These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.

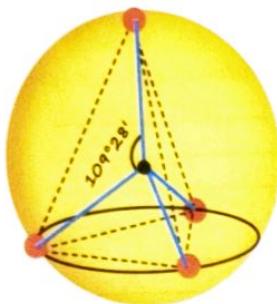
2 electron pairs are localised on spherical surface at maximum distance, when angle between them is 180° .



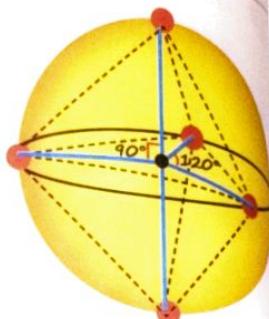
3 electron pairs are localised on spherical surface at maximum distance, when they are placed at corners at triangle.



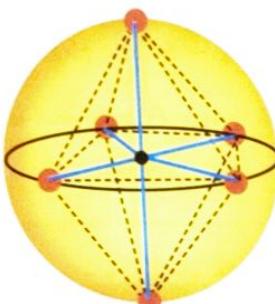
4 electron pairs are localised on spherical surface at maximum distance, when they are placed at corners of tetrahedron.



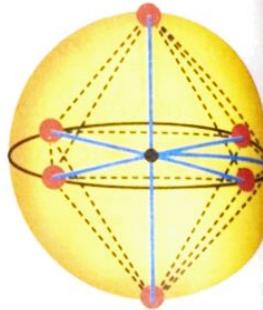
5 electron pairs are localised on spherical surface of central atom at maximum distance when 3 are placed at equatorial position [at angle 120°] and 2 are placed at axial position [at angle 90°]



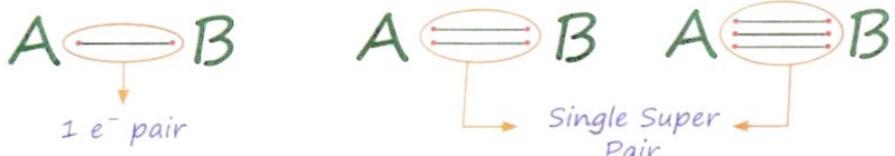
6 electron pairs are localised on spherical surface at maximum distance, when they are placed at corners of octahedron.



7 electron pairs at maximum distance is shown in figure



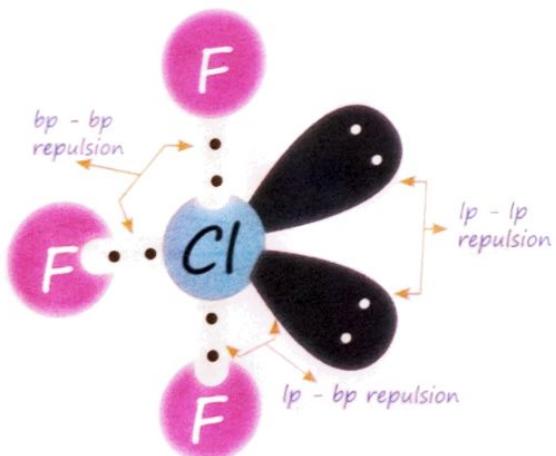
- A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of multiple bond are treated as a single super pair.



- Where two or more resonance structures can represent a molecule, the VSEPR model is applied to any such structure.

The repulsive interaction of electron pairs decrease in the order:

Lone pair (lp) - Lone pair (lp) > Lone pair (lp) - Bond pair (bp) > Bond pair (bp) - Bond pair (bp)



- The lone pair are localized on the central atom, each bonded pair is shared between two atoms. As a result, the lone pair electrons in a molecule occupy more space as compared to the bonding pairs of electrons.

- We can represent any molecule in AB_xL_y form where, A → Central atom, B → Side atom, L → Lone pair
- Number of valence shell electron pair decides the geometry of a molecule.

Valence shell electron pair [VSEP] = $x + y$

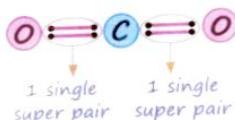
AB_2 Type Molecule



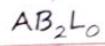
- Valence shell electron pair = 2
- Geometry → Linear
- Bond angle → 180°



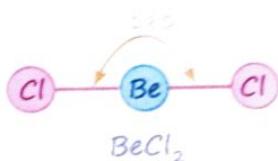
$$\begin{array}{l} x = 2 \\ y = 0 \end{array}$$



- Valence shell electron pair = 2
- Geometry → Linear
- Bond angle → 180°



$$\begin{array}{l} x = 2 \\ y = 0 \end{array}$$



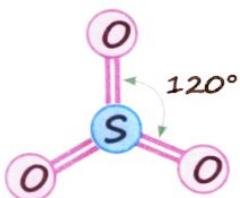
AB_3 Type Molecule



- Valence shell electron pair = $3 + 0 = 3$
- Geometry → Trigonal planar
- Bond angle → 120°



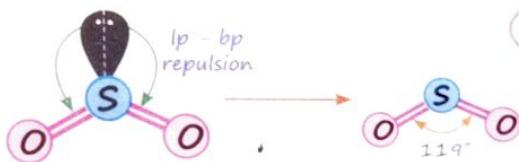
$$\begin{array}{l} x = 3 \\ y = 0 \end{array}$$



- Valence shell electron pair = $2 + 1 = 3$
- Due to lp - bp repulsion, bond angle reduces from 120° to 119°



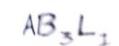
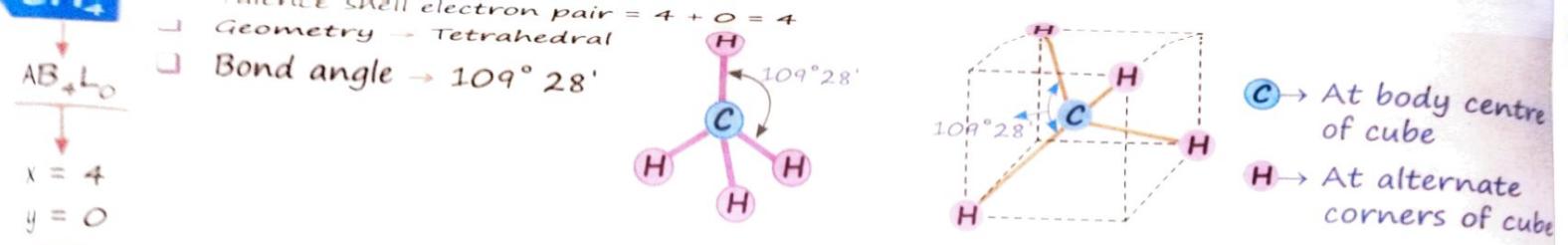
$$\begin{array}{l} x = 2 \\ y = 1 \end{array}$$



Geometry → Trigonal planar

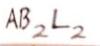
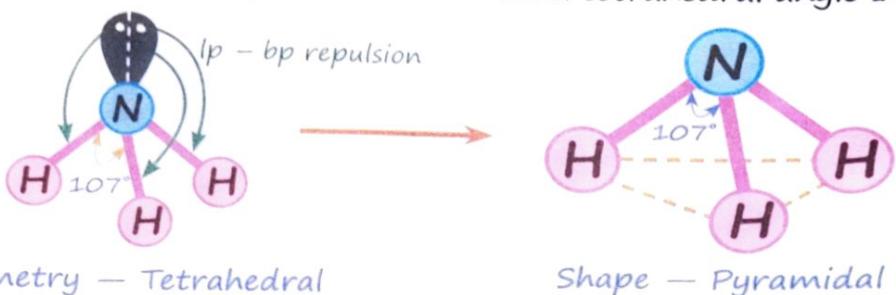
Shape → Bent

Structure with lone pair → Geometry
Structure without lone pair → Shape



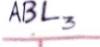
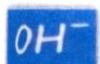
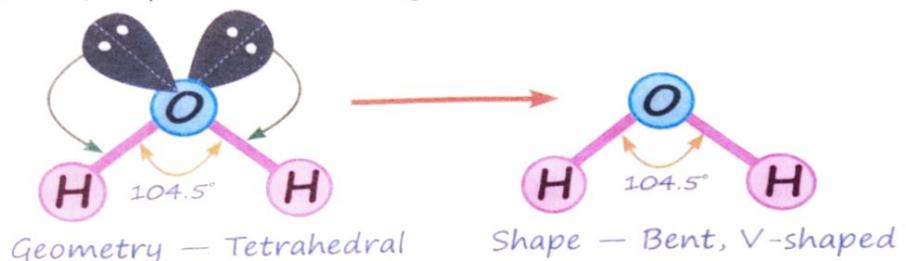
$x = 3$
 $y = 1$

- Valence shell electron pair = $3 + 1 = 4$
- Due to $lp - bp$ repulsion, bond angle reduces from ideal tetrahedral angle $109^\circ 28'$ to 107°



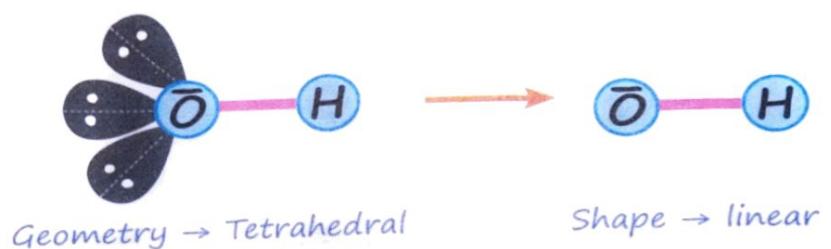
$x = 2$
 $y = 2$

- Valence shell electron pair = $2 + 2 = 4$
- Due to more $lp - bp$ repulsion, bond angle reduces from $109^\circ 28'$ to 104.5°



$x = 1$
 $y = 3$

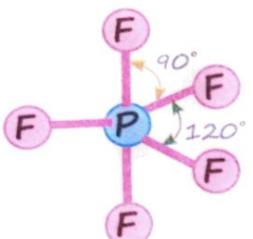
- Valence shell electron pair = $1 + 3 = 4$



AB₅ Type Molecule



- Valence shell electron pair = $5 + 0 = 5$
- Geometry \rightarrow Trigonal bipyramidal
- $\theta \rightarrow 90^\circ$ and 120°

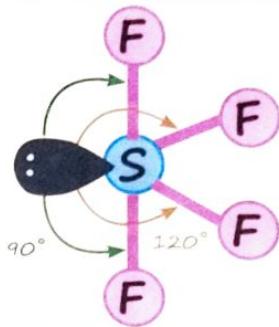




- Valence shell electron pair = $4 + 1 = 5$

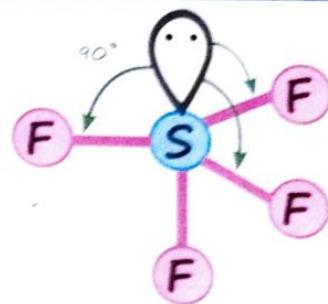
Case-1

If lp is present at equatorial position

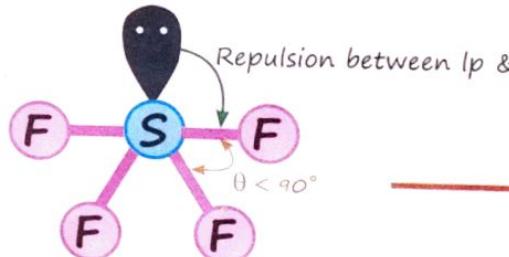


Case-2

If lp is present at axial position



- There are 2 lp - bp repulsions at 90° and 2 lp - bp repulsions at 120° .
- Repulsions at 90° are more effective than 120° . So we are going to compare on the basis of repulsions at 90° .
- Case - 1 structure is more favorable than case-2 due to less repulsion.
- So, case - 1 structure is Acceptable on the basis of postulates of VSEPR theory.



Geometry — TBP

Shape — See Saw

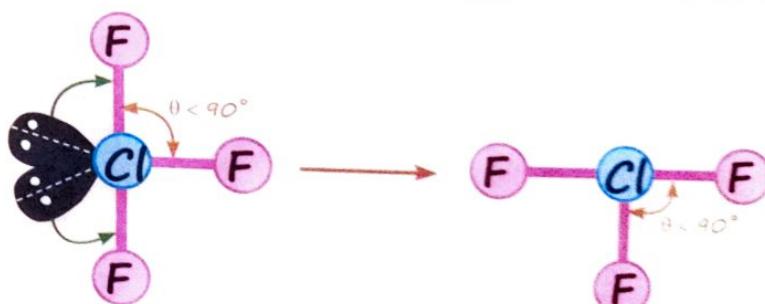
Note

In TBP geometry due to less repulsion, more favorable position for lone pair is equatorial position.



- Valence shell electron pair = $3 + 2 = 5$

$$\begin{array}{c} \downarrow \\ AB_3L_2 \\ \hline x = 3 \\ y = 2 \end{array}$$

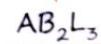


TBP Geometry

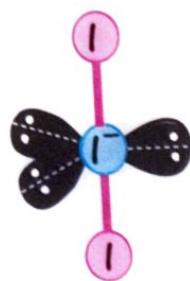
Bent T shaped



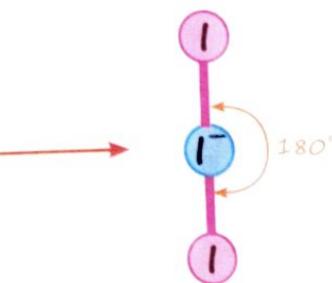
- Valence shell electron pair = $2 + 3 = 5$



$$\begin{array}{l} x = 2 \\ y = 3 \end{array}$$



TBP Geometry

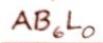


Linear shape

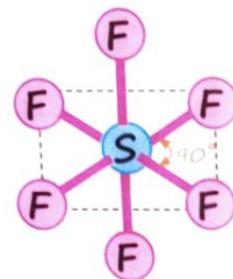
AB₆ Type Molecule



- Valence shell electron pair = $6 + 0 = 6$
- Geometry → Octahedral
- Bond angle → 90°



$$\begin{array}{l} x = 6 \\ y = 0 \end{array}$$



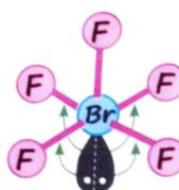
- Valence shell electron pair = $5 + 1 = 6$
- All bond angles are less than 90°

The lone pair would force the Br-F bond pairs upward, and all Br-F bond angles would contract.



$x = 5$

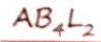
$y = 1$



Geometry - Octahedral Shape → Square Pyramid

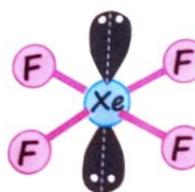


- Valence shell electron pair = $4 + 2 = 6$
- Bond angle → 90°

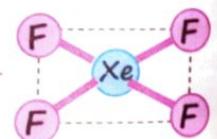


$x = 4$

$y = 2$

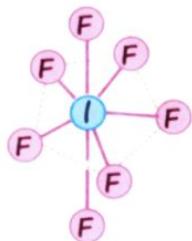
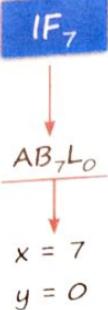


Geometry - octahedral

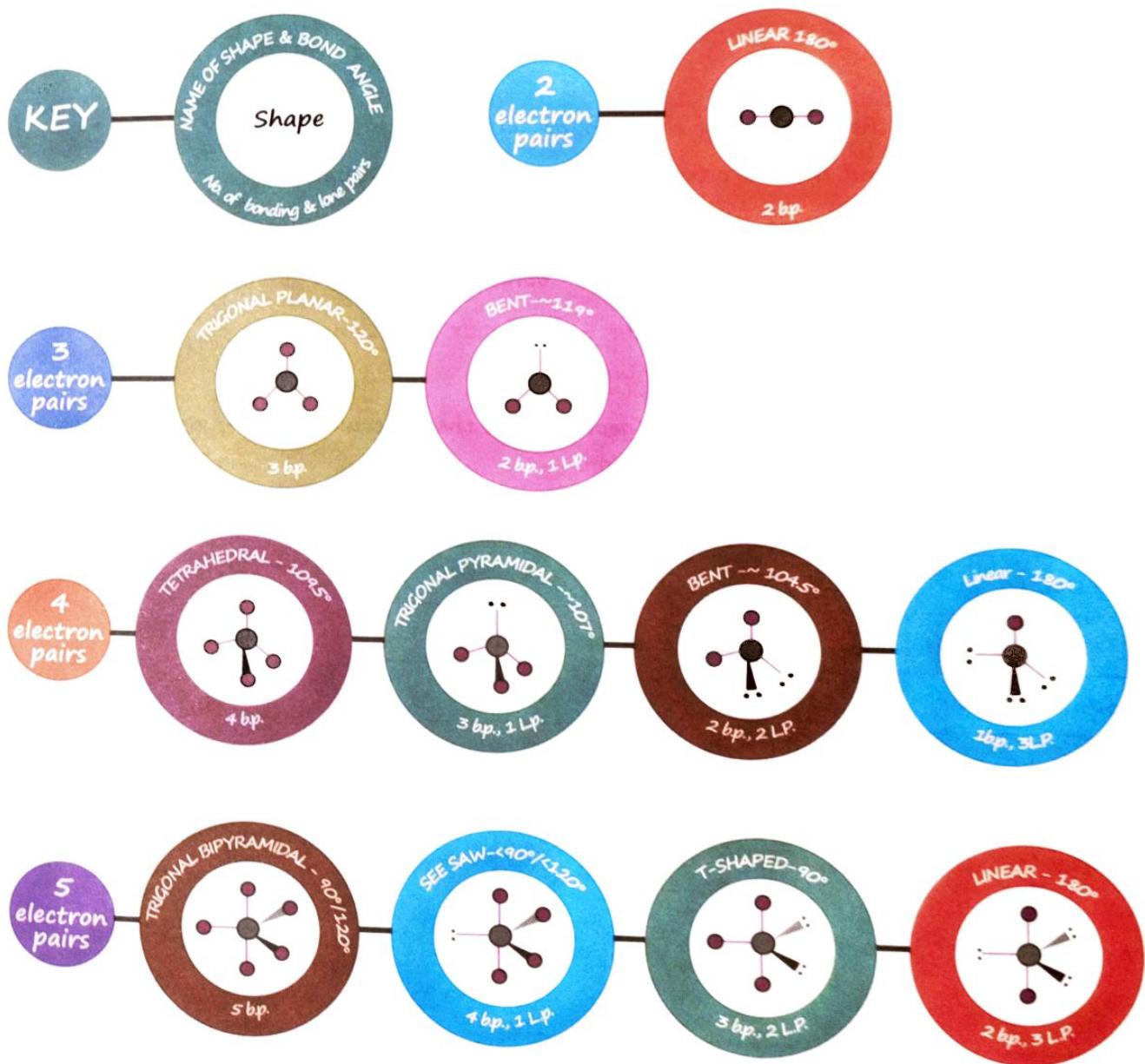


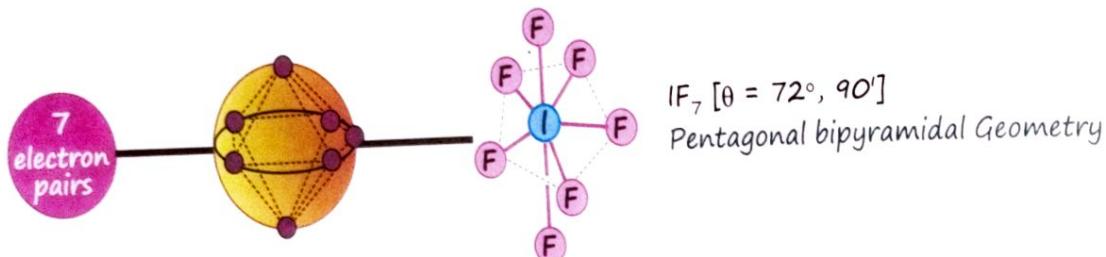
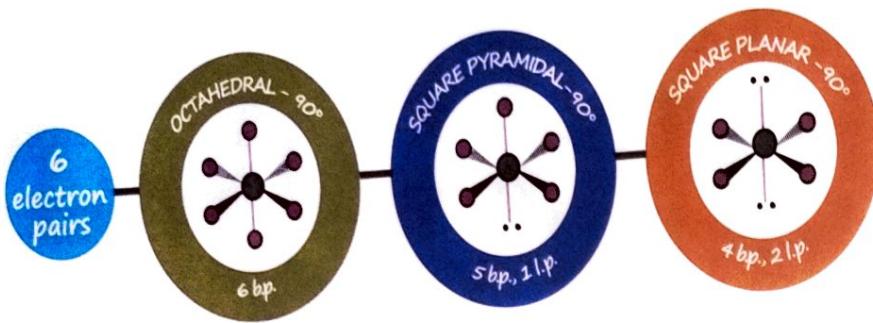
shape - Square planar

AB₇ Type Molecule



IF_7 [$\theta = 72^\circ, 90^\circ$]
Pentagonal bipyramidal Geometry





6. In the structure of SF_4 , the lone pair of electrons on S is

[27 June, 2022 (Shift-I)]

- (a) Equatorial position and there are two lone pair - bond pair repulsions at 90°.
- (b) Equatorial position and there are three lone pair - bond pair repulsions at 90°.
- (c) Axial position and there are three lone pair - bond pair repulsion at 90°.
- (d) Axial position and there are two lone pair - bond pair repulsion at 90°.

Sol. (a)

7. Based upon VSEPR theory, match the shape (geometry) of the molecules in List-I with the molecules in List-II and select the most appropriate option.

[27 June, 2022 (Shift-I)]

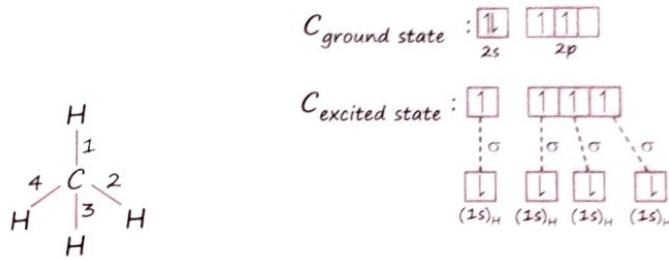
List-I (Shape)		List-II (Molecules)
A. T-shaped	I.	XeF_4
B. Trigonal planar	II.	SF_4
C. Square planar	III.	ClF_3
D. See-saw	IV.	BF_3

- (a) (A)-(I), (B)-(II), (C)-(III), (D)-(IV)
- (b) (A)-(III), (B)-(IV), (C)-(I), (D)-(II)
- (c) (A)-(III), (B)-(IV), (C)-(II), (D)-(I)
- (d) (A)-(IV), (B)-(III), (C)-(I), (D)-(II)

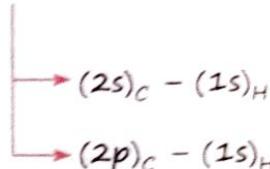
Sol. (b)

NEED OF NEW CONCEPT → (HYBRIDISATION)

Bonding in CH_4 according to VBT



□ 2 different types of overlapping

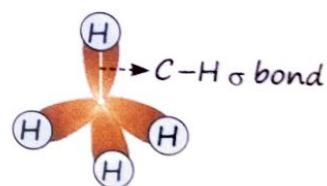
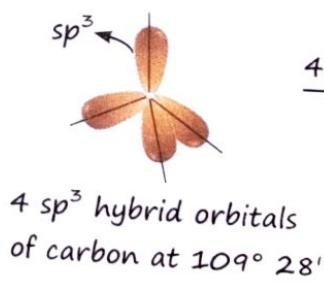
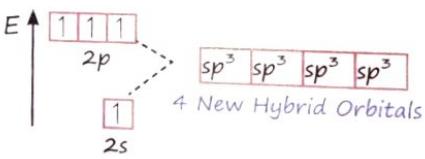
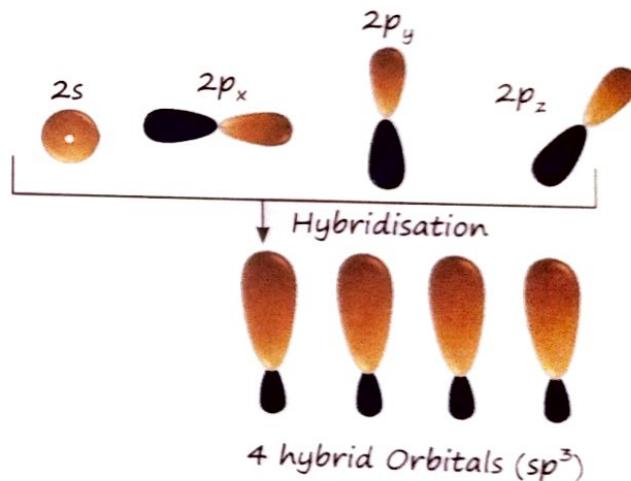
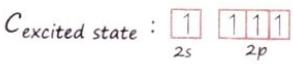


□ 2 Different bond lengths.

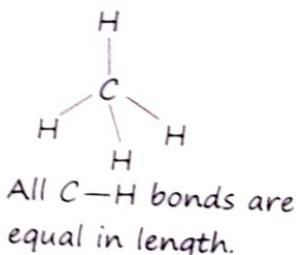
VBT predicts that the 3 bonds formed through s-p overlap would be the same and differ from the 4th bond formed through s-s overlap. This difference in bond types would result in unequal bond lengths which is not what is observed in methane.

Experimental Fact All C – H bonds are same in CH_4 . → This fact can be explained by new theory ⇒ Hybridisation

Hybridisation in CH_4



Overlapping between sp^3 hybrid orbital of carbon and $1s$ atomic orbital of hydrogen



HYBRIDISATION

Inter Mixing of pure atomic orbitals before bonding to produce new hybrid orbitals, specially for bonding purpose.

Postulates

- (i) It is a hypothetical concept.
- (ii) Only those orbitals can take part in hybridisation which have comparable (almost equal) energies.
- (iii) The number of hybrid orbitals generated will be equal to the number of pure atomic orbitals taking part in hybridisation.
- (iv) All 3 type of orbitals (having a pair of electrons or having a unpaired electron or completely empty) can take part in hybridisation.
- (v) The hybrid orbital generated will be represented by

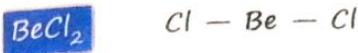
 Bigger lobe will be used for bonding.

Steric Number Rule

Steric number = No. of lone pairs + No. of side atoms

SN	Geometry	Hybridisation	Bond Angle
1	Linear	sp	$\theta = 180^\circ$
2	Trigonal planar	sp^2	$\theta = 120^\circ$
3	Tetrahedral	sp^3	$\theta = 109^\circ 28'$
4	Trigonal bi-pyramidal	sp^3d	$\theta = 90^\circ, 120^\circ$
5	Octahedral	sp^3d^2	$\theta = 90^\circ$
6	Pentagonal bi-pyramidal	sp^3d^3	$\theta = 90^\circ, 72^\circ$

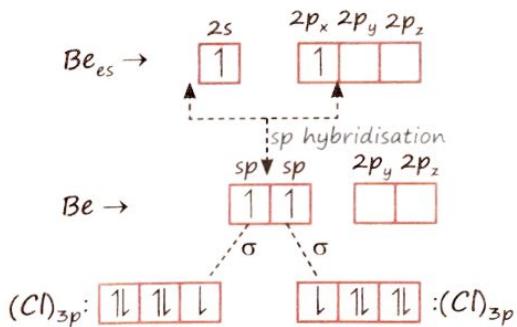
sp Hybridisation



□ $\text{SN} = \text{LP} + \text{SA} = 0 + 2$

= ② → sp hybridisation

□



□ 2 $\text{Be} - \text{Cl} \sigma$ bonds: $(\text{sp})_{\text{Be}} - (\text{3p})_{\text{Cl}}$

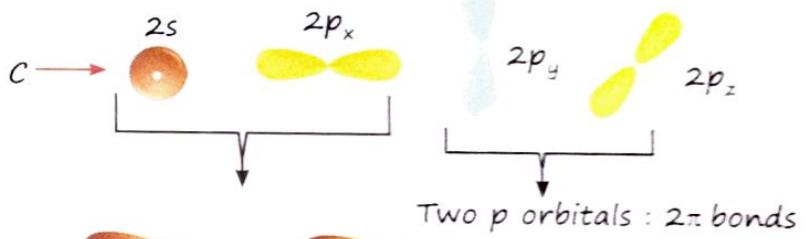
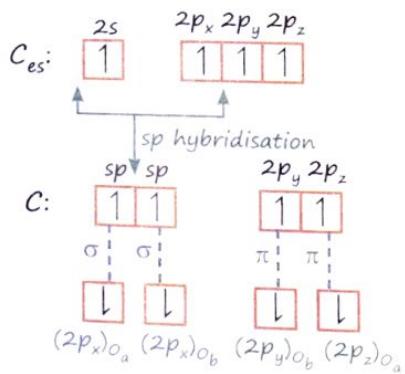
□ 2 vacant orbitals ($2p_y$ and $2p_z$) at Be.



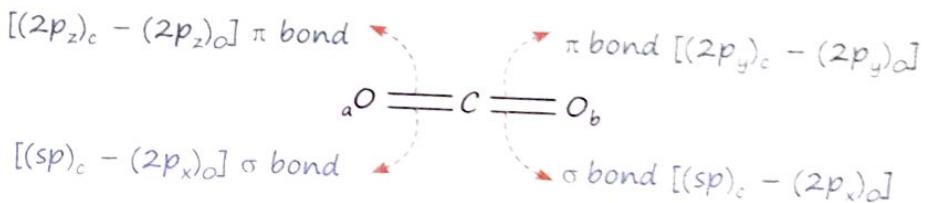
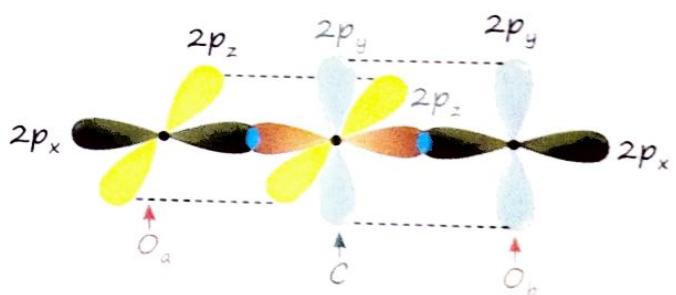
□ $\text{SN} = \text{LP} + \text{SA}$

= 0 + 2

= 2 → sp hybridisation



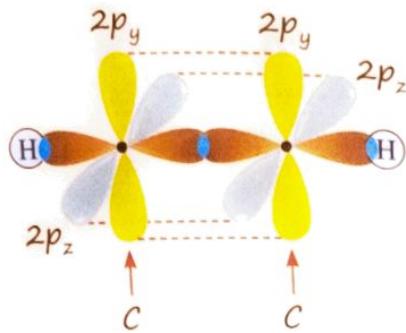
Two sp hybrid orbitals : 2σ bonds





- 2 C-H σ bonds : $(sp)_c - (1s)_H$
- 1 C-C σ bond : $(sp)_c - (sp)_c$
- 2 C-C π bonds : $(2p_y)_c - (2p_y)_c$ and $(2p_z)_c - (2p_z)_c$

Molecular plane \rightarrow $H-C \equiv C-H$



sp^2 Hybridisation

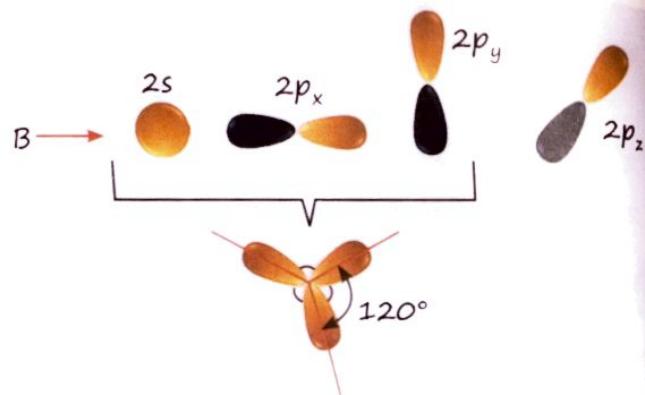


- B_{gs} :

2s	2p _x 2p _y 2p _z
1	1 1
 - B_{es} :

2s	2p _x 2p _y 2p _z
1	1 1 1
 - B_{es} :

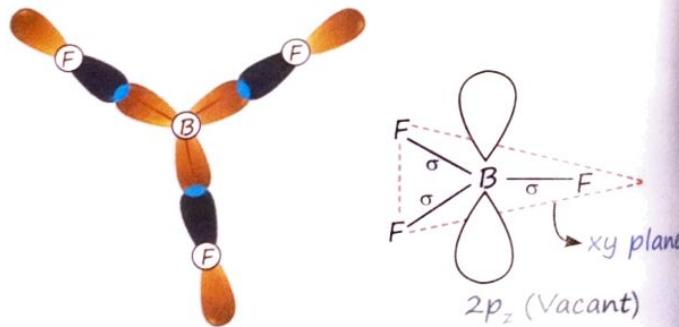
1 1 1	2p _z
-------	-----------------
- sp² Hybridisation
- 3, sp² hybrid orbitals



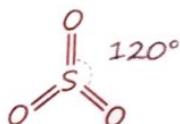
- 3 sp² hybrid orbitals are arranged at 120° before bonding.

- F:

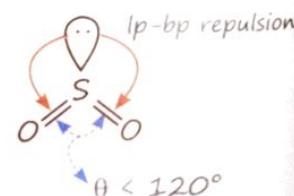
2s	2p _x 2p _y 2p _z
1 1	1 1 1
- 3 σ B - F bonds: $(sp^2)_B - (2p_x)_F$
- $sp^2 \equiv s + p_x + p_y$



- $SN = O + 3 = 3$
- $hyb^n = sp^2$
- Shape = Trigonal planar

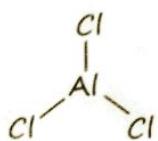


- $SN = 1 + 2 = 3$
- sp^2
- v shaped



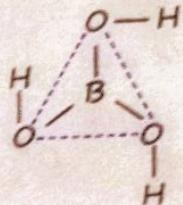
AlCl_3

- $SN = O + 3 = 3$
- sp^2
- Trigonal planar

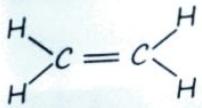


H_3BO_3

- $SN = O + 3 = 3$
- sp^2
- Trigonal planar

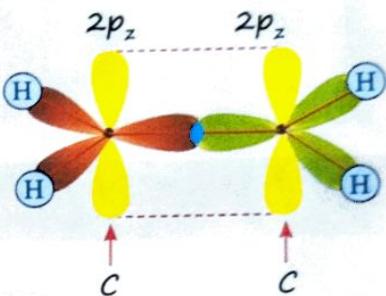
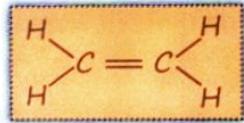


C_2H_4



- $sp^2 \equiv s + p_x + p_y$
- 4 C-H σ bonds : $(sp^2)_c - (1s)_H$
- 1 C-C σ bond : $(sp^2)_c - (sp^2)_c$
- 1 C-C π bond : $(2p)_c - (2p)_c$

- Molecular plane \rightarrow

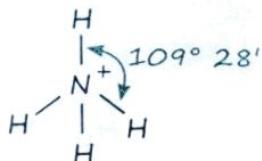


- Max. no of atoms in a plane = 6

sp^3 Hybridisation \rightarrow Geometry : Tetrahedral

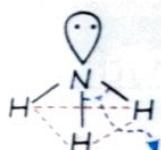
NH_4^+

- $SN = O + 4$
- sp^3
- Tetrahedral



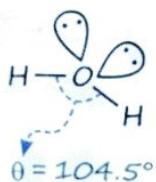
NH_3

- $SN = 1 + 3 = 4$
- sp^3
- Pyramidal



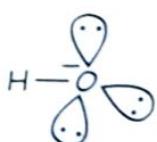
H_2O

- $SN = LP + SA$
 $= 2 + 2 = 4$
- sp^3
- V shape



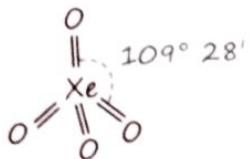
HO^-

- $SN = 3 + 1 = 4$
- sp^3
- Linear



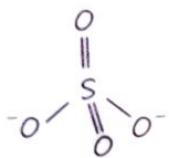
XeO_4

- ◻ $\text{SN} = \text{O} + 4 = 4$
- ◻ sp^3
- ◻ Tetrahedral



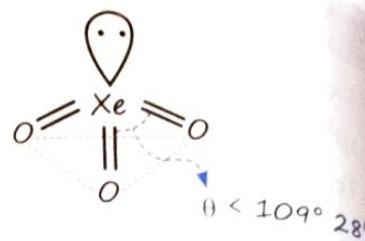
SO_4^{2-}

- ◻ $\text{SN} = \text{O} + 4 = 4$
- ◻ sp^3
- ◻ Tetrahedral



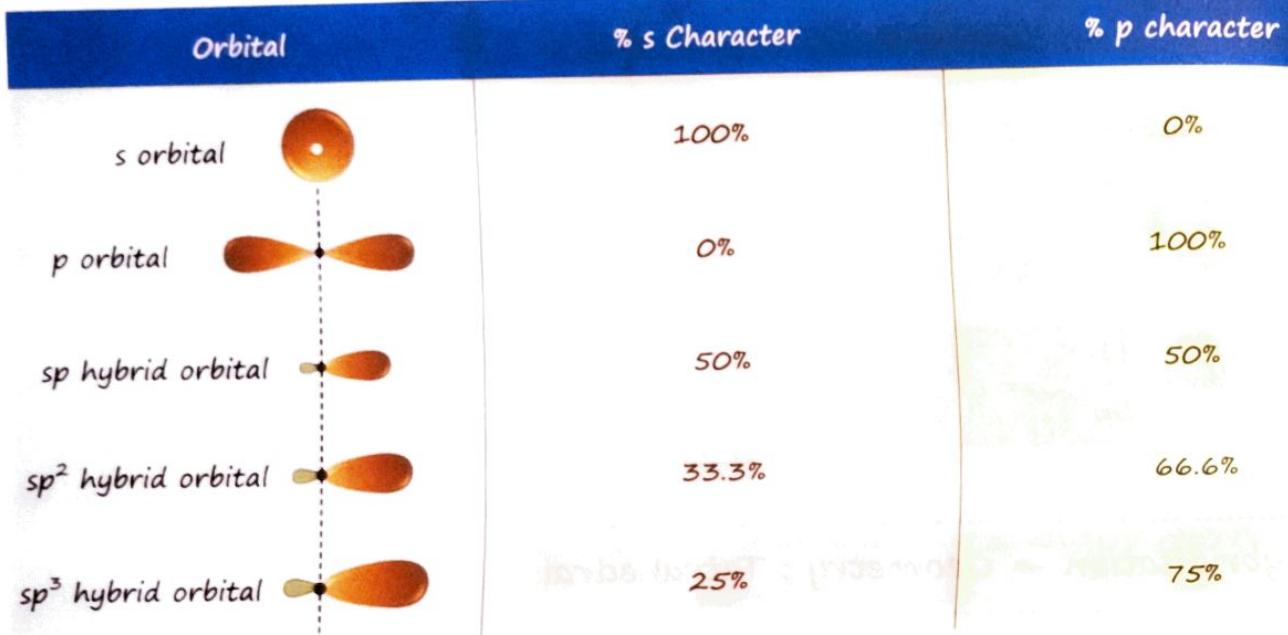
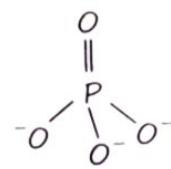
XeO_3

- ◻ $\text{SN} = 1 + 3 = 4$
- ◻ sp^3
- ◻ Pyramidal



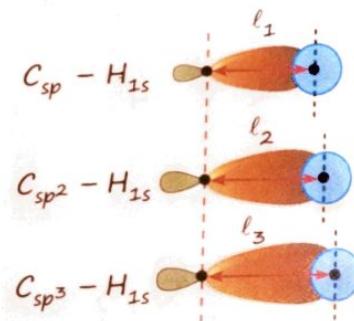
PO_4^{3-}

- ◻ $\text{SN} = \text{O} + 4 = 4$
- ◻ sp^3
- ◻ Tetrahedral



Bond Length & % s Character

- ◻ % s character: $C_{\text{sp}} > C_{\text{sp}^2} > C_{\text{sp}^3}$
- ◻ Bond length: $\ell_1 < \ell_2 < \ell_3$
- ◻
$$\text{Bond length} \propto \frac{1}{\% \text{ s character}} \propto \% \text{ p character}$$

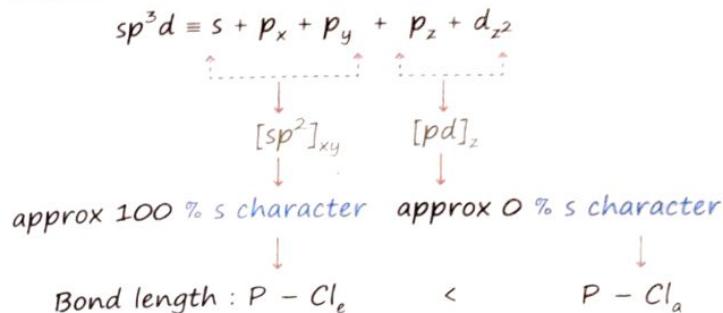


Electronegativity & % s Character

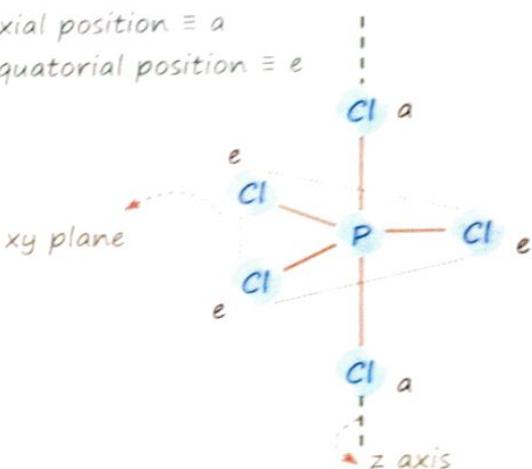
- ◻ $\text{EN} \propto \% \text{ s character}$
- ◻ % s character: $C_{\text{sp}} > C_{\text{sp}^2} > C_{\text{sp}^3}$
- ◻ Electronegativity: $C_{\text{sp}} > C_{\text{sp}^2} > C_{\text{sp}^3}$

sp^3d Hybridisation \rightarrow Geometry: Trigonal bipyramidal (TBP)

PCl_5



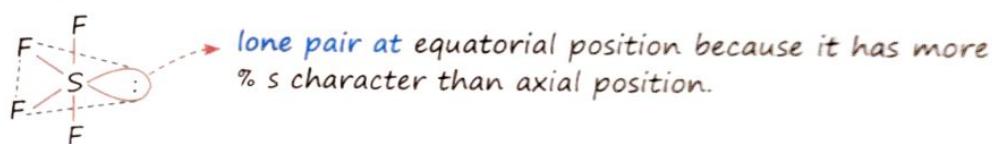
axial position $\equiv a$
equatorial position $\equiv e$



Bent's Rule

(1) Lone pair of electron prefers to occupy those hybrid orbitals which has greater % of s character.

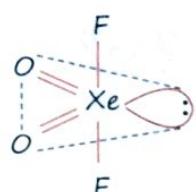
SF_4



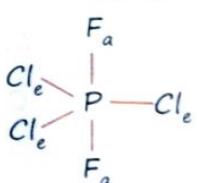
(2) A more electronegative atom prefers to occupy that hybrid orbital which has smaller % of s character (axial position).

XeO_2F_2

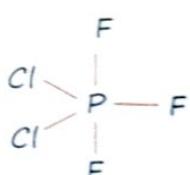
- $SN = LP + SA = 1 + 4 = 5$
- Geometry - TBP
- Shape - see saw



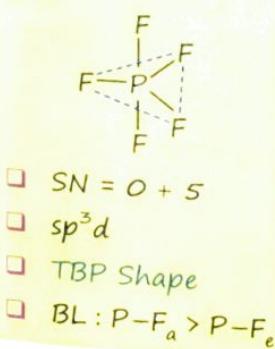
PCl_3F_2



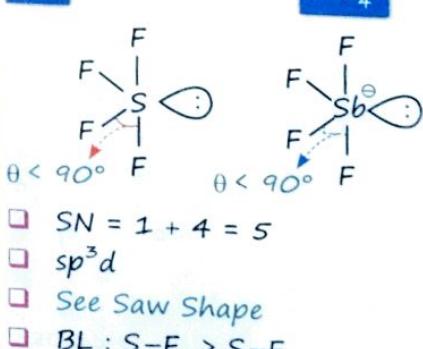
PCl_2F_3



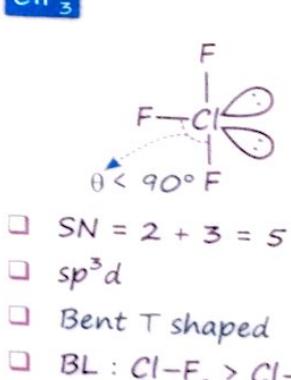
PF_5



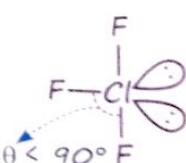
SF_4



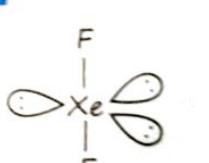
SbF_4^-



CIF_3

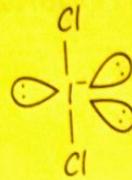


XeF_2

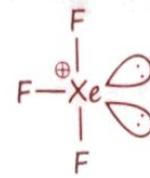


I₃⁻

- SN = 3 + 2 = 5
- sp³d
- Linear Shape

ICl₂⁻

- SN = 3 + 2 = 5
- sp³d
- Linear Shape

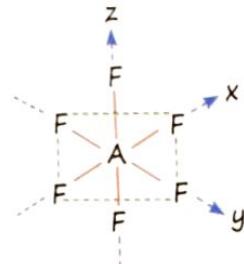
XeF₃⁺

- SN = LP + SA
= 2 + 3 = 5
- Bent T shaped

sp³d² Hybridisation: Geometry → Octahedral

AF₆

SF₆
PF₆⁻
SiF₆²⁻
AlF₆³⁻



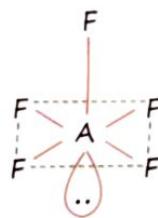
$$\text{sp}^3\text{d}^2 \equiv s + p_x + p_y + d_{x^2-y^2} + p_z + d_{z^2}$$

xy plane z axis

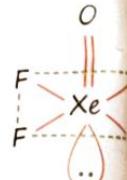
A	S	Si ²⁻	P ⁻	Al ³⁻
Valence shell electrons	6 4+2 5+1 3+3			

BrF₅, XeF₅⁺, ClF₅, IF₅, SF₅⁻

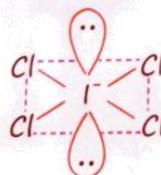
- AB₅ → A = Br, Xe⁺, I, Cl, S⁻
- SN = 1 + 5 = 6
- sp³d²
- Square pyramidal → shape
- No of bond angles at 90° → zero

XeOF₄

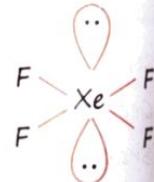
- SN = 1 + 5 = 6
- Square pyramidal → shape

ICl₄⁻

- SN = 2 + 4 = 6 (sp³d²)
- Square planar → shape

XeF₄

- Square planar → shape



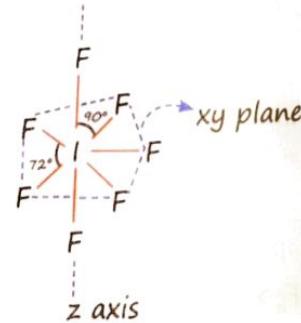
sp³d³ Hybridisation

IF₇

$$\text{s} + \text{p}_x + \text{p}_y + \text{d}_{x^2-y^2} + \text{d}_{xy} + \text{p}_z + \text{d}_{z^2}$$

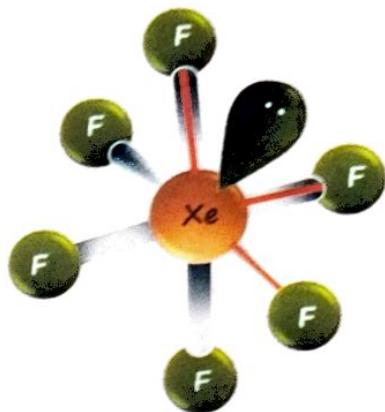
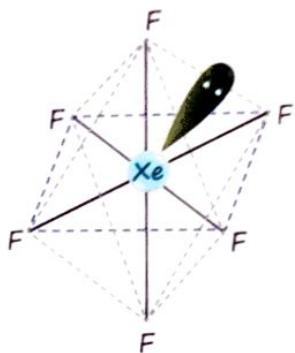
xy plane z axis

- SN = LP + SA = 0 + 7 = 7
- Pentagonal bipyramidal → shape
- θ → 90°/72°

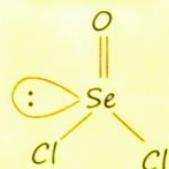
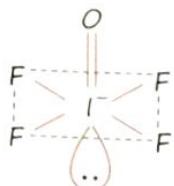
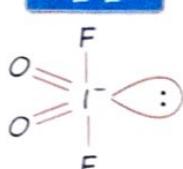
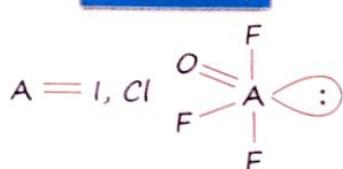
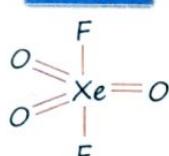
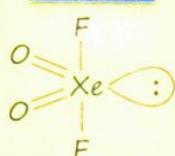
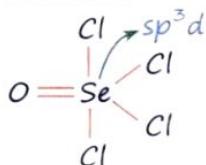
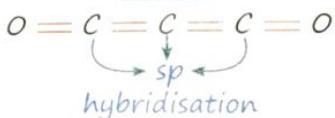
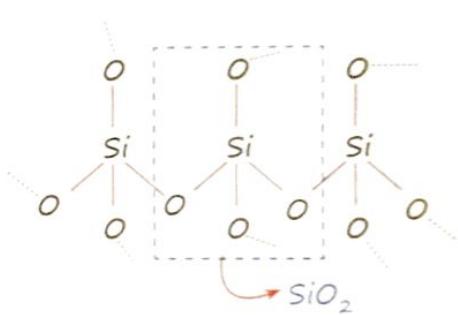
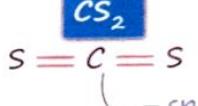
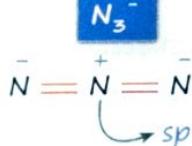




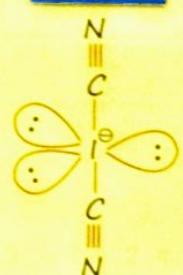
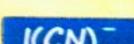
- SN = LP + SA = 1 + 6 = 7
- Shape → Distorted octahedral
Capped octahedral



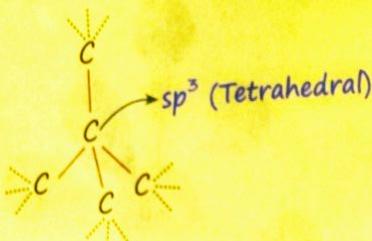
Some Important Molecules-



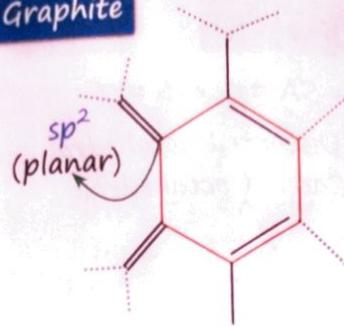
- Structure is like HCN



Diamond



Graphite



8. Number of lone pair(s) in $XeOF_4$ is/are

(a) 0

(b) 1

(c) 2

(d) 3

(IIT JEE 2004)

Sol. (b)

9. Molecular shape of SF_4 , CF_4 and XeF_4 are

(IIT JEE 2000)

(a) the same, with 2, 0 and 1 lone pair of electrons respectively

(b) the same, with 1, 1 and 1 lone pair of electrons respectively

(c) the different, with 0, 1 and 2 lone pair of electrons respectively

(d) the different, with 1, 0 and 2 lone pair of electrons respectively

Sol. (d)

10. Based on VSEPR theory, the number of 90° F-Br-F angles in BrF_5 is _____. (IIT JEE 2010)

Sol. [0]

11. The hybridisation of atomic orbitals of nitrogen in NO_2^+ , NO_3^- and NH_4^+ are

(IIT JEE 2000)

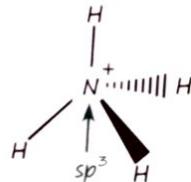
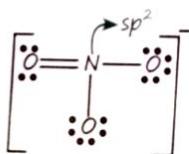
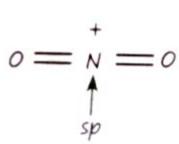
(a) sp , sp^3 and sp^2 respectively

(b) sp , sp^2 and sp^3 respectively

(c) sp^2 , sp and sp^3 respectively

(d) sp^3 , sp^3 and sp respectively

Sol. (b)



12. Match List-I with List-II:

List-I (Species)	List-II (Number of lone pairs of electrons on the central atom)
A. XeF_2	I. 0
B. XeO_2F_2	II. 1
C. XeO_3F_2	III. 2
D. XeF_4	IV. 3

Choose the most appropriate answer from the options given below:

- (a) (A)-(IV), (B)-(I), (C)-(II), (D)-(III)
 (c) (A)-(III), (B)-(IV), (C)-(II), (D)-(I)

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

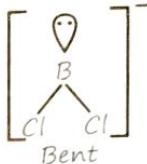
(d) (A)-(IV), (B)-(II), (C)-(I), (D)-(III)

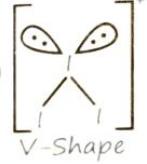
Sol. (d) XeF_2 Lone Pair = 3 XeO_2F_2 Lone Pair = 1 XeO_3F_2 Lone Pair = 0 XeF_4 Lone Pair = 2

13. Amongst the following, the number of species having the linear shape is ____.

XeF_2 , I_3^+ , C_3O_2 , I_3^- , CO_2 , SO_2 , BeCl_2 and BCl_2^-

[30 Jan, 2023 (Shift-I)]

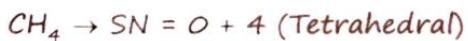
Sol. [5] (i)  Bent
 (ii) $\text{Cl}-\text{Be}-\text{Cl}$ Linear
 (iii)  Linear
 (iv) XeF_2 - Linear

(v)  V-Shape
 (vi) CO_2 - Linear
 (vii) C_3O_2 ($\text{O}=\text{C}=\text{C}=\text{O}$) Linear
 (viii) SO_2 - Bent

Iso-structural Species and Iso-electronic Species

Iso-structural Species

- Species having same shape



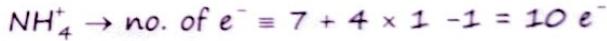
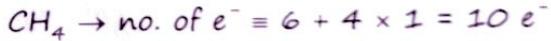
- Shape \rightarrow Distorted octahedral

$$\text{Xe} \equiv \text{Br}^- \equiv \text{Se}^{2-} \equiv \text{Te}^{2-}$$

No. of e^- in valence shell $\rightarrow 8$

Iso-electronic Species

- Species having same no. of electrons

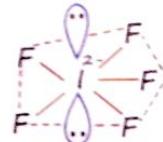


- $\text{Xe} \equiv \text{I}^{2-} \rightarrow 8e^-$ in valence shell

- Shape \rightarrow Pentagonal planar

$$\text{no. of } e^- \text{ in } \text{XeF}_5^- \equiv 54 + 5 \times 9 + 1 = 100$$

$$\text{no. of } e^- \text{ in } \text{IF}_5^{2-} \equiv 53 + 5 \times 9 + 2 = 100$$

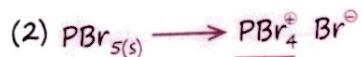


Hybridisation in Solid State

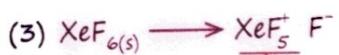


hybⁿ of cationic part of $\text{PCl}_5 \equiv \text{PCl}_4^+ \equiv \text{sp}^3$ [Tetrahedral]

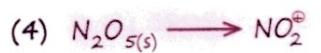
hybⁿ of anionic part of $\text{PCl}_5 \equiv \text{PCl}_6^- \equiv \text{sp}^3 \text{d}^2$ [Octahedral]



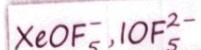
sp³ hybⁿ [Tetrahedral]



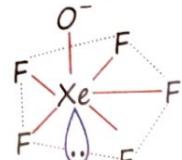
sp³d² [Sq. Pyramidal]



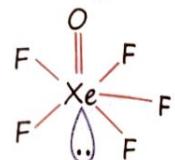
Cation	Anion
$\begin{array}{c} \text{O}=\overset{+}{\text{N}}=\text{O} \\ \text{sp hybrid} \\ \text{Linear} \end{array}$	$\begin{array}{c} \text{O}-\overset{\circ}{\text{N}}=\text{O} \\ \text{sp}^2 \text{ hybrid} \\ \text{Trigonal planar} \end{array}$



Pentagonal Pyramidal shape



(-)ve charge at oxygen



(-)ve charge at xenon

Both structures are acceptable.

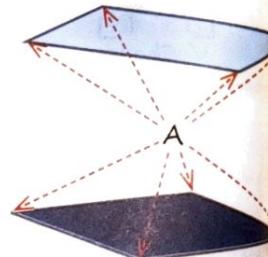
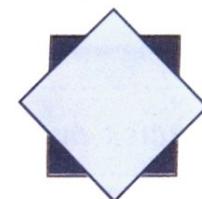
Pentagonal Pyramid



A pentagonal pyramid has 5 vertices, ten edges, and six faces.

Square antiprismatic molecular geom

- TaF_8^{3-}
- IF_8^-
- XeF_8^{2-}



Ideal square antiprism

14. Which of the following contains a maximum number of lone pairs on the central atom?

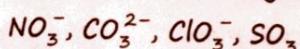
(IIT JEE 2005)

- (a) ClO_3^- (b) XeF_4^- (c) SF_4 (d) I_3^-

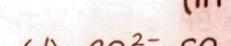
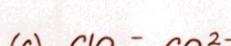
Sol. (d)

15. Which of the following are isoelectronic and isostructural?

(IIT JEE 2005)



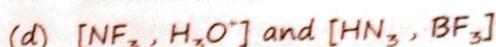
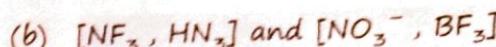
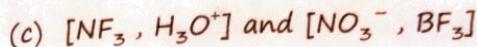
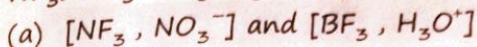
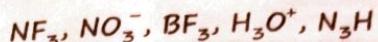
- (a) $\text{NO}_3^-, \text{CO}_3^{2-}$ (b) $\text{SO}_3, \text{NO}_3^-$



Sol. (a)

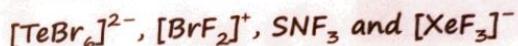
16. Among the following species, identify the isostructural pairs.

(IIT JEE 1996)



Sol. (c)

17. The sum of the number of lone pairs of electrons on each central atom in the following species is



(Atomic numbers : N = 7, F = 9, S = 16, Br = 35, Te = 52, Xe = 54)

(JEE Adv. 2017)

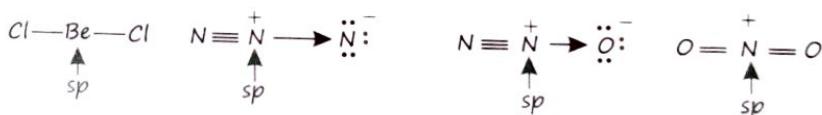
Sol. [6]

S.N.	Species	No. of σ - bonds with central atom	No. of LP at central atom
(i)	$[TeBr_6]^{2-}$	6	1
(ii)	$[BrF_2]^+$	2	2
(iii)	SNF_3	4	0
(iv)	$[XeF_3]^-$	3	3

18. Among the triatomic molecules/ions $BeCl_2$, N_3^- , N_2O , NO_2^+ , O_3 , SCl_2 , ICl_2^- , I_3^- and XeF_2 , the total number of linear molecules/ion(s) where the hybridisation of the central atom does not have contribution from the d-orbitals(s) is [atomic number of S = 16, Cl = 17, I = 53 and Xe = 54]

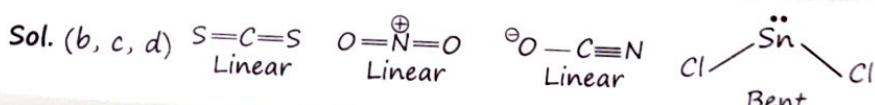
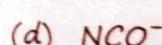
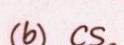
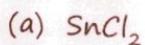
(JEE Adv. 2015)

Sol. [4]



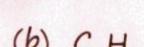
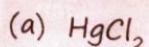
19. The linear structure assumed by

(IIT JEE 1991)



20. CO_2 is isostructural with

(IIT JEE 1986)



Sol. (a, b) CO_2 , $HgCl_2$, C_2H_2 are all linear.

NO. OF $p\pi - p\pi$ BONDS/NO. OF $p\pi - d\pi$ BONDS

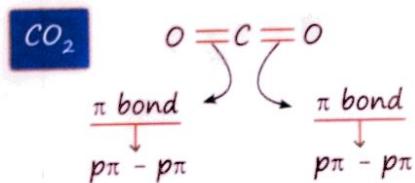
Orbital	π Bond
s	Can not form π bond
p	Can form π bond
d	Can form π bond

Period no = 2

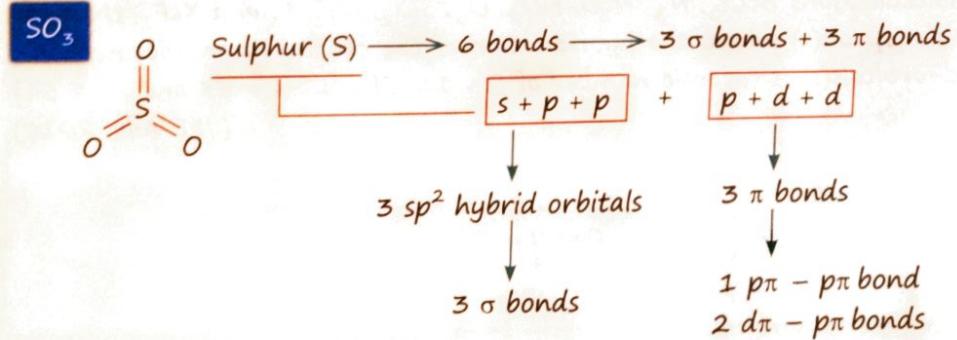
s	X
p	✓
d	not available in 2 nd period elements.

Period no > 2	π Bond
s	X
p	✓
d	✓

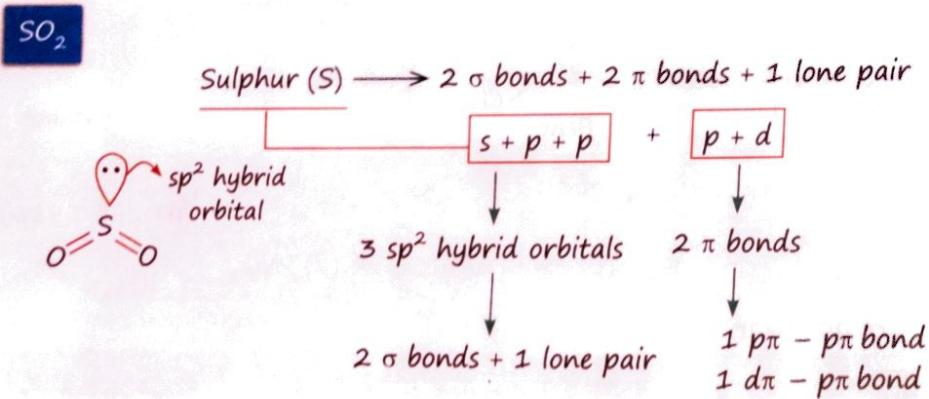
- If central atom or side atom is from period no 2 (B,C,N,O) then only p orbital can make π bond.
- If central atom or side atom is from period no > 2 (Al, Si, P, S, Cl, Xe) then p and d both can make π bond.



- overlapping between p orbital of carbon and p orbital of oxygen makes π bond.
- No. of $p\pi - p\pi$ bonds = 2

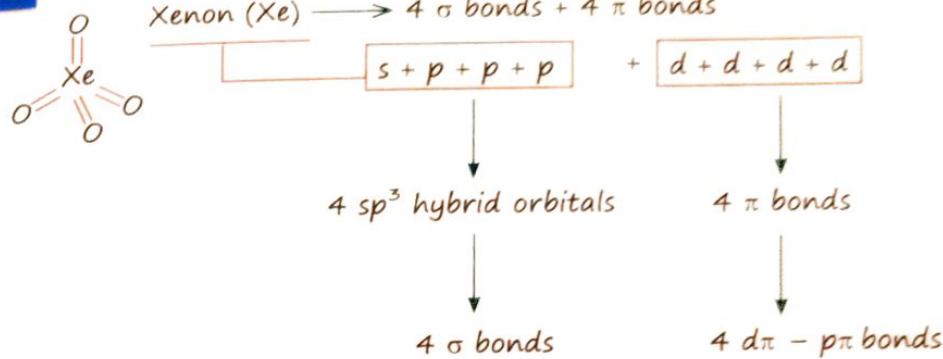


3 π bonds	
Sulphur	Oxygen
1. p	p
2. d	p
3. d	p



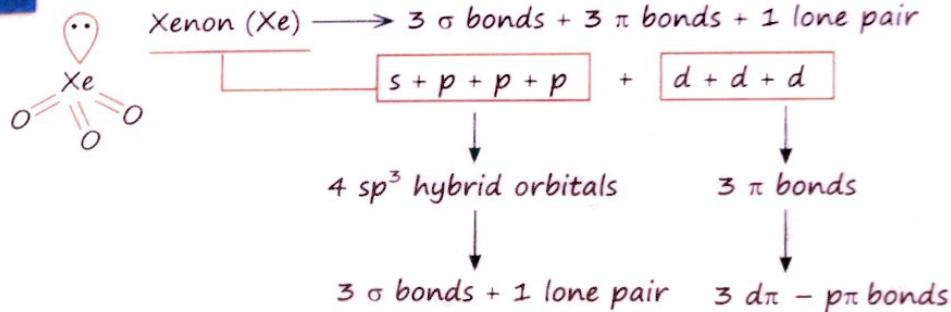
2 π bonds	
Sulphur	Oxygen
1. p	p
2. d	p

XeO_4



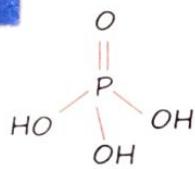
4 π bonds	
Xenon	Oxygen
1. d	p
2. d	p
3. d	p
4. d	p

XeO_3

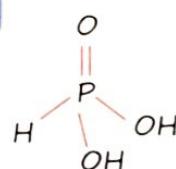


4 π bonds	
Xenon	Oxygen
1. d	p
2. d	p
3. d	p

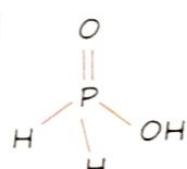
H_3PO_4



H_3PO_3



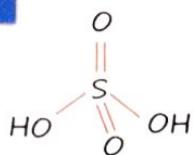
H_3PO_2



◻ Hybridisation of P : sp^3

◻ 1 $p\pi - d\pi$ bond

H_2SO_4



◻ Hybridisation of S : sp^3

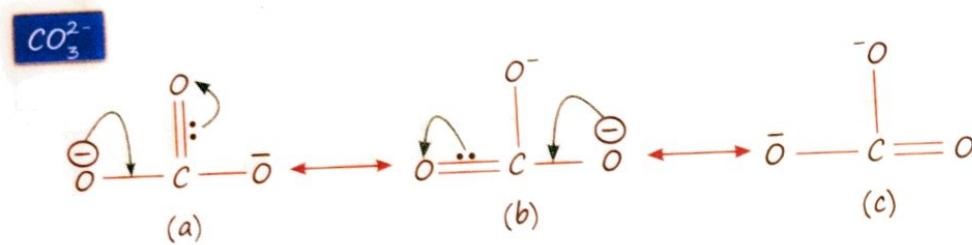
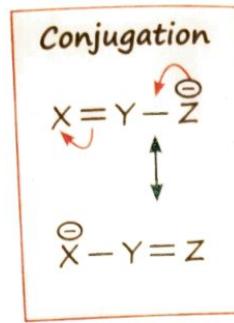
◻ 2 $p\pi - d\pi$ bond

H_2SO_3

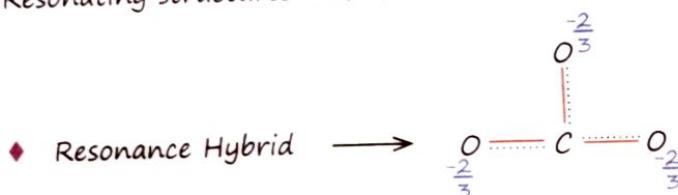


RESONANCE

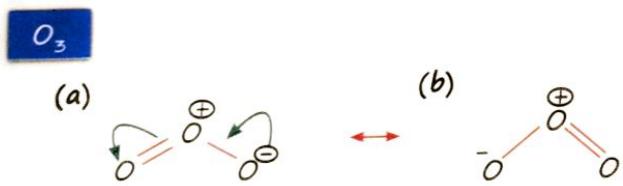
- ❑ Delocalisation of pi electrons
 - ❑ Conjugation - Necessary condition for resonance



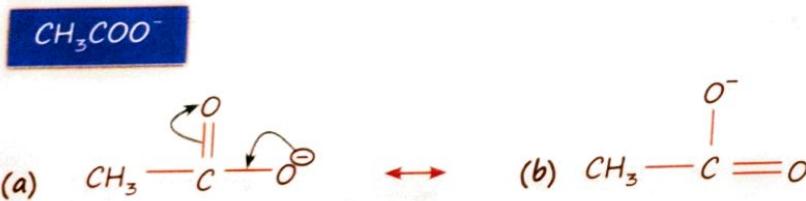
- Resonating structures $\equiv a, b, c$



- ❑ No. of bonds b/w 2 atoms [Bond order] = $\frac{\sigma + \pi}{\sigma} = \frac{3 + 1}{3} = 1.33 \rightarrow 1\sigma \text{ bond} + \frac{1}{3}\pi \text{ bonds.}$
 - ❑ Formal charge on oxygen = $\frac{-2}{3}$
 - ❑ Bond length = All C - O bonds are same due to resonance

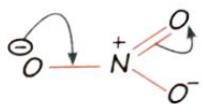
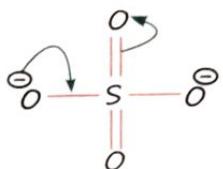
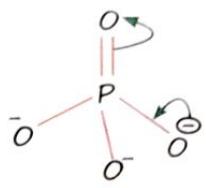


- ❑ Resonating structures = a & b
 - ❑ Resonance Hybrid = 
 - ❑ Bond order = $\frac{\sigma + \pi}{\sigma} = \frac{2 + 1}{2} = 1.5$
 - ❑ Bond length = All O - O bonds are same.



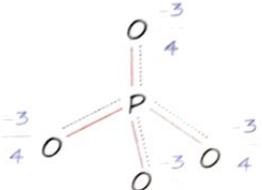
- Resonance Hybrid - 
 - CO bond order = $\frac{\sigma + \pi}{\sigma} = \frac{2 + 1}{2} = 1.5$
 - Bond length \equiv All $C - O$ bonds are same

Resonance Hybrid

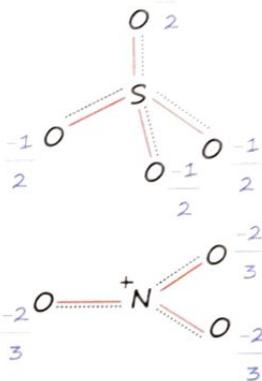


Bond Order

$$BO = \frac{\sigma + \pi}{\sigma} = \frac{4+1}{4} = 1.25$$

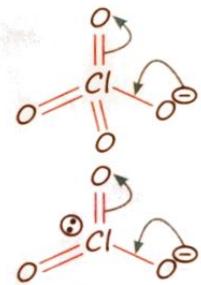
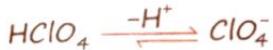


$$BO = \frac{4+2}{4} = 1.5$$



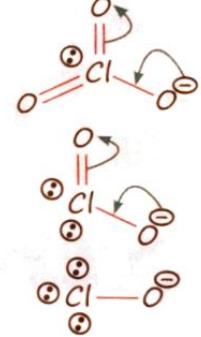
$$BO = \frac{\sigma + \pi}{\sigma} = \frac{3+1}{3} = 1.33$$

Formal Charge



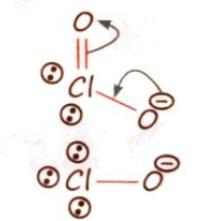
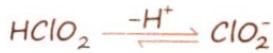
$$\frac{-1}{4}$$

$$BO = \frac{\sigma + \pi}{\sigma} = \frac{4+3}{4} = 1.75$$



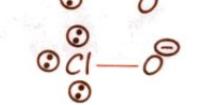
$$\frac{-1}{3}$$

$$BO = \frac{3+2}{3} = 1.66$$



$$\frac{-1}{2}$$

$$BO = \frac{2+1}{2} = 1.5$$



$$-1$$

$$BO = 1$$

- Acidity \propto Stability of conjugate base $\propto \frac{1}{\text{formal charge}}$
- Acidic Strength : $a > b > c > d$

(JEE. Adv 2015)

21. The correct statement(s) regarding,

- HClO , (ii) HClO_2 , (iii) HClO_3 and (iv) HClO_4 is (are)
- The number of $\text{Cl}=\text{O}$ bonds in (ii) and (iii) together is two
 - the number of lone pair of electrons on Cl in (ii) and (iii) together is three
 - the hybridisation of Cl in (iv) is sp^3
 - amongst (i) to (iv), the strongest acid is (i)

Sol. (b, c)

DRAGO COMPOUNDS

- In some cases (like group 15, 16 hydrides from 3rd or higher period), the central atom does not participate in hybridisation.
- Bonding occurs through pure p orbitals, leading to a bond angle of approximately 90° .



bond angle θ is near to ideal angle $109^\circ 28'$ of sp^3 hybridisation.

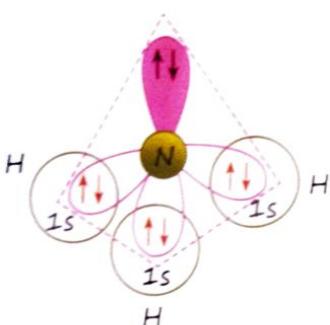
PH_3	93.6°	H_2S	92°
ASH_3	91.8°	H_2Se	91°
SbH_3	91.3°	H_2Te	90°

bond angle $\theta \approx 90^\circ$

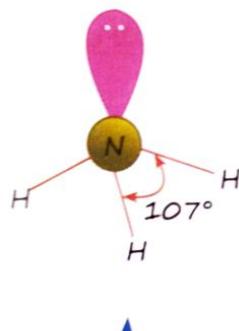
No, Hybridisation

Pure p orbital of central atom overlap
1s atomic orbital of side atom H.

Bonding in NH_3

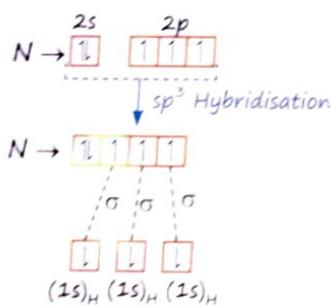


Orbital overlap in NH_3

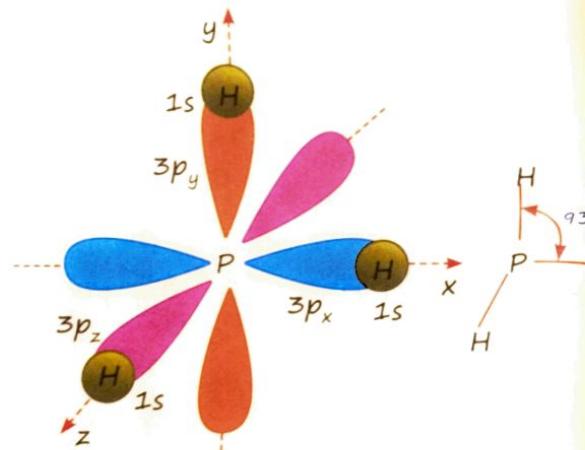


Pyramidal shape

In order to make N - H bonds sp^3 hybrid orbitals of nitrogen overlap with 1s atomic orbital of hydrogens.

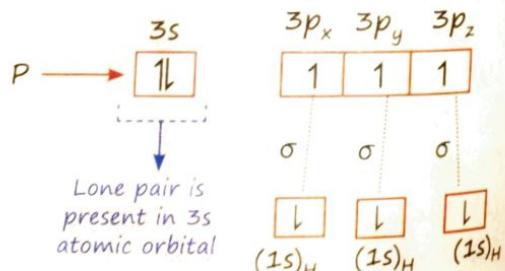


- 3 N - H σ bonds : $(sp^3)_N - (1s)_H$
- 1 lone pair in sp^3 hybrid orbital of nitrogen.



Orbital overlap in PH_3

In order to make P - H bonds p - atomic orbitals (p_x, p_y, p_z) of phosphorus overlap with 1s atomic orbital of hydrogens.



BOND ANGLE

Angle between two bonds.

Molecules without Lone Pair

Hybridisation $\rightarrow \theta : sp > sp^2 > sp^3$

$\theta : CO_2 > CO_3^{2-} > CH_4$



$\theta : CF_4 = CH_4 = NH_4^+ = XeO_4 = 109^\circ 28'$ [sp³ hybridisation]

$\theta : NO_2^+ = CO_2 > SO_3 > XeO_4$



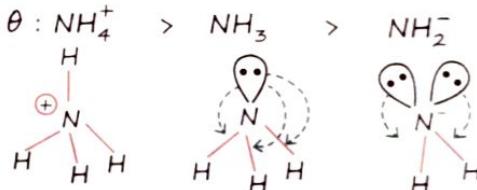
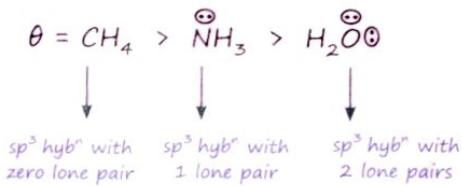
$\theta : BF_3 = BCl_3 = BBr_3 = 120^\circ$

[sp² hybridisation]



Molecules with Lone Pair

1. If same Hybridisation \rightarrow No of lone pair $\uparrow : \theta \downarrow$



2. No. of lone pair : same \Rightarrow Size of CA $\uparrow : \text{Bond angle} \downarrow$

$\theta : \ddot{N}H_3 > \ddot{P}H_3 > \ddot{As}H_3 > \ddot{Sb}H_3$

$\theta : \ddot{N}Cl_3 > \ddot{P}Cl_3 > \ddot{As}Cl_3 > \ddot{Sb}Cl_3$

$\theta : OF_2 > SF_2$

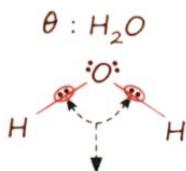
$\theta : OCl_2 > SCl_2 > SeCl_2 > TeCl_2$

$\theta : NF_3 > PF_3 > AsF_3 > SbF_3$

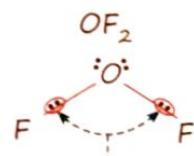
3. No of lone pair : same

E.N. of S.A. $\uparrow : \text{Bond angle} \downarrow$

$\theta : NH_3 > NF_3$



$>$



Bond pair - bond pair repulsion \uparrow

Bond angle \uparrow

$\theta = 104.5^\circ$

Bond pair - bond pair repulsion \downarrow

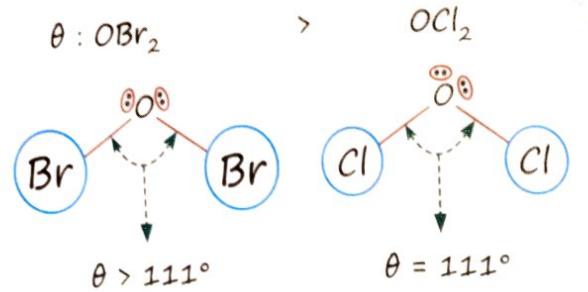
Bond angle \downarrow

$\theta < 104.5^\circ$

4.

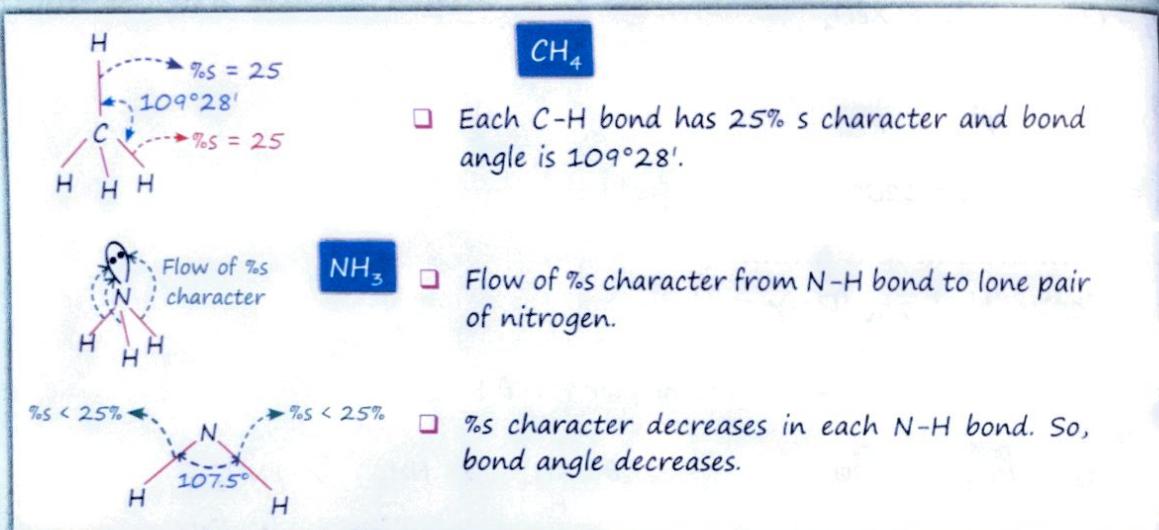
No of lone pair : same

Size of S.A.↑ : Bond angle↑

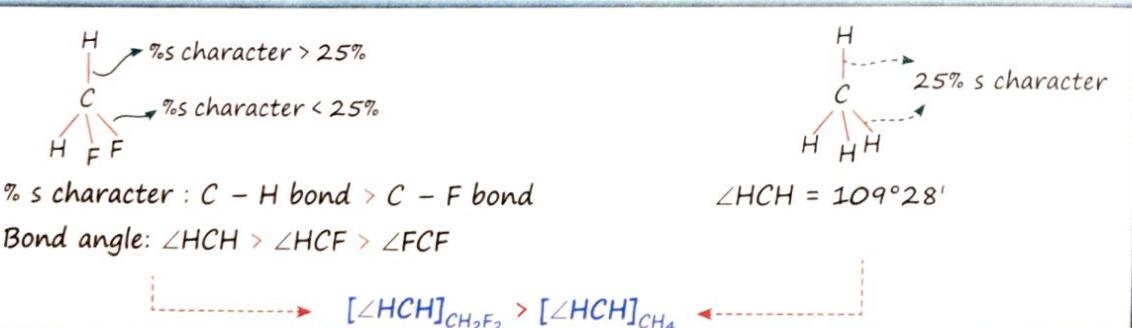
 $\theta : \ddot{\text{P}}\text{Br}_3 > \ddot{\text{P}}\text{Cl}_3 > \ddot{\text{P}}\text{F}_3$ **Note****Bent's Rule**

% s character ↑ : Bond Angle ↑

1. Lone pair orbitals must adopt a higher s character to stabilise the unshared, tightly bound nonbonding electrons.



2. Electronegative element prefer hybrid orbital having less s character and more p character while less electronegative substituents prefer hybrid orbital having more s character.



(IIT JEE 1999)

22. In compounds of type ECl_3 , where E = B, P, As or Bi, the angles $\text{Cl}-\text{E}-\text{Cl}$ is in order

(a) $\text{B} > \text{P} = \text{As} = \text{Bi}$ (b) $\text{B} > \text{P} > \text{As} > \text{Bi}$ (c) $\text{B} < \text{P} = \text{As} = \text{Bi}$ (d) $\text{B} < \text{P} < \text{As} < \text{Bi}$

Sol. (b)

23. For OF_2 molecule, consider the following:

- (A) Number of lone pairs on oxygen is 2.
- (C) Oxidation state of O is -2.
- (E) Molecular geometry is linear.

(B) FOF angle is less than 104.5° .

(D) Molecule is bent 'V' shaped.

Correct options are:

- (a) C, D, E only
- (b) B, E, A only
- (c) A, C, D only
- (d) A, B, D only

Sol. (d)

Bond Length

Size \uparrow : Bond length \uparrow

$\text{H} - \text{F} < \text{H} - \text{Cl} < \text{H} - \text{Br} < \text{H} - \text{I}$: Bond length

$\text{C} - \text{F} < \text{C} - \text{Cl} < \text{C} - \text{Br} < \text{C} - \text{I}$: Bond length

Bond order \downarrow : Bond length \uparrow

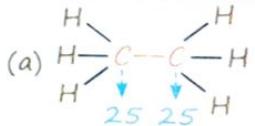
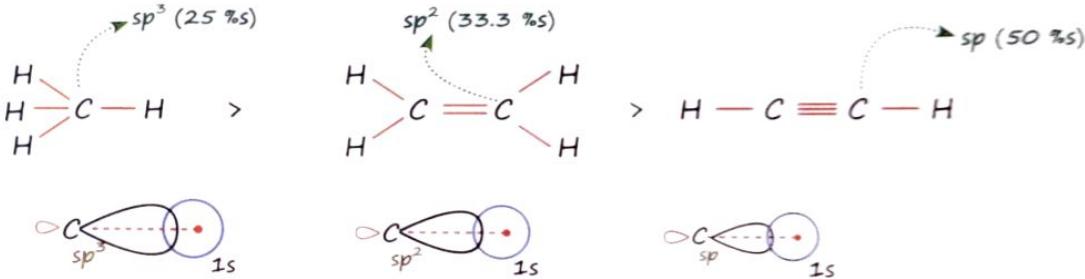
$\text{C} \equiv \text{C} < \text{C} = \text{C} < \text{C} - \text{C}$

$\text{C} \equiv \text{N} < \text{C} = \text{N} < \text{C} - \text{N}$

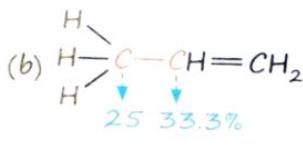
$\text{N} \equiv \text{N} < \text{N} = \text{N} < \text{N} - \text{N}$

%s character \uparrow : Bond length \downarrow

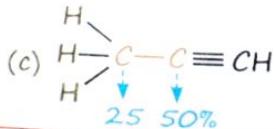
C-H Bond length :



- %s character : c > b > a
- C-C Bond length : c < b < a



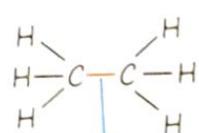
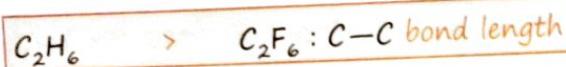
- (i) $\text{H}_2\text{C}=\text{HC}-\text{CH}=\text{CH}_2$
- 33.3% 33.3%



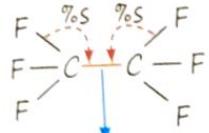
- (ii) $\text{H}_2\text{C}=\text{HC}-\text{C}\equiv\text{CH}$
- 33.3% 50%
- (iii) $\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}$
- 50% 50%

- %s character : iii > ii > i
- Bond length : iii < ii < i

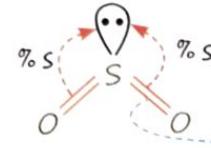
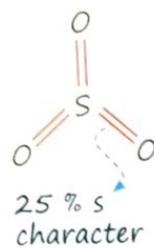
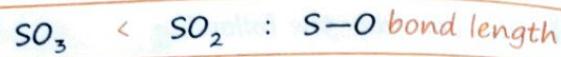
Bond length : a > b > c > i > ii > iii



less % s character

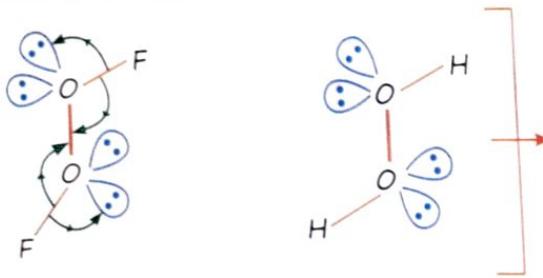
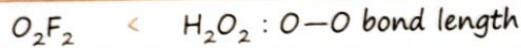


% s character Concentrates in C - C bond

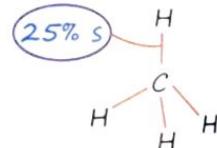
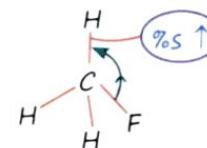
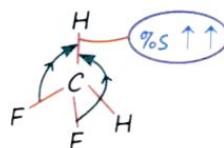
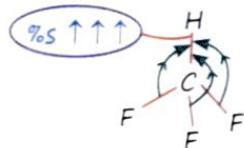
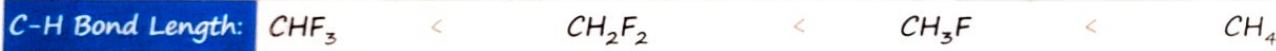
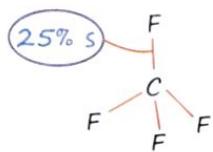
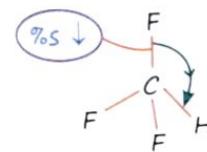
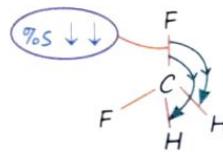
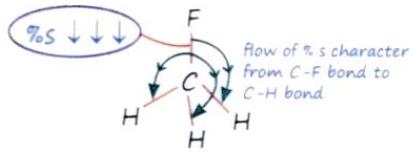


❑ % s character < 25%

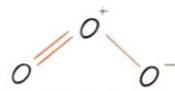
❑ Less % s character → more bond length



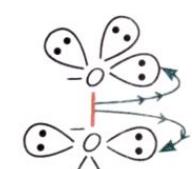
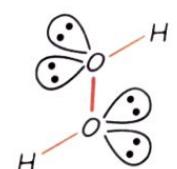
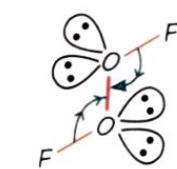
- ❑ Order of % s character in O - O bond : $O_2F_2 > H_2O_2$
- ❑ O - O bond length : $O_2F_2 < H_2O_2$
- ❑ % s character : $O - F < O - H$
- Bond length : $O - F > O - H$



$$BO = 2$$



$$BO = \frac{\sigma + \pi}{\sigma} = \frac{2+1}{2} = 1.5$$

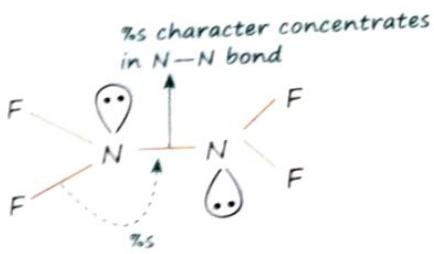
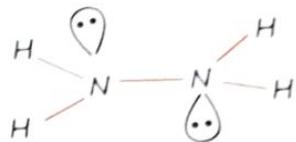


Order of %s character in O-O bond: $O_2F_2 > H_2O_2$

O-O bond length: $O_2F_2 < H_2O_2$

Less %s character in O-O bond in O_2^{2-} than O_2F_2 and H_2O_2

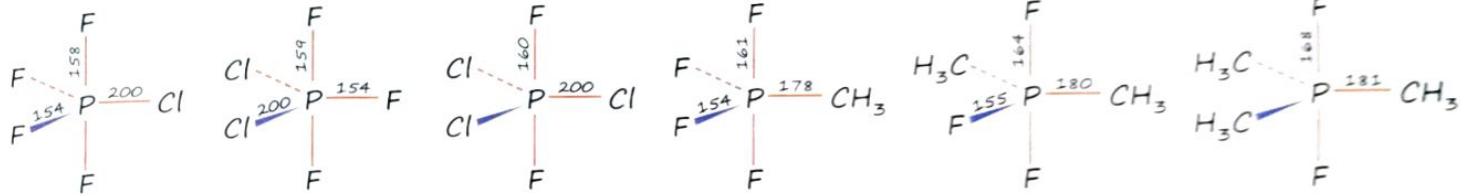
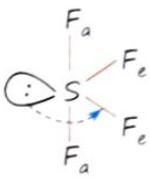
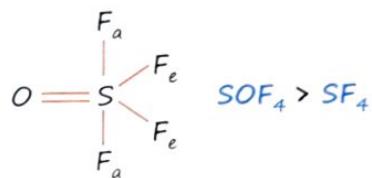
N-N Bond length: $N_2H_4 > N_2F_4$



O-F Bond length: $O_2F_2 > OF_2$



S-F(eq) Bond length:



24. O-O bond length in H_2O_2 is X than the O-O bond length in F_2O_2 . The O-H bond length in H_2O_2 is Y than that of the O-F bond in F_2O_2 .

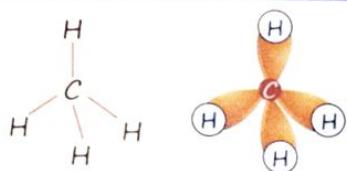
Choose the correct option for X and Y from the given below.

[1 Feb, 2023 (Shift-I)]

- (a) X - shorter, Y - shorter
- (b) X - shorter, Y - longer
- (c) X - longer, Y - longer
- (d) X - longer, Y - shorter

Sol. (d)

Equivalent Hybrid Orbitals

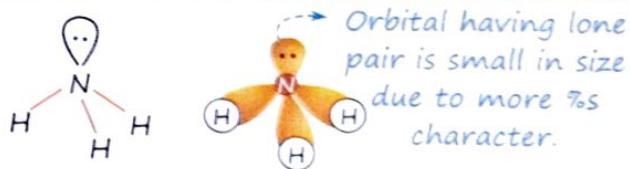


- All 4 hybrid orbitals are equivalent in energy and size.

- Central atom without lone pair and attached with same side atoms

Example: XeO_4 , $BeCl_2$, BF_3

Non-equivalent Hybrid Orbitals



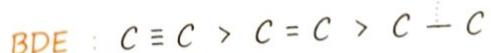
- CA with LP or attached with different side atoms

Example: H_2O , NH_3 , CH_2F_2

Bond Dissociation Energy

Minimum energy required to break a bond is known as bond dissociation energy.

(1) $BDE \propto \text{Bond Order}$



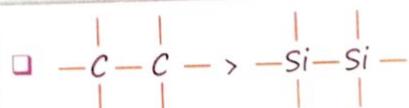
Easy to break : $BDE \downarrow$

(2) $BDE \downarrow : \text{Bond Length} \uparrow$

□ Bond length: $C \equiv C > C \equiv N > N \equiv N$

(Size: $C > N$)

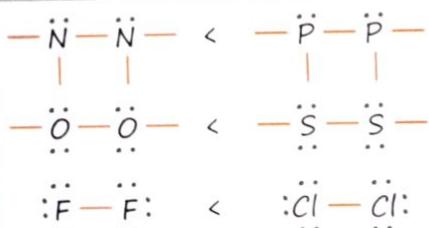
$BDE : C \equiv C < C \equiv N < N \equiv N$



Order of bond length: $C-C < Si-Si$

Bond dissociation energy: $C-C > Si-Si$

(3) $BDE \downarrow : \text{LP-LP Repulsion} \uparrow$



- In these 3 cases, bonded atoms have lone pair(s) so, are going to consider lone pair-lone pair repulsion as a major factor in order to compare the bond dissociation energy.
- Lone pair-lone pair repulsion is more when bonded atoms are small in size, so it will be easy to break the bond.

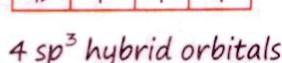
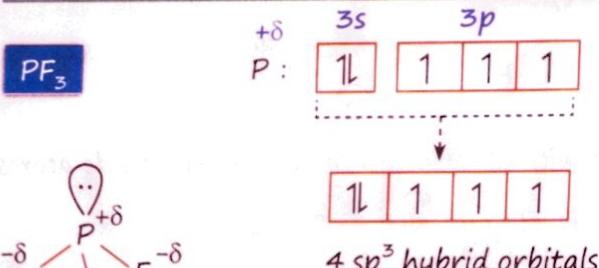
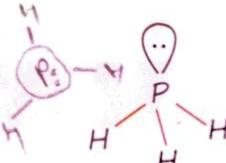
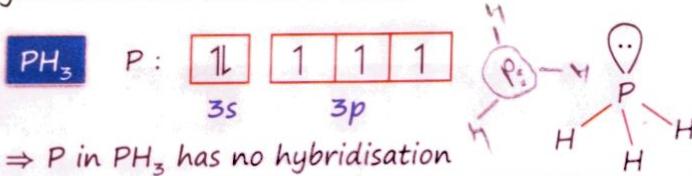
Note

$\begin{array}{cccc} Cl_2 & Br_2 & F_2 & I_2 \\ \text{BDE: } Cl-Cl > Br-Br > F-F > I-I \\ \text{काला} & \text{बन्दर} & \text{फिर} & \text{India में!} \end{array}$

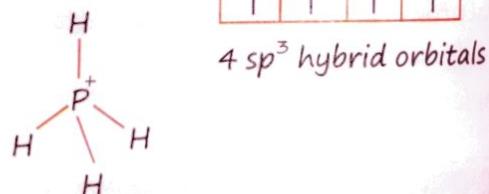
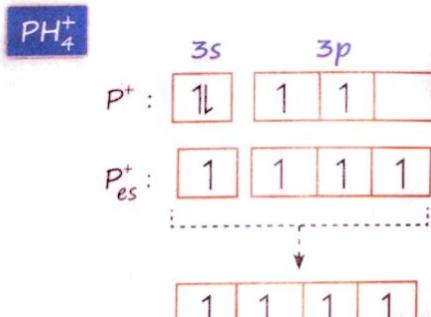


PH₃ HAS NO HYBRIDISATION BUT PF₃ & PH₄⁺ HAS? WHY?

Complete or partial +ve charge on central atom supports ORBITAL CONTRACTION, which hybridisation of atomic orbitals.



⇒ P in PF₃ is sp³ hybridised



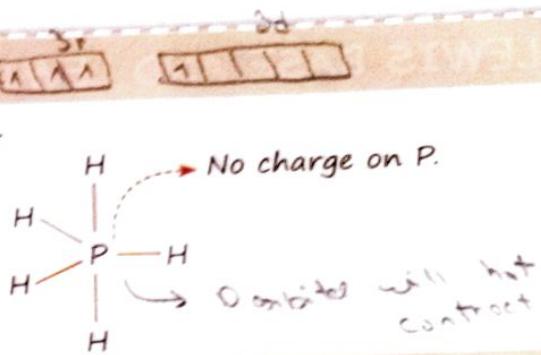
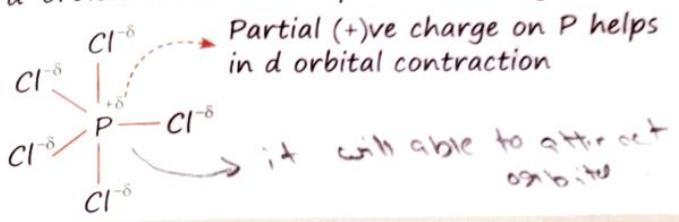
⇒ P in PH₄⁺ is sp³ hybridised

Bond Angle: PH₃ < PF₃ < PH₄⁺

[θ ≈ 90°] [θ > 90°] [θ = 109°28']

25. PCl_5 exists but not PH_5 ?

Sol. d-orbital contraction is possible in PCl_5 but not in PH_5



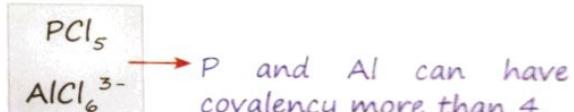
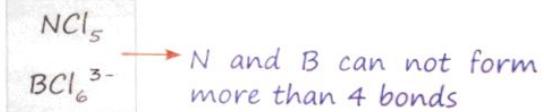
26. SF_6 exists but not SH_6 ?

Sol. d-orbital contraction is possible in SF_6 but not in SH_6 .

EXISTENCE & NON-EXISTENCE

- 2nd Period elements → B/C/N/O/F → Can have maximum $8e^-$ in valence shell
 - max. covalency $\equiv 4$
 - d orbitals are not available
 - Possible hybridisation are - sp , sp^2 , sp^3

- 3rd/4th/5th/6th/7th Period elements → Al/Si/P/S etc.
 - d orbitals are available of bonding
 - Possible hybridisation are sp , sp^2 , sp^3 , sp^3d , sp^3d^2 , sp^3d^3
 - These elements can form more than 4 bonds.



Note

Molecules That Do Not Exist

(1) SF_4 , SF_6 & PF_5 , exist while OF_4 , OF_6 , NF_5 do not exist

(2) (a) PI_5 (vap) & SCl_6 do not exist

(b) SCl_6 does not exist while TeCl_6 exist due to steric effect.

(c) PI_5 (solid) exist as PI_3 and I_2 .

(3) SF_6 , PF_5 , XeF_6 , XeF_4 & XeF_2 exist while SH_6 , PH_5 , XeH_6 , XeH_4 , XeH_2 do not exist.



LEWIS BASE AND LEWIS ACID

Lewis Acid \rightarrow Electron pair acceptor

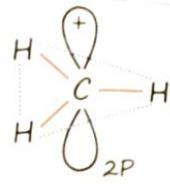
CA having vacant orbital:

(i) Vacant p orbital: BF_3
 $B(OH)_3$
 $AlCl_3$

(ii) Vacant d orbital: SiF_4 ,
 PCl_5

CA with +ve charge having vacant orbital:

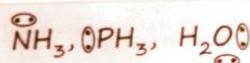
(i) Vacant s orbital: H^+
(ii) Vacant p orbital: CH_3^+



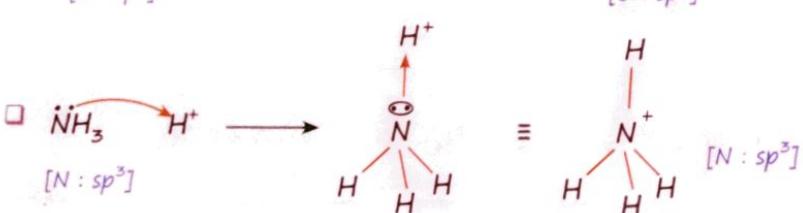
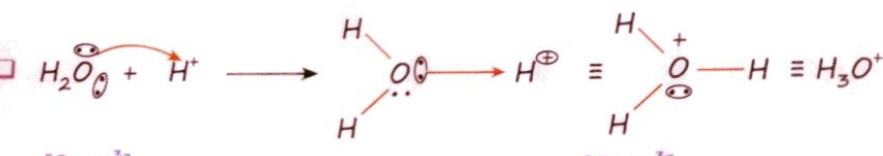
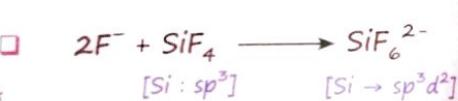
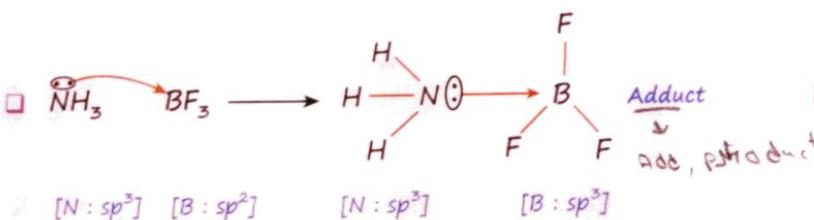
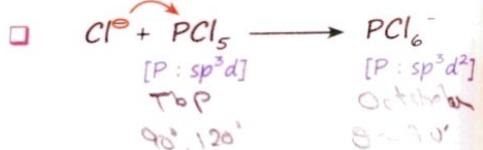
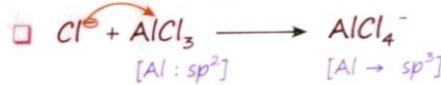
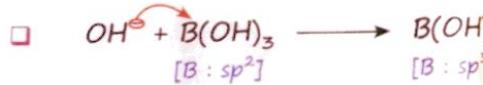
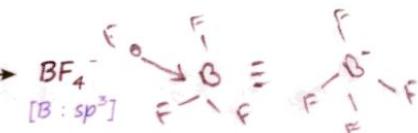
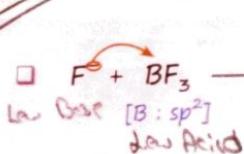
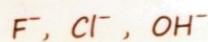
NH_4^+ \longrightarrow not a Lewis Acid because there is no vacant orbital in N.

Lewis Base \rightarrow Electron pair donor

CA with lone pair:

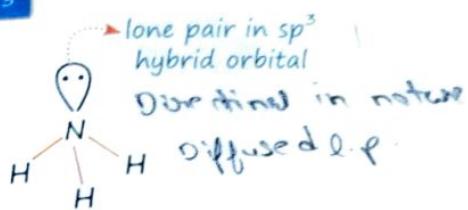


CA with -ve charge:

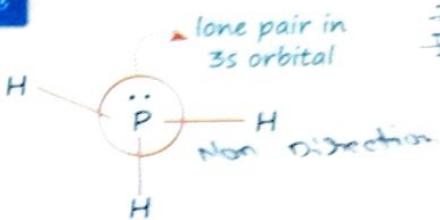


Lewis Basicity NH_3 vs PH_3

NH_3



PH_3



$\text{H} \quad \text{P} \quad \text{H}$



♦ $K_{b1} \gg K_{b2}$

♦ Lewis basicity: $\boxed{\text{NH}_3 > \text{PH}_3}$

Order of Lewis basicity is due to fact that lone pair on N is in sp^3 hybrid orbital which is more diffused and directional. But lone pair on P is present in a 's' orbital which is contracted and non-directional.

diffused = opp of contracted

(IIT JEE 2002)

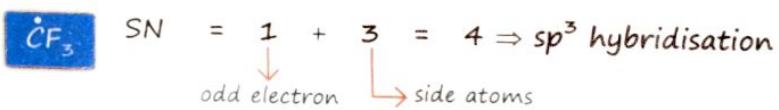
27. Specify the coordination geometry around and hybridising N and B atoms in a 1 : 1 complex of BF_3 and NH_3 .

- (a) N: tetrahedral, sp^3 ; B: tetrahedral, sp^3 (b) N: pyramidal, sp^3 ; B: pyramidal, sp^3
 (c) N: pyramidal, sp^3 ; B: planar, sp^2 (d) N: pyramidal, sp^2 ; B: tetrahedral, sp^2

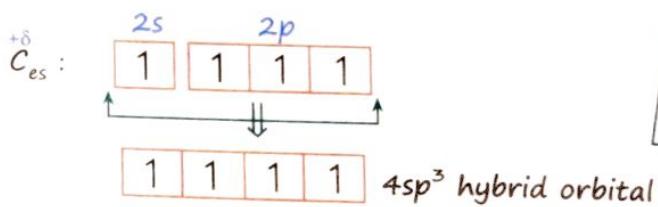
Sol. (a)

HYBRIDISATION IN ODD ELECTRON SPECIES

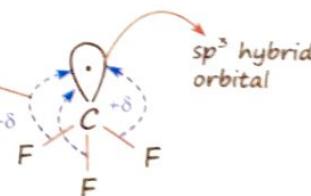
When side atoms are more electronegative than central atom then odd electrons are considered in steric number to find hybridisation.



+8 it attract the orbital;



Flow of %s character from C-F bonds to the orbital having an odd electron.

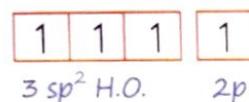
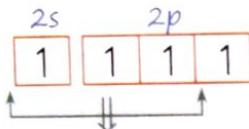




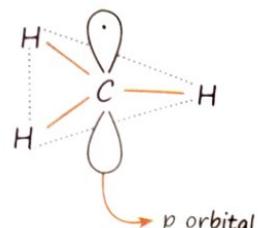
$\text{SN} = \text{O} + 3 = 3 \Rightarrow \text{sp}^2 \text{ hybridisation}$

[odd electron is not considered because side atom H is less electronegative than central atom C]

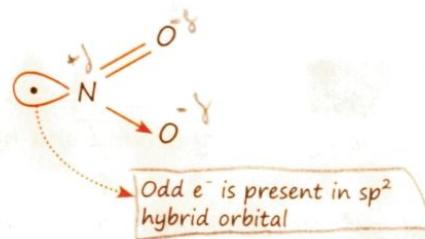
H will not give %s charge



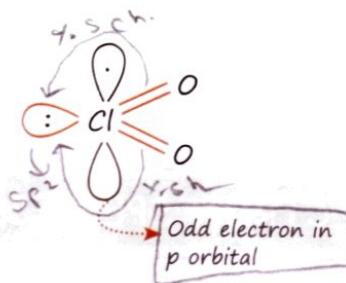
Odd e⁻ is present in 2p orbital of C



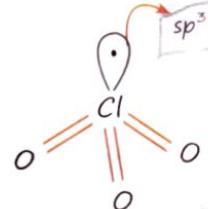
- $\text{SN} = 1 + 2 = 3$
- sp^2 hybridisation



- $\text{SN} = 1 + 2 = 3$
- sp^2 hybridisation



- $\text{SN} = 1 + 3 = 4$
- sp^3



Odd e⁻ molecule

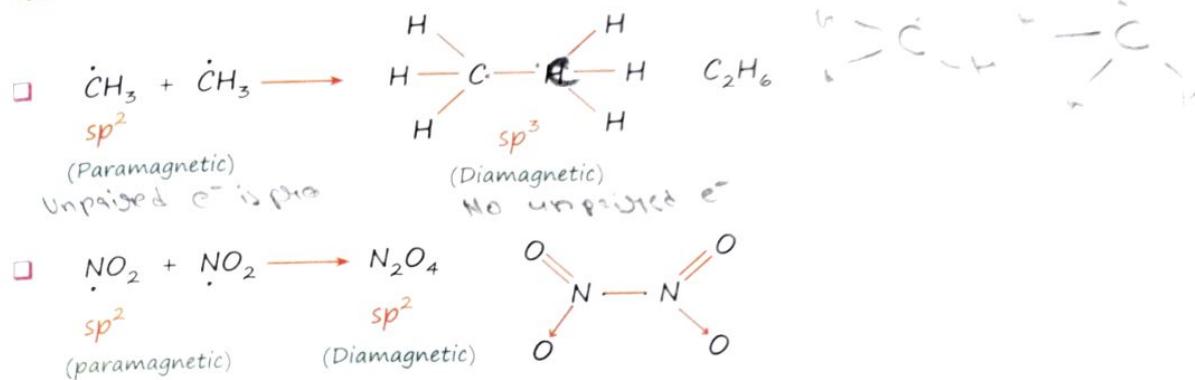
Orbital having odd electron

hybⁿ of central atom

$\dot{\text{C}}\text{H}_3$	p	sp^2
$\dot{\text{C}}\text{F}_3$	sp^3	sp^3
$\dot{\text{N}}\text{O}_2$	sp^2	sp^2
$\dot{\text{ClO}}_3$	sp^3	sp^3
$\dot{\text{ClO}}_2$	p	sp^2

Dimer Formation - Hybridisation Change & Magnetic Behaviour

$\begin{smallmatrix} \uparrow \\ 2 \end{smallmatrix}$ unit



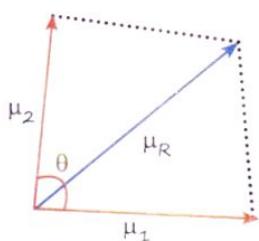
DIPOLE MOMENT

Product of the magnitude of the charge and the distance between the centers of the positive and negative charges.

Dipole moment = charge . distance of separation

$$\text{Dipole moment } \mu = q \cdot l$$

Dipole moment is a vector quantity when 2 vectors (μ_1 & μ_2) are separated by θ then we can calculate resultant μ_R .



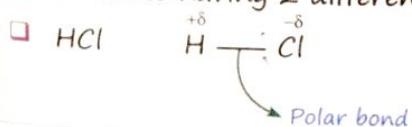
- $\mu_R^2 = \mu_1^2 + \mu_2^2 + 2\mu_1 \cdot \mu_2 \cos\theta$
- $\cos\theta \uparrow : \mu_R \uparrow$
- $\theta \uparrow : \cos\theta \downarrow : \mu_R \downarrow$

Unit $\equiv C \cdot m$
 $\equiv \text{esu} \cdot \text{cm}$
 $\equiv \text{Deby} [\text{D}]$
 $C \rightarrow \text{Coulomb}$
 $m \rightarrow \text{metre}$
 $\text{esu} \rightarrow \text{Electrostatic unit of charge}$

1 Deby $= 10^{-18} \text{ esu cm}$
 $\text{Charge on } e^- \rightarrow q_e = 1.6 \times 10^{-19} \text{ C}$
 $= 4.8 \times 10^{-10} \text{ esu}$

Polar Molecule ($\mu_R \neq 0$)

- Hetero-nuclear diatomic
- Molecule having 2 different atoms



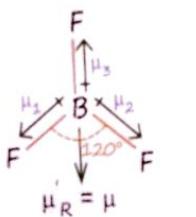
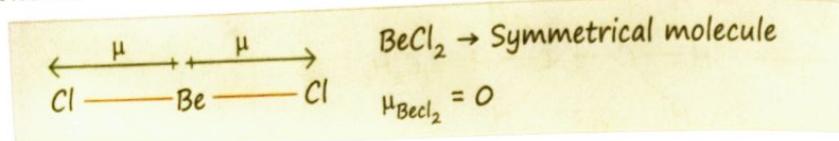
Non-polar Molecule ($\mu_R = 0$)

- Homonuclear diatomic
- Molecule having 2 same atoms



Symmetry and Dipole Moment

A polyatomic molecule having polar covalent bonds and symmetrical structure indicates the zero dipole moment of the molecule.



- $\text{BF}_3 \rightarrow \text{Symmetrical molecule}$
- $\mu_{\text{BF}_3} = 0$
- $\text{BF}_3 \rightarrow \text{Non polar molecule}$

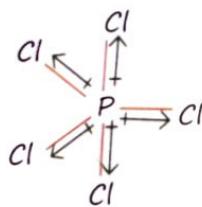
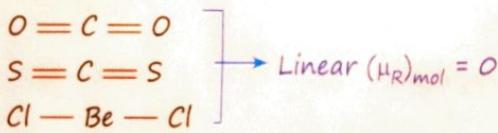
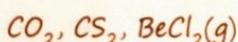
$$\begin{aligned} \mu_R'^2 &= \mu_1^2 + \mu_2^2 + 2\mu_1 \cdot \mu_2 \cos 120^\circ \\ \mu_R' &= \mu \quad [\mu_1 = \mu_2 = \mu] \end{aligned} \quad \boxed{\mu_R' \text{ is cancelled by } \mu_3 (= \mu).}$$

Symmetrical Molecule

- Symmetrical molecules are non-polar molecules.

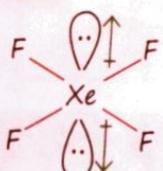
$$\square (\mu_R)_{\text{molecule}} = 0$$

1. Molecule having no lone pair on central atom and having same side atoms.

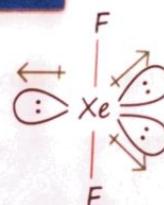


Non-Polar molecule

2. Molecule having lone pairs on central atom but in such a way that they can cancel each others dipole moment.



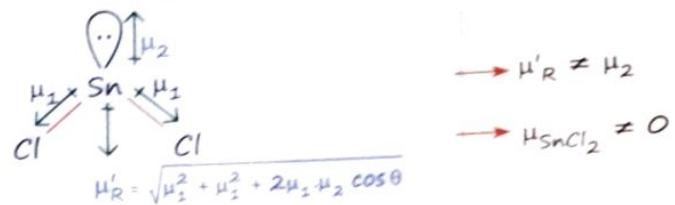
- Non polar molecule
- $\mu_R = 0$



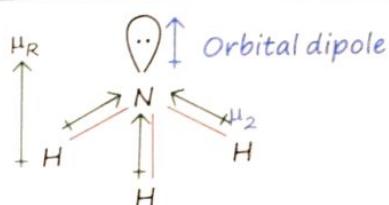
Unsymmetrical Molecule

Molecule having lone pairs on central atom but in such a way that they can not cancel each others dipole moment.

$\ddot{S}nCl_2$, \ddot{PbCl}_2 , \ddot{SO}_2 : Angular mol. : Polar
 \ddot{NH}_3 , $H_2\ddot{O}$, \ddot{NF}_3 , \ddot{SF}_4 , $H_2\ddot{S}$: Polar molecule

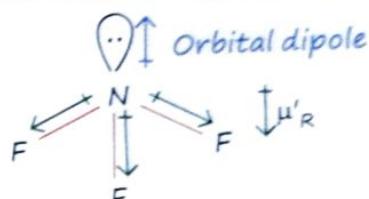


NH_3



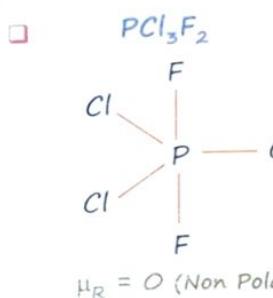
In case of NH_3 , the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the N - H bonds.

NF_3 : Dipole moment

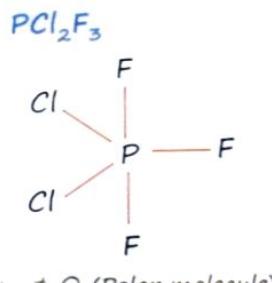


In NF_3 , the orbital dipole is in the direction opposite to the resultant dipole moment of the three N-F bonds.

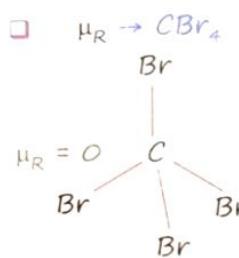
The orbital dipole because of lone pair decreases the effect of the resultant N - F bond moments, which results in the low dipole moment of NF_3 .



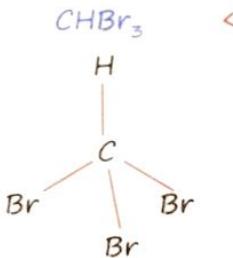
$\mu_R = 0$ (Non Polar)



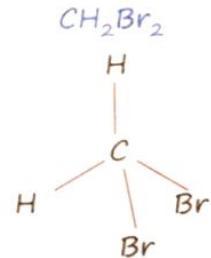
$\mu_R \neq 0$ (Polar molecule)



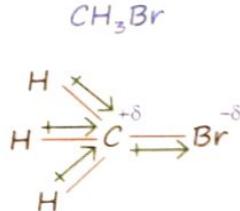
$\mu_R = 0$



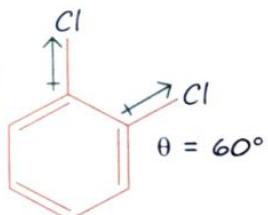
$\mu_R = 0$



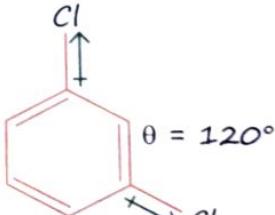
$\mu_R = 0$



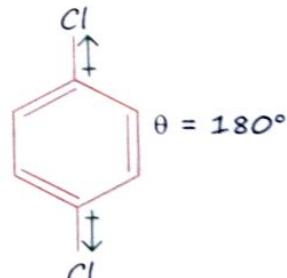
$\mu_R \uparrow : \theta \downarrow : \cos\theta \uparrow$



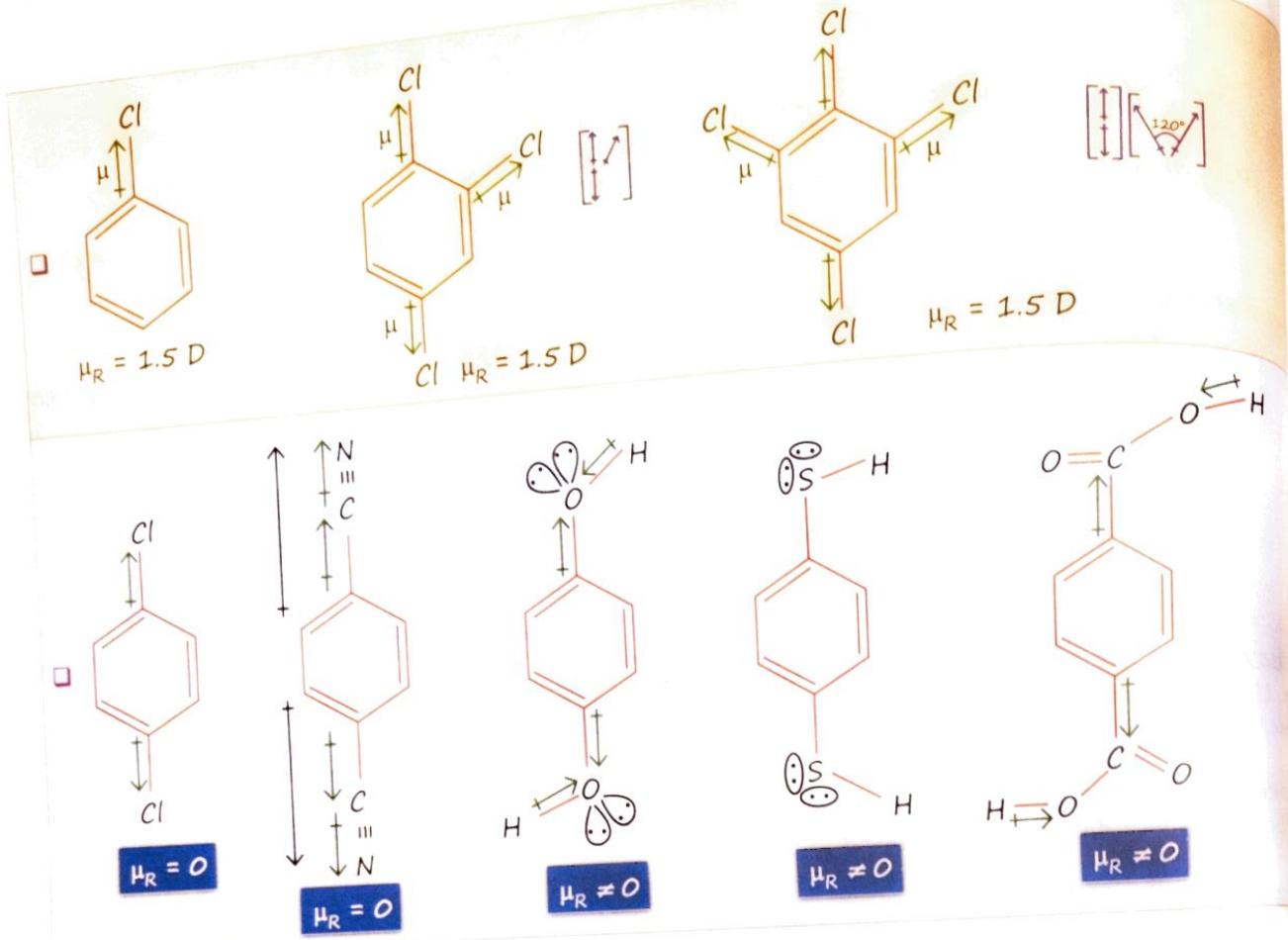
μ_R : ortho - dichlorobenzene



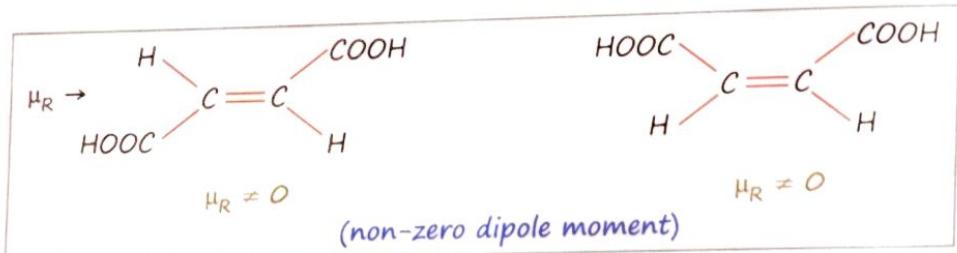
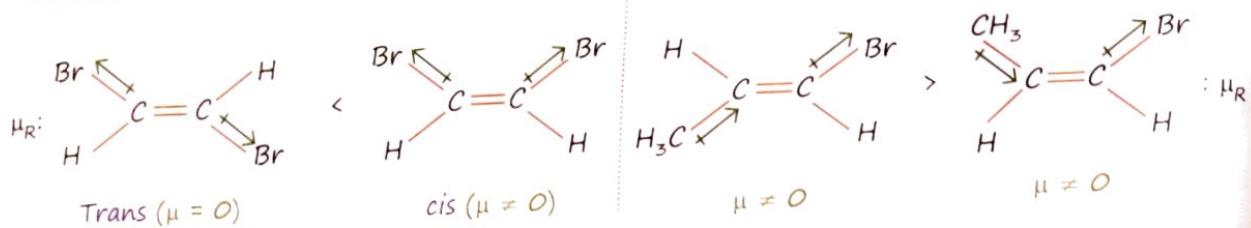
> meta-dichlorobenzene



> para-dichlorobenzene



Cis & Trans



μ_R \longrightarrow $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$

length factor dominates over charge factor.

μ_R \longrightarrow $\text{CH}_3\text{F} < \text{CH}_3\text{Cl} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$

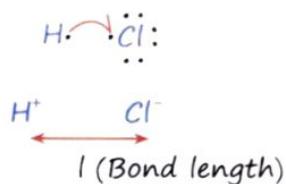
charge factor dominates over length factor.

μ_R \longrightarrow $\text{CH}_3-\text{Cl} > \text{CH}_3\text{F} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$

% Ionic Character in Covalent Bond

$$\% \text{ ionic character} = \frac{\mu_{(\text{exp/obs})}}{\mu_{(\text{cal/theo})}} \times 100$$

$\mu_{\text{experiment}}$ = given \rightarrow $\boxed{H - \overset{-\delta}{Cl}}$ $\rightarrow \mu_{\text{calculated}} = q.l = (4.8 \times 10^{-10} \text{ esu})$. Bond length



□ For 100% ionic character-

It is assumed that 1 electron is completely transferred from one atom to another.

28. For HCl gas molecule $\mu = 1.03 \text{ D}$ and bond distance = 1.275 \AA . Calculate the % ionic character.

Sol. $\mu_{\text{exp}} = 1.03 \text{ D}$

$$l = 1.275 \times 10^{-8} \text{ cm}$$

$$\mu_{\text{cal}} = ?$$

$$\square \mu_{\text{cal}} = q_e \cdot l$$

$$= (4.8 \times 10^{-10} \text{ esu}) \cdot (1.275 \times 10^{-8} \text{ cm})$$

$$= (4.8 \times 1.275) \cdot (10^{-18} \text{ esu} \cdot \text{cm}) = (4.8 \times 1.275) \text{ D}$$

$$\begin{aligned} \% \text{ ionic character} &= \frac{1.03}{(4.8 \times 1.275)} \times 100\% \\ &= 0.1683 \times 100 = 16.83\% \end{aligned}$$

29. Among the following, the molecule with the highest dipole moment is

(IIT JEE 2003)

(a) CH_3Cl

(b) CH_2Cl_2

(c) $CHCl_3$

(d) CCl_4

Sol. (a)

30. Each of the following options contains a set of four molecules. Identify the option(s) where all four molecules possess permanent dipole moment at room temperature. (JEE Adv. 2019)

(a) SO_2 , C_6H_5Cl , H_2Se , BrF_5

(b) $BeCl_2$, CO_2 , BCl_3 , $CHCl_3$

(c) NO_2 , NH_3 , $POCl_3$, CH_3Cl

(d) BF_3 , O_3 , SF_6 , XeF_6

Sol. (a, c)

31. Which one of the following molecules has maximum dipole moment? [04 April, 2024 (Shift-I)]

(a) NF_3

(b) CH_4

(c) NH_3

(d) PF_5

Sol. (c)

32. Given below are two statements: one is labelled as Assertion (A) and the other is labelled as Reason (R).
- Assertion (A):** NH_3 and NF_3 molecule have pyramidal shape with a lone pair of electrons on nitrogen atom. The resultant dipole moment of NH_3 is greater than that of NF_3 .
- Reason (R):** In NH_3 , the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the N-H bonds. F is the most electronegative element.

In the light of the above statements, choose the correct answer from the options given below

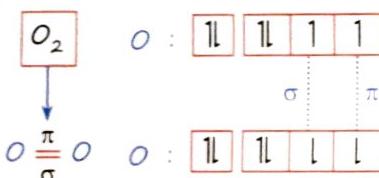
[05 April, 2024 (Shift-II)]

- (a) Both (A) and (R) are true and (R) is the correct explanation of (A)
- (b) (A) is false but (R) is true
- (c) (A) is true but (R) is false
- (d) Both (A) and (R) are true but (R) is NOT the correct explanation of (A)

Sol. (a)

MOLECULAR ORBITAL THEORY

According to VBT



- All electrons are paired.
- O_2 is a diamagnetic molecule

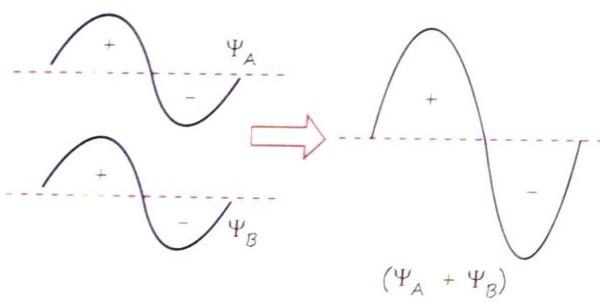
Need of new theory

- Experimental fact → (i) O_2 is a paramagnetic molecule
(ii) O_2 has 2 unpaired electrons



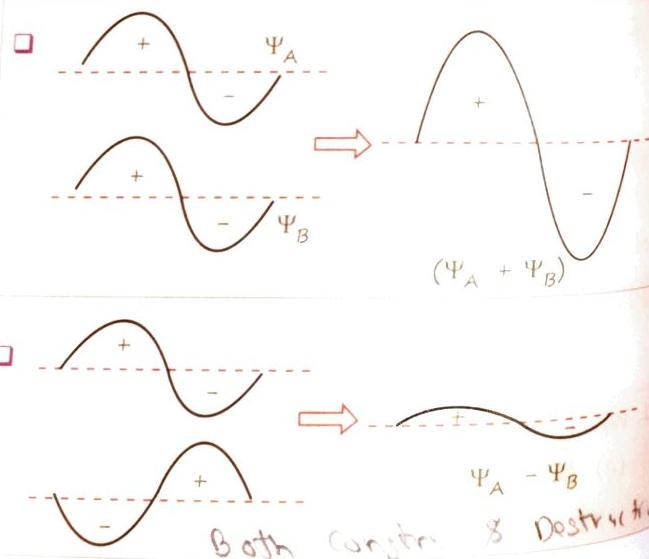
- Interaction between liq. O_2 and magnetic field.

Valence Bond Theory



Only constructive

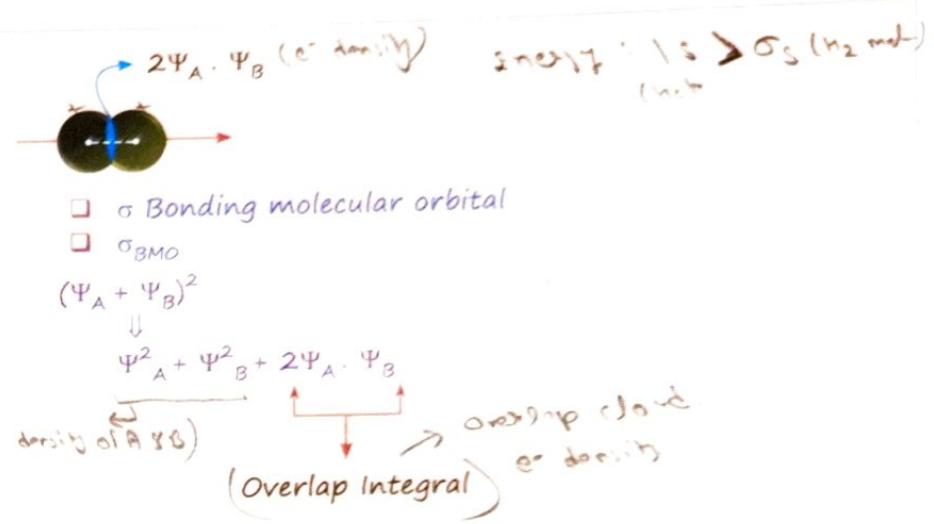
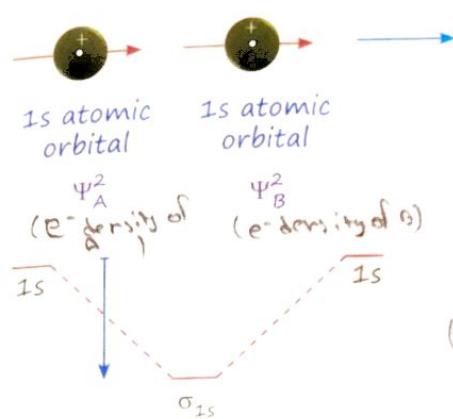
Molecular Orbital Theory



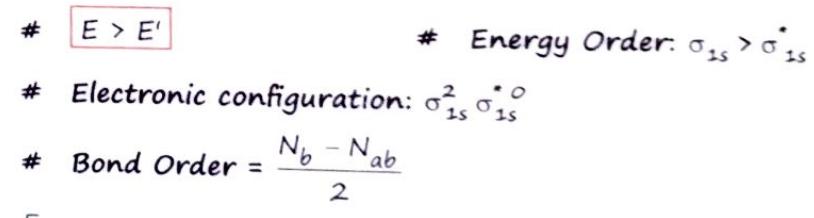
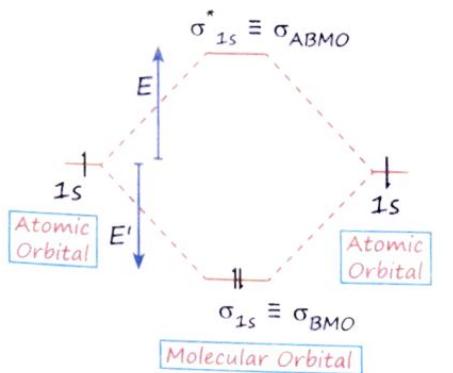
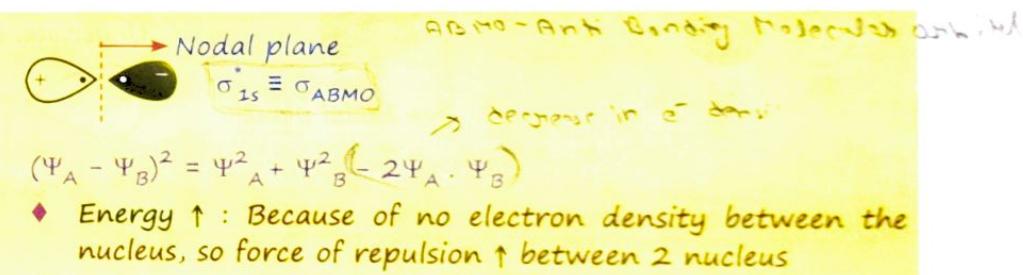
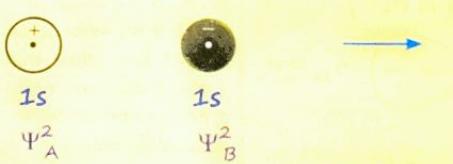
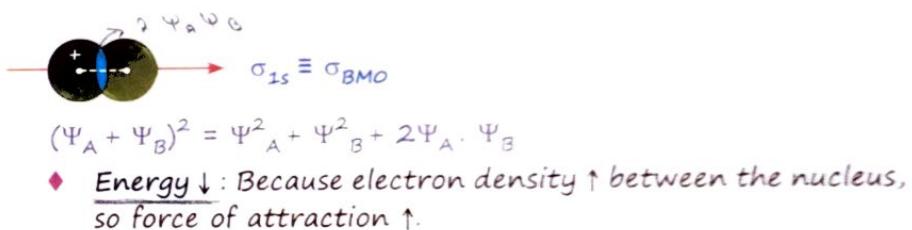
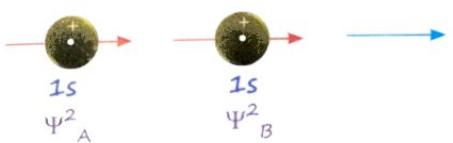
- VBT & MOT both are quantum mechanical theories of chemical bonding.

Bond order = No. of bonds

VBT

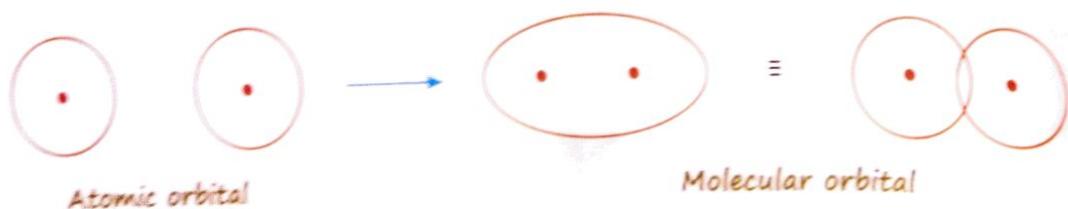


MOT



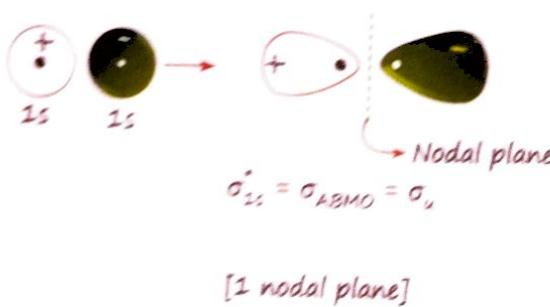
$[N_b = \text{no. of electrons in bonding molecular orbital}]$
 $[N_{ab} = \text{no. of electrons in anti bonding molecular orbital}]$

Energy order: $\sigma_{1s} < 1s < \sigma_{1s}^*$



- An atomic orbital is monocentric while a molecular orbital is polycentric.
- Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by molecular orbital.
- The molecular orbitals like the atomic orbitals are filled in accordance with the Aufbau principle, obeying the Pauli Exclusion principle and the Hund's Rule of Maximum Multiplicity. But the order of these molecular orbitals is always experimentally decided.
- To construct such molecular orbitals we need to combine the atomic orbitals of the atoms that make up the molecule. This approach is known as the Linear Combination of Atomic Orbitals [LCAO].

* s-s overlapping



* Symmetry Term

- Gerade : Centre of symmetry is present



COS is present

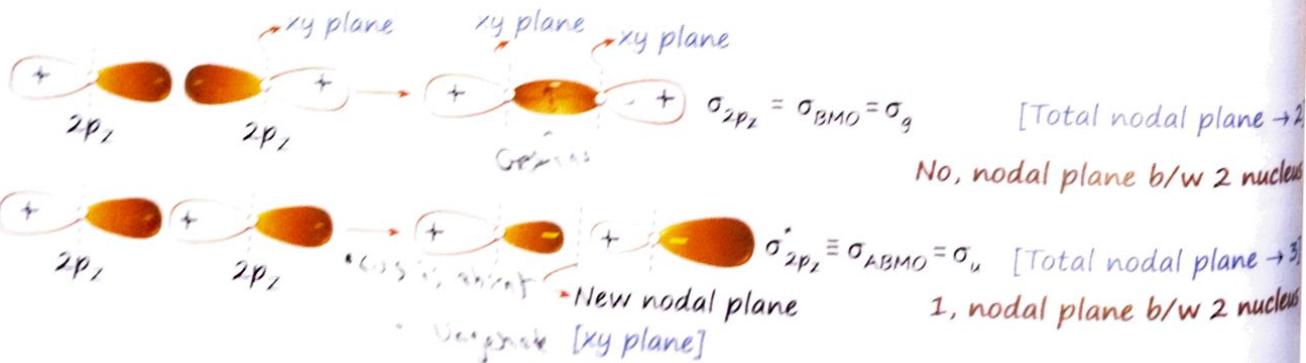
- Ungerade: COS is not present



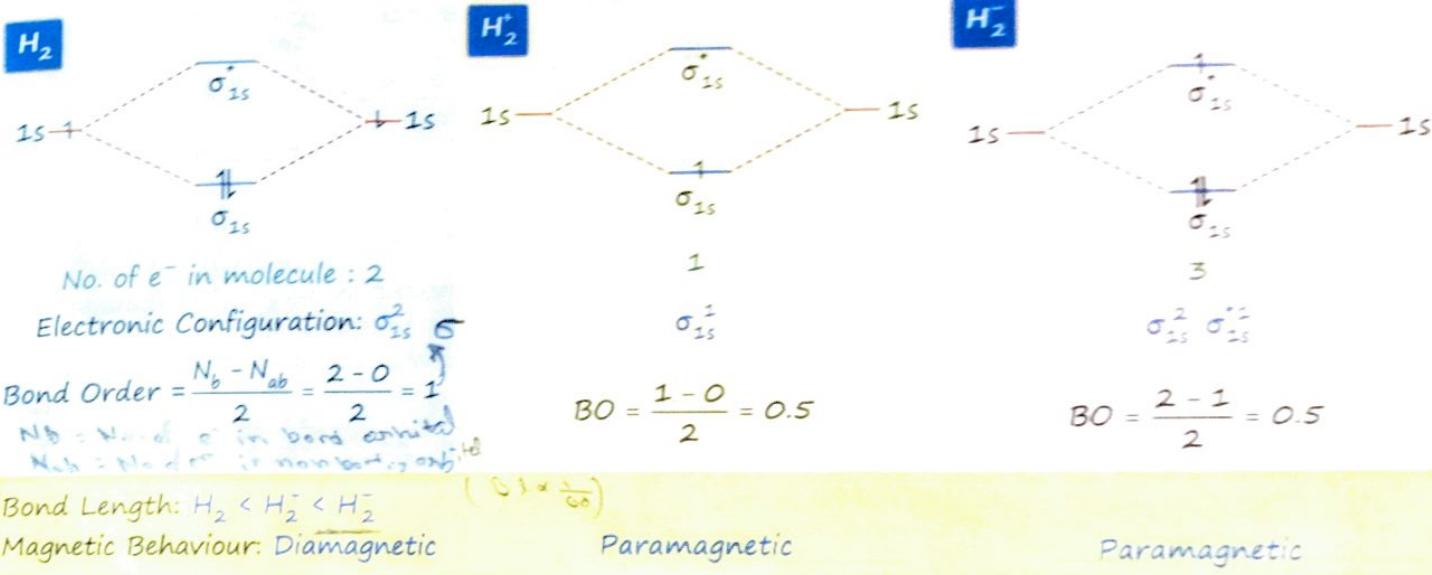
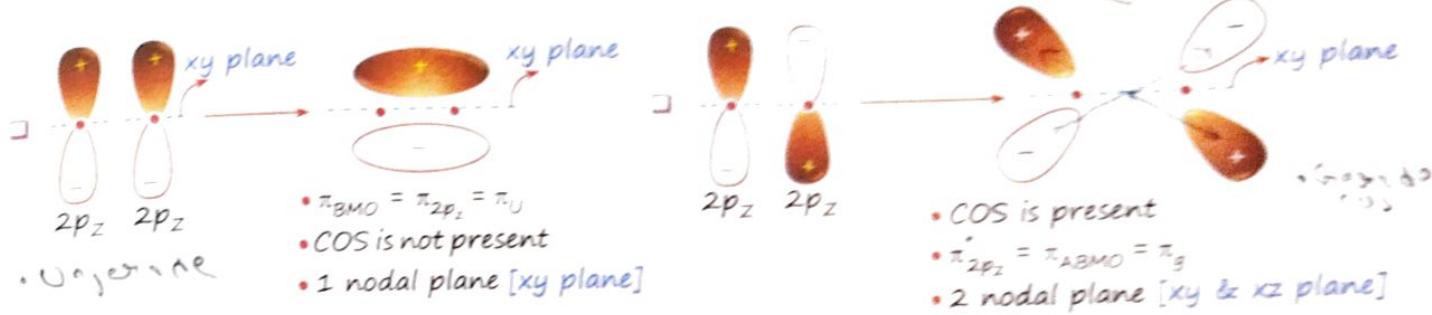
COS is not present

COS : A molecular orbital has a centre of symmetry when, for any molecular orbital in the molecule, identical lobes (phase + or -) exists diametrically opposite to this centre at an equal distance.

* p-p overlapping

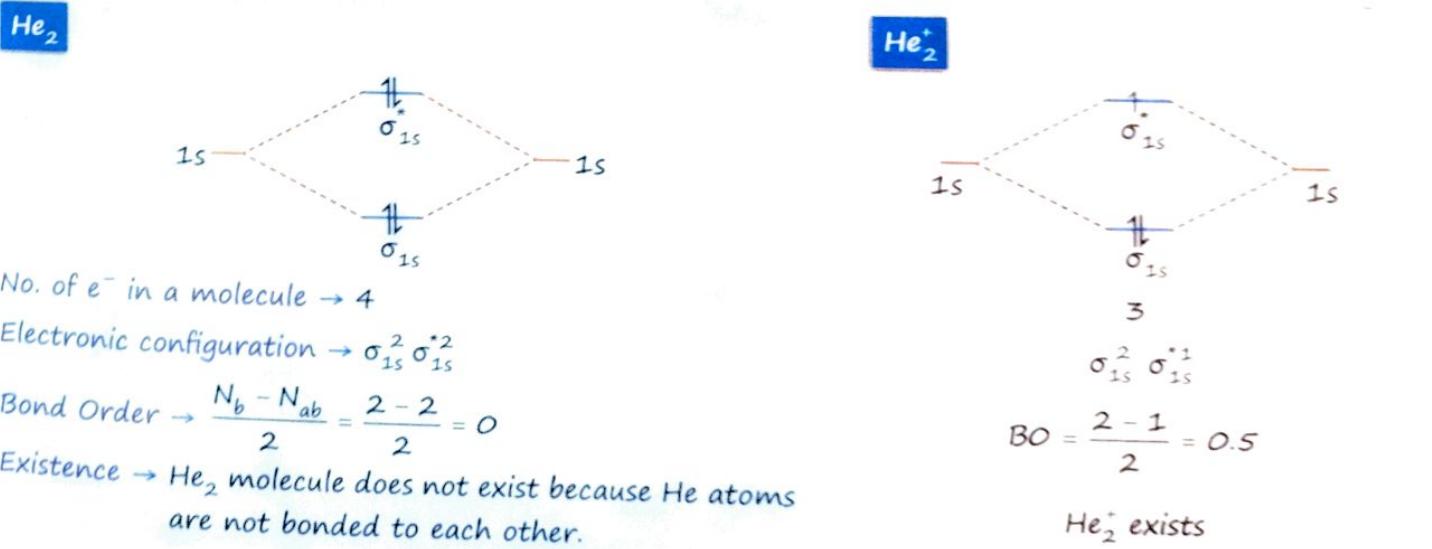


p-p overlapping



Note

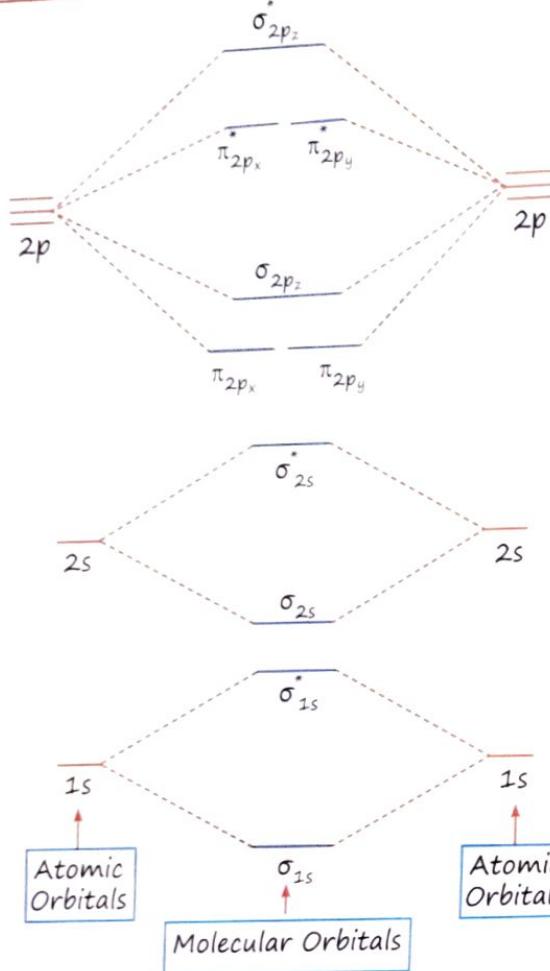
If bond order is same $\rightarrow N_{ab} \uparrow : BL \uparrow$



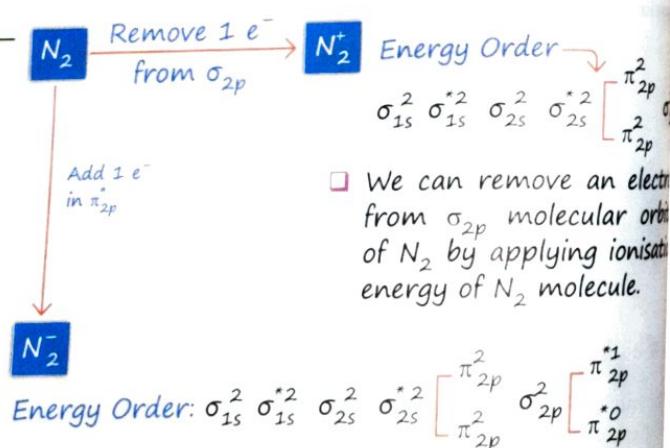
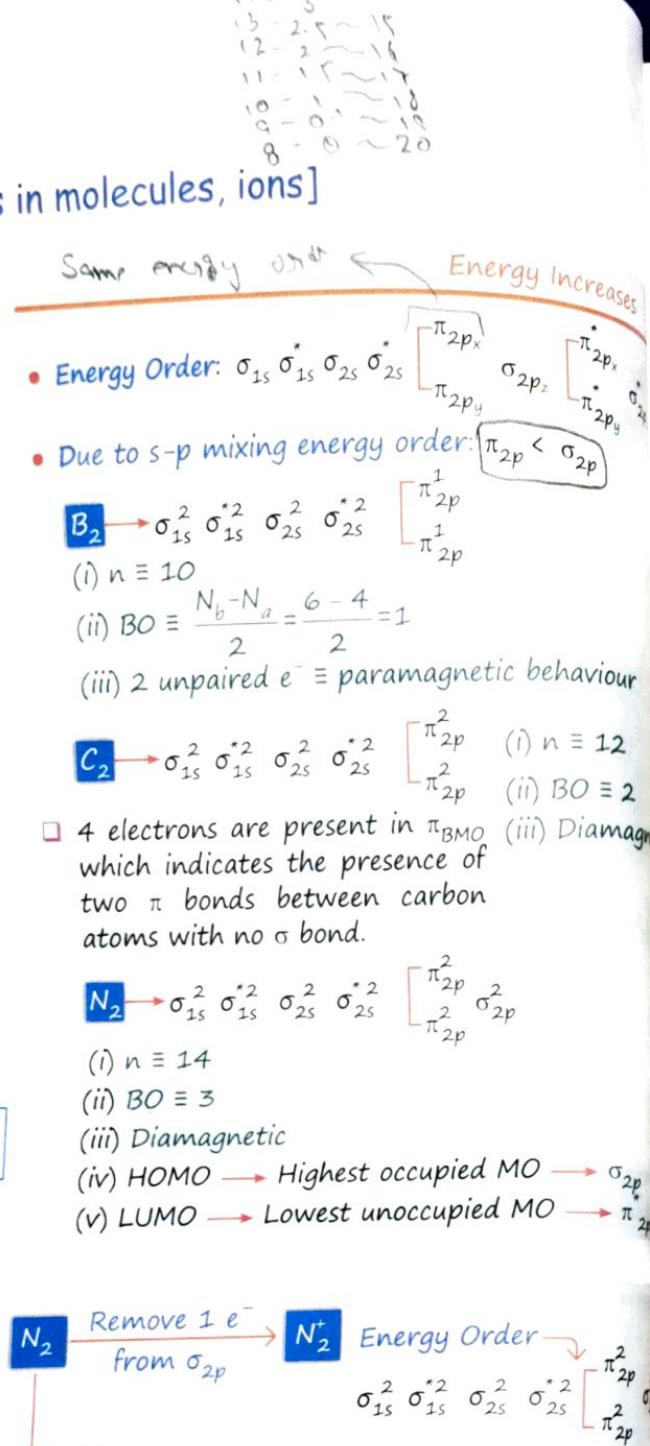
Electronic Configuration

$n \leq 14$

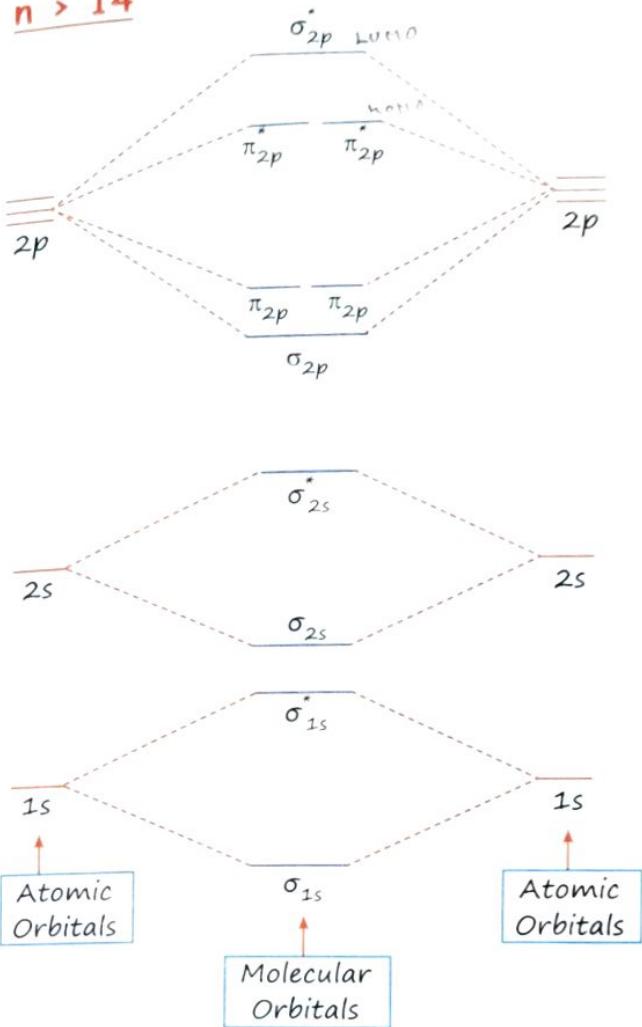
[$n \rightarrow$ no. of electrons in molecules, ions]



	N ₂	N ₂ ⁺	N ₂ ⁻
N _b	10	9	10
N _{ab}	4	4	5
Bond Order	3	2.5	2.5
Bond Length	N ₂ < N ₂ ⁺ < N ₂ ⁻		
Bond Strength	N ₂ > N ₂ ⁺ > N ₂ ⁻		
Bond Dissociation Energy	N ₂ > N ₂ ⁺ > N ₂ ⁻		
Magnetic Behaviour	Dia	Para	Para
Unpaired e ⁻ is present in	-	σ_{2p}	π_{2p}^*



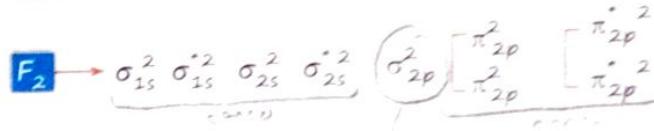
n > 14



Energy Increases →

• Energy Order: $\sigma_{1s} \sigma^*_{1s} \sigma_{2s} \sigma^*_{2s} \sigma_{2p} \pi_{2p} \pi^*_{2p}$

• No, s-p mixing → Energy: $\sigma_{2p} < \pi_{2p}$



(i) $n = 18$

$$(ii) BO \equiv \frac{10 - 8}{2} = 1$$

(iii) HOMO → Highest occupied MO → π_{2p}^2 & $\sigma^*_{2p}^2$

(iv) LUMO → Lowest unoccupied MO → σ_{2p}^2 & $\pi^*_{2p}^2$

(v) Colour → Pale yellow [HOMO to LUMO electronic transition is the reason behind colour]

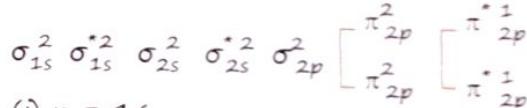
(vi) Magnetic Behaviour: Diamagnetic

□ F_2 , Cl_2 , Br_2 and I_2 , all 4 are diamagnetic in nature and are colored (due to transition of electron from HOMO to LUMO $\equiv \pi^* \text{ to } \sigma^*$).

	O_2^{2+}	O_2^+	O_2	O_2^-	O_2^{2-}
N_b	10	10	10	10	10
N_{ab}	4	5	6	7	8
Bond order	3	2.5	2	1.5	1
Bond length	$O_2^{2+} < O_2^+ < O_2 < O_2^- < O_2^{2-}$				
Bond strength	$O_2^{2+} > O_2^+ > O_2 > O_2^- > O_2^{2-}$				
Bond energy	$O_2^{2+} > O_2^+ > O_2 > O_2^- > O_2^{2-}$				
Magnetic Behaviour	Dia	Para	Para	Para	Dia
No. of Unpaired e ⁻	0	1	2	1	0



Electronic Configuration of O_2

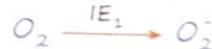


(i) $n = 16$

(ii) Bond order = 2

(iii) 2 unpaired electrons → O_2 is paramagnetic in nature

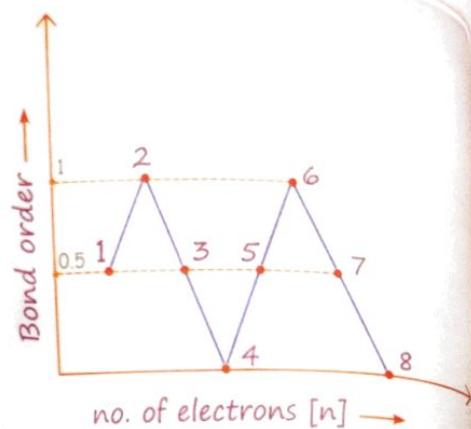
□ We can remove an electron from π_{2p}^* molecular orbital of O_2 by applying 1st ionisation energy of O_2 molecule.



□ S_2 molecule is also paramagnetic with 2 unpaired electrons as O_2 molecule.

Note

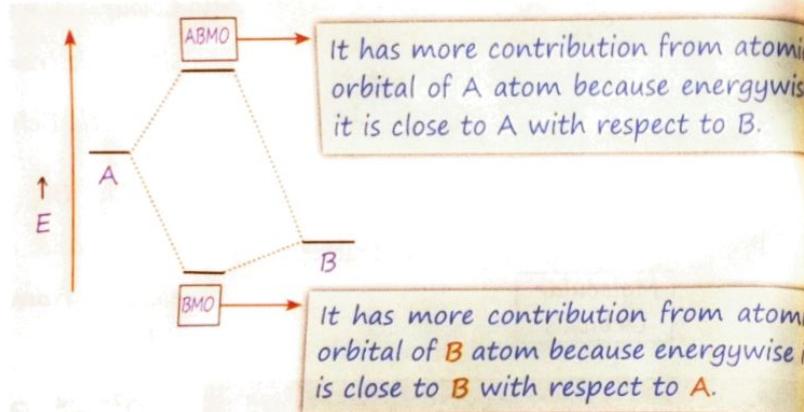
Bond Order		n
n		n
14	3	15
13	2.5	16
12	2	17
11	1.5	18
10	1	19
9	0.5	20
8	0	



MOT for Heteronuclear Diatomic

AB molecule Type [CO, NO, CN⁻, NO⁺]

- Electronegativity: A < B
- Energy of same orbital: A > B



Isoelectronic Species

N_2 (7+7=14e ⁻)	CO (6+8=14e ⁻)	NO ⁺ (7+8-1=14e ⁻)	CN ⁻ (6+7+1=14e ⁻)	Bond order = 3
----------------------------------	-------------------------------	--	--	----------------

N_2^- (14+1=15e ⁻)	NO (7+8=15e ⁻)	Bond order = 2.5
-------------------------------------	-------------------------------	------------------

Box-1a	BaO ₂ Ba ²⁺ O ₂ ²⁻ (18e ⁻)	O ₂ (16e ⁻)	NaO ₂ Na ⁺ O ₂ ⁻ (17e ⁻)
Bond Order → 1	2	1.5	
Bond Length → O ₂ ²⁻ > O ₂ ⁻ > O ₂	[O - O]		

Box-1b	O ₂ (16e ⁻)	O ₃ O=O O	O ₂ ⁺ (15e ⁻)
2 BO = $\frac{\sigma + \pi}{\sigma} = \frac{2 + 1}{2} = 1.5$		2.5 ← Bond Order	
O ₃ > O ₂ > O ₂ ⁺ : Bond Length			

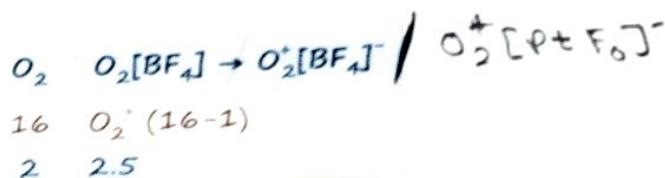
Box-2



No. of e^- in oxygen containing species $\rightarrow O_2^- (16+1)$

Bond Order $\rightarrow 1.5$

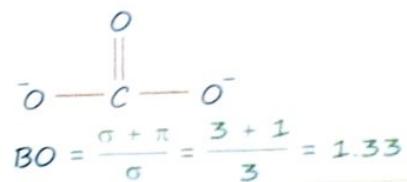
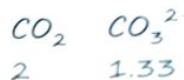
Bond Length $\rightarrow O_2^+ < O_2^- < O_2^-$
 $[O - O]$



Box-3



Bond Order $\rightarrow 3$



C-O Bond Length $\rightarrow CO < CO_2 < CO_3^{2-}$

Box-4

□ Bond Length: $NO > NO^+$
 Bond order = 2.5 Bond order = 3

CO $> CO^+$: Bond length



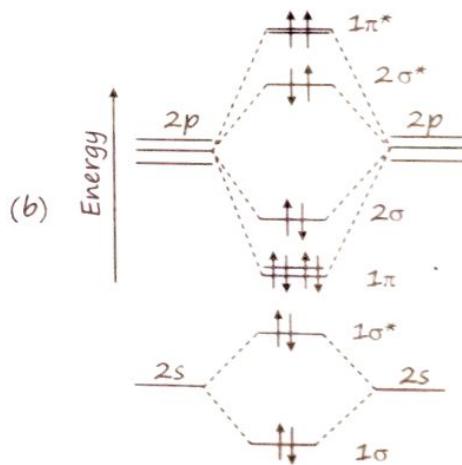
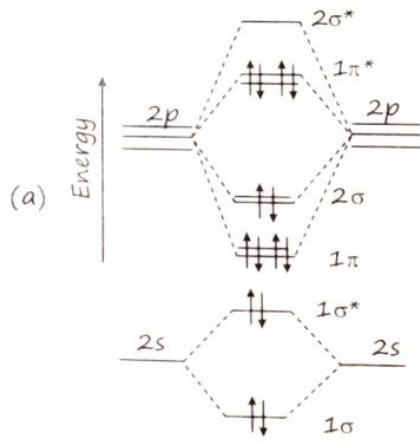
33. Assuming 2s-2p mixing is not operative, the paramagnetic species among the following is (JEE Adv. 2014)

- (a) Be_2 (b) B_2 (c) C_2 (d) N_2

Sol. (c) Assuming that no 2s - 2p mixing takes place the MO electronic configuration can be written as

- (a) $Be_2 \rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2$ (diamagnetic)
 (b) $B_2 \rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_{z}^2$, (diamagnetic)
 (c) $C_2 \rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_{z}^2, \pi 2p_x^1, \pi 2p_y^1$ (paramagnetic)
 (d) $N_2 \rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_{z}^2, \pi 2p_x^2, \pi 2p_y^2$ (diamagnetic)

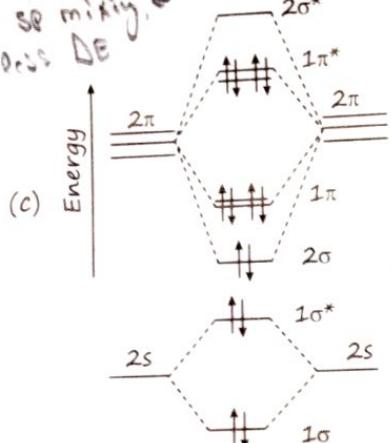
34. The correct molecular orbital diagram for F_2 molecule in the ground state is (JEE Adv. 2023)



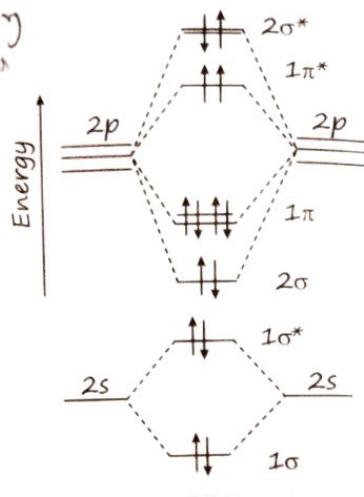
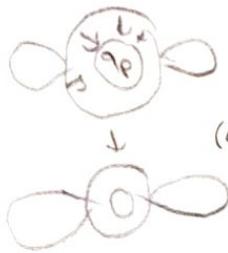
Atoms : 2¹ He 3² Li 4³ Be 5⁴ B 6⁵ C 7⁶ N 8⁷ O 9⁸ F 10⁹ Ne

$\Delta E_{(2p_2s)}$ 1.8 2.8 4.5 5.3 6.0 15.0 50.5 26.7

sp mixing
over DE



No 2s & 2p mixing
Due to ΔE_{rel}



Sol. (c)

35. The species having bond order different from that in CO is-

- (a) NO^- (b) NO^+ (c) CN^- (d) N_2

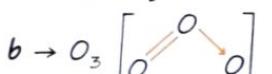
(IIT JEE 2000)

36. Among the following, the paramagnetic compound is

- (a) Na_2O_2 (b) O_3 (c) N_2O (d) KO_2

(IIT JEE 2000)

Sol. (d) a $\rightarrow 2\text{Na}^+ [10 \text{ e}^- : \text{all paired}], \text{O}_2^{2-} [18 \text{ e}^- : \text{all paired}]$,



All electrons are paired



All electrons are paired

d $\rightarrow \text{K}^+ [18 \text{ e}^- : \text{all paired}], \text{O}_2^- [17 \text{ e}^- : 1 \text{ unpaired}]$

37. Match the orbital overlap figures shown in Column-I with the description given in Column-II a select the correct answer using the codes given below the Columns.

(JEE Adv. 2000)

Column-I		Column-II	
A.		1.	p-d π antibonding
B.		2.	d-d σ bonding
C.		3.	p-d π bonding
D.		4.	d-d σ antibonding

Codes:

A	B	C	D
(a) 4	3	2	1
(b) 1	2	3	4
(c) 2	3	1	4
(d) 4	1	2	3

Sol. (c)

δ_{C-C} in C_2 (1.76\AA) $> \delta_{C-C}$ in O_2 (1.25\AA)

38. For diatomic molecules, the correct statement(s) about the molecular orbitals formed by the overlap of two $2p_z$ orbitals is(are) (JEE Adv 2022)

- (a) σ orbital has a total of two nodal planes.
- (b) σ^* orbital has one node in the xz -plane containing the molecular axis.
- (c) π orbital has one node in the plane which is perpendicular to the molecular axis and goes through the center of the molecule.
- (d) π^* orbital has one node in the xy -plane containing the molecular axis.

Sol. (a, d)

39. According to molecular orbital theory, which of the following statements is(are) correct? (JEE Adv. 2016)

- (a) C_2^{2-} is expected to be diamagnetic
- (b) O_2^{2+} is expected to have a longer bond length than O_2^-
- (c) N_2^+ and N_2^- have the same bond order
- (d) He_2^+ has the same energy as two isolated He atoms

Sol. (a, c)

40. Among H_2 , He_2^+ , Li_2 , Be_2 , B_2 , C_2 , N_2 , O_2^- and F_2 , the number of diamagnetic species is (Atomic numbers : H = 1, He = 2, Li = 3, Be = 4, B = 5, C = 6, N = 7, O = 8, F = 9) (JEE Adv. 2017)

Sol. [6] (H_2 , Li_2 , Be_2 , C_2 , N_2 , F_2) are diamagnetic.

41. During the change of O_2 to O_2^- , the incoming electron goes to the orbital:

[10 April, 2019 (Shift-I)]

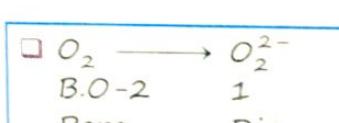
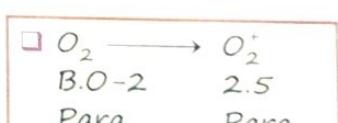
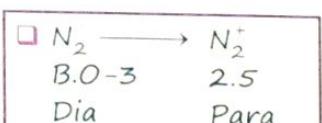
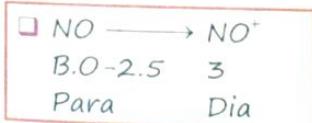
- (a) σ^*2p_z
- (b) $\pi 2p_y$
- (c) π^*2p_x
- (d) $\pi 2p_x$

Sol. (c)

42. In which of the following processes, the bond order has increased and paramagnetic character has changed to diamagnetic? [9 Jan, 2019 (Shift-II)]

- (a) $NO \rightarrow NO^+$
- (b) $N_2 \rightarrow N_2^+$
- (c) $O_2 \rightarrow O_2^+$
- (d) $O_2 \rightarrow O_2^{2-}$

Sol. (a)



43. AX is a covalent diatomic molecule where A and X are second row elements of periodic table. Based on molecular orbital theory, the bond order of AX is 2.5. The total number of electrons in AX is _____. (Round off to the nearest integer). [18 March, 2021 (Shift-I)]

Sol. [15] Given: $\text{AX} \Rightarrow$ Diatomic molecule

Bond order is 2.5

According to the given data, the compound is NO .

Total number of electrons in it = 15

(\therefore Number of electrons in $\text{N} = 7$, Number of electron in $\text{O} = 8$)

44. Amongst the following, the number of oxide(s) which are paramagnetic in nature is

$\text{Na}_2\text{O}, \text{KO}_2, \text{NO}_2, \text{N}_2\text{O}, \text{ClO}_2, \text{NO}, \text{SO}_2, \text{Cl}_2\text{O}$ (Nearest Integer)

[27 July, 2022 (Shift-I)]

Sol. [4] Paramagnetic species = $\text{KO}_2, \text{NO}_2, \text{ClO}_2, \text{NO}$

45. Match List-I with List-II.

[27 July, 2022 (Shift-I)]

List-I		List-II	
A. $\Psi_{MO} = \Psi_A - \Psi_B$	I.	Dipole moment	
B. $\mu = Q \times r$	II.	Bonding molecular orbital	
C. $\frac{N_b - N_a}{2}$	III.	Anti-bonding molecular orbital	
D. $\Psi_{MO} = \Psi_A + \Psi_B$	IV.	Bond order	

Choose the correct answer from the options given below

- (a) (A)-(II), (B)-(I), (C)-(IV), (D)-(III) (b) (A)-(III), (B)-(IV), (C)-(I), (D)-(II)
(c) (A)-(III), (B)-(I), (C)-(IV), (D)-(II) (d) (A)-(III), (B)-(IV), (C)-(II), (D)-(I)

Sol. (c)

46. The linear combination of atomic orbitals to form molecular orbitals takes place only when combining atomic orbitals

- A. have the same energy
B. have the minimum overlap
C. have same symmetry about the molecular axis
D. have different symmetry about the molecular axis

Choose the most appropriate from the options given below:

- (a) A, B, C only (b) A and C only (c) B, C, D only (d) B and D only

Sol. (b)

47. Bonding in which of the following diatomic molecule(s) become(s) stronger, on the basis of Theory, by removal of an electron?

- (A) NO (B) N_2 (C) O_2 (D) C_2 (E) B_2

Choose the most appropriate answer from the options given below:

- (a) (A), (B), (C) only (b) (B), (C), (E) only
(c) (A), (C) only (d) (D) only

Sol. (c)

[31 Jan, 2024 (Shift-I)]

[25 June, 2022 (Shift-I)]

48. Given below are two statements:

Statement-I: A π bonding MO has lower electron density above and below the inter-nuclear axis.

Statement-II: The π^* antibonding MO has a node between the nuclei.

In the light of the above statements, choose the most appropriate answer from the options given below:

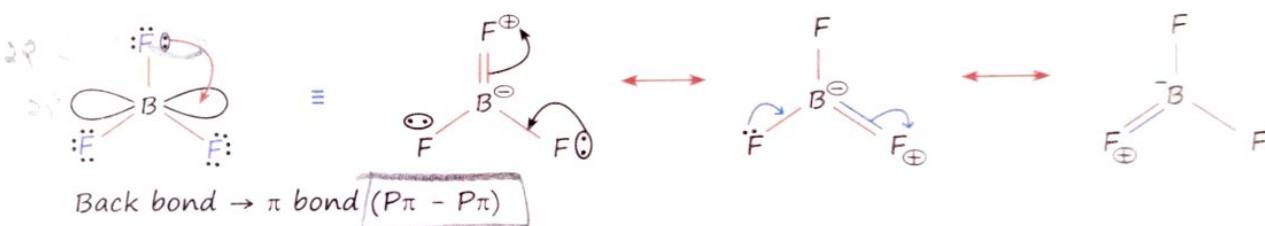
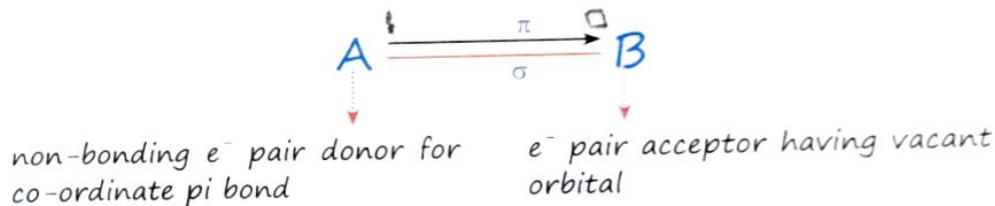
[01 Feb, 2024 (Shift-II)]

- (a) Both Statement-I and Statement-II are false
- (b) Both Statement-I and Statement-II are true
- (c) Statement-I is false but Statement-II is true
- (d) Statement-I is true but Statement-II is false

Sol. (c) A pi bonding molecular orbital exhibits higher electron density both above and below the internuclear axis.

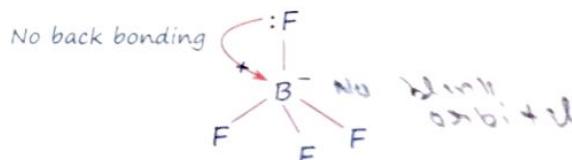
BACK BONDING

Coordinate pi bond



Back bonding increases the bond strength and decreases the bond length.

B-F Bond length: $BF_3 < BF_4^-$



Condition for Excellent Back Bonding

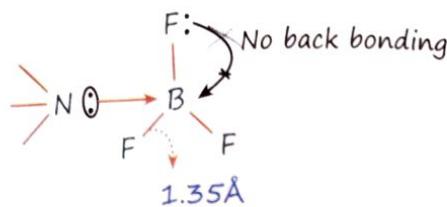
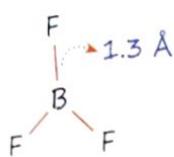
1. One atom from 2nd period

2. Second atom from 2nd/3rd period

π bond strength [back bond strength]: $2p - 2p > 2p - 3d > 2p - 3p > 3p - 3p$

49. The B - F bond length in $\text{Me}_3\text{N} \cdot \text{BF}_3$ is 1.35 \AA , much longer than 1.30 \AA in BF_3 . Explain?

Sol.



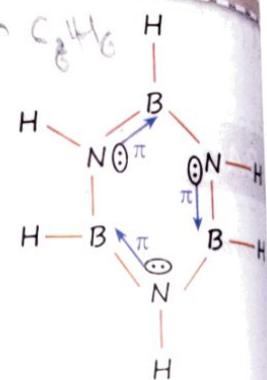
- back bonding from F to B \rightarrow small B - F bond

- No back bonding \rightarrow large B - F bond

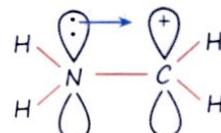
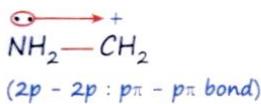
Inorganic Benzene ($\text{B}_3\text{N}_3\text{H}_6$)

- Back bonding from N to B.
- 3π bonds [6 π electrons]
- All nitrogen and boron are sp^2 hybridised.
- Molecule is planar.
- It is an aromatic compound and isoelectronic as benzene [C_6H_6].

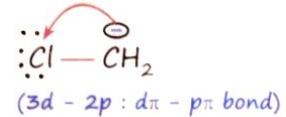
$6\pi e^-$ in $\text{B}_3\text{N}_3\text{H}_6$ in C_6H_6



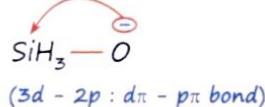
(1)



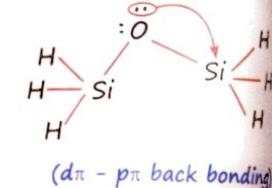
(2)



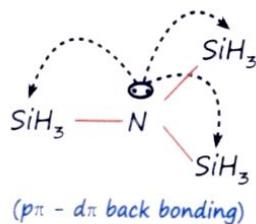
(3)



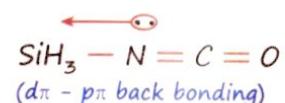
(4)



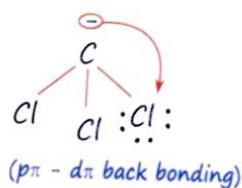
(5)



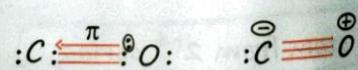
(6)



(7)



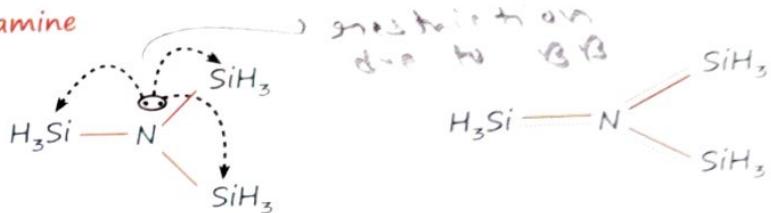
CO Molecule



(JEE Adv. 2005)

50. Trisilylamine is a planar molecule and does not act as a Lewis base while trimethylamine is pyramidal and act as Lewis base!

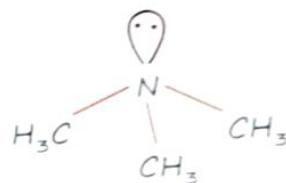
Sol. $N(SiH_3)_3 \rightarrow$ Trisilylamine



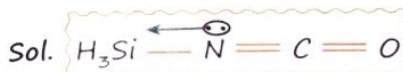
- ◆ Back bonding from N to Si
- ◆ Lone pair on nitrogen is delocalised as it is participating in back bonding with Si, so does not act as lewis base.
- ◆ Steric no = LP + SA = 0 + 3 = 3
- ◆ sp^2 hybridisation (planar molecule)

$N(CH_3)_3 \rightarrow$ Trimethylamine

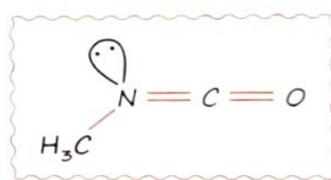
- ◆ No back bonding
- ◆ Lone pair is localised on nitrogen, so act as lewis base
- ◆ Steric No = LP + SA = 1 + 3 = 4
- ◆ sp^3 hybridisation (pyramidal shape)



51. Silyl isocyanate (SiH_3NCO) is linear but methyl isocyanate (CH_3NCO) is bent explain!



- ◆ Steric number of N : LP + SA = $0 + 2 = 2$
- ◆ sp hybⁿ : Linear
- ◆ Back bonding from N to Si



- ◆ No back bonding
- ◆ $SN \equiv 1 + 2 \equiv 3$
- ◆ sp^2 hybⁿ
- ◆ Bent shape

Lewis Basicity

$N(SiH_3)_3$

<

$P(SiH_3)_3$

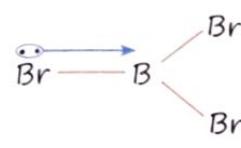
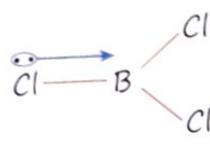
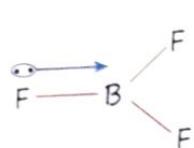
<

$N(CH_3)_3$: Lewis Basicity

<input type="checkbox"/> Lone pair on nitrogen is not available for donation due to back bonding, so it is less basic.	<input type="checkbox"/> Lone pair on P is present in a pure s orbital (near to the nucleus), so donation of e ⁻ pair is tough.	<input type="checkbox"/> Lone pair on N is present in sp^3 hybrid orbital (which is directional in nature). sp^3 hybrid orbital has only 33.3 %s character.
<input type="checkbox"/> Donation of e ⁻ pair is easy from sp^3 hybrid orbital w.r.t. pure s orbital.		

Lewis Acidic Character

$\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$: Lewis Acidity [Lone pair accepting tendency]



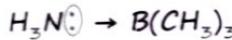
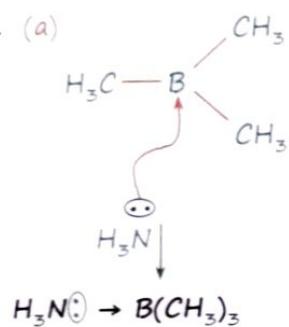
Extent of overlapping: $2p - 2p > 3p - 2p > 4p - 2p > 5p - 2p$
(Back Bonding)

Lewis acidity: $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$

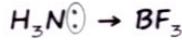
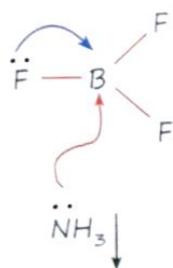
52. Find the order of reactivity towards NH_3 in following molecules?

- (a) $\text{B}(\text{CH}_3)_3$ (b) BF_3 (c) $\text{B}(\text{OH})_3$ (d) $\text{B}(\text{NH}_2)_3$

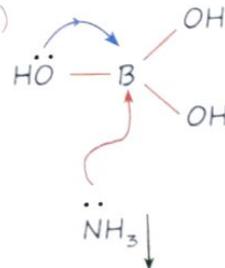
Sol. (a)



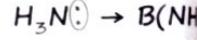
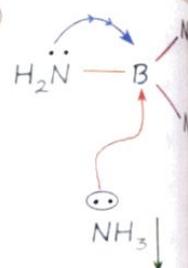
(b)



(c)



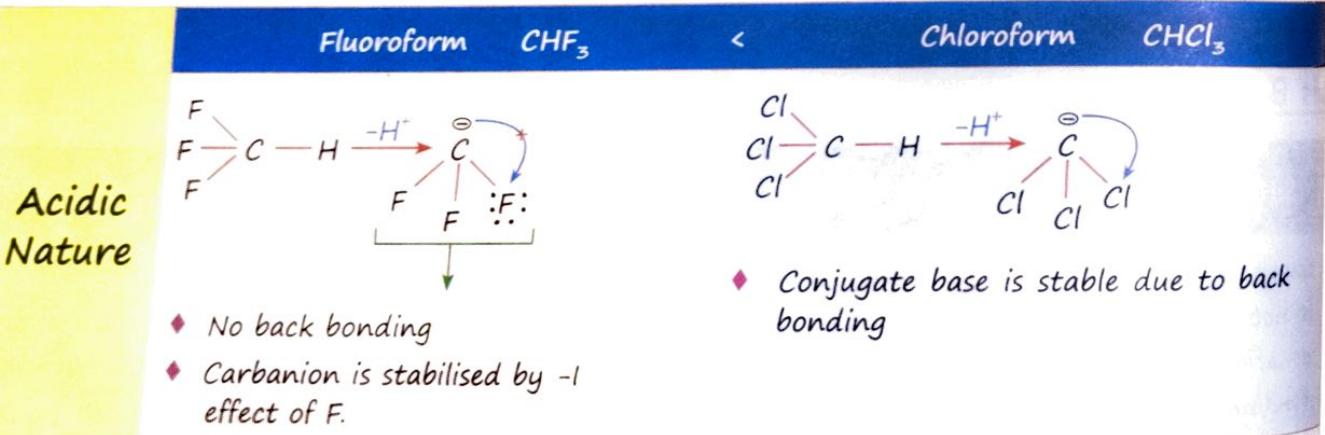
(d)



♦ Extent of back bonding $\rightarrow \text{B}(\text{CH}_3)_3 < \text{BF}_3 < \text{B}(\text{OH})_3 < \text{B}(\text{NH}_2)_3$

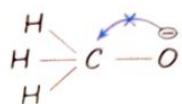
♦ Lewis Acidity $\rightarrow \text{B}(\text{CH}_3)_3 > \text{BF}_3 > \text{B}(\text{OH})_3 > \text{B}(\text{NH}_2)_3$

♦ Order of reactivity towards NH_3 (Lewis base): a > b > c > d (Rate of reaction)



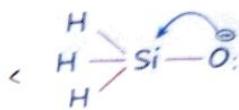
- ♦ No back bonding
- ♦ Carbanion is stabilised by $-I$ effect of F.

Methanol CH_3OH



♦ No back bonding

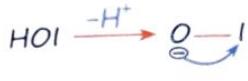
Silanol SiH_3-OH



Stability of conjugate base

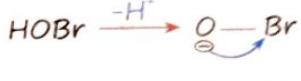
♦ Stable due to back bonding

HOI



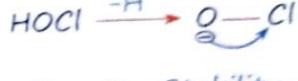
$\text{O}-\text{I}$

HOBr



$\text{O}-\text{Br}$

HOCl



$\text{O}-\text{Cl}$: Stability of conjugate base

Acidic Nature

(IIT JEE. 1996)

53. The following acids have been arranged in the order of decreasing acid strength. Identify the correct order.



(a) I > II > III

(b) II > I > III

(c) III > II > I

(d) I > III > II

Sol. (a)

DIMER FORMATION

mer \equiv Unit,

Dimer \equiv Combination of 2 unit

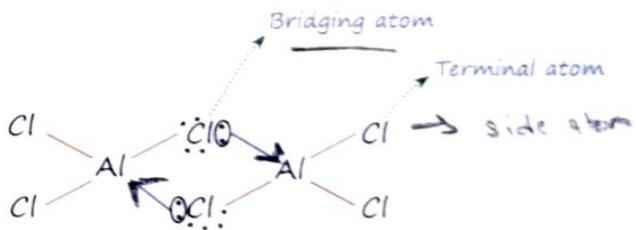
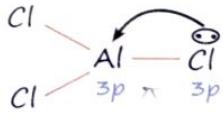
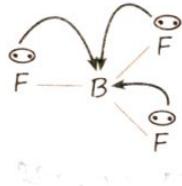
mono-mer \equiv Single Unit

Poly-mer \equiv Combination of more than 2 unit

BF_3

vs

AlCl_3



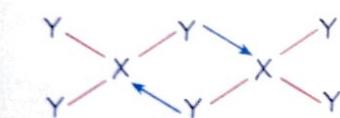
■ monomer is stable due to excellent back bonding $[2p - 2p]$

- Monomer is not stable because back bonding from Cl to Al $[3p - 3p]$ is not so good \rightarrow because $2p - 2p \pi$ bond is more strong
- Dimer formation takes place through bridge bonding to attain stability
- $[\text{AlCl}_3]_2 \equiv \text{Al}_2\text{Cl}_6$

BRIDGE BONDING

Type-1

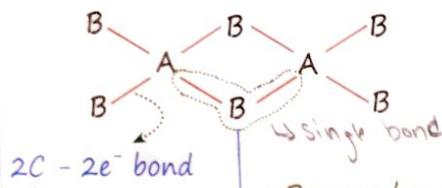
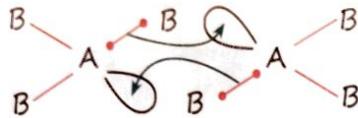
- Side atom has lone pair (Br, Cl)



- All bonds have $2e^-$ in it
[2 centre - $2e^-$ bond]

Type-2

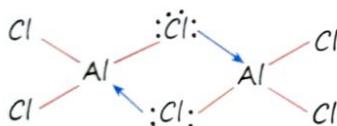
- Side atom or group has no lone pair (-H, -CH₃, -C₆H₅)



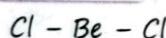
Single bond
 Banana bond
 3C - $2e^-$ bond
 Electron deficient bond

Type-1

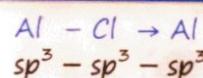
Type-1



BeCl_2 at high temperature → Monomer



Hybridisation



Max. No. of atoms in same plane

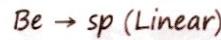
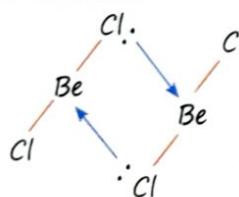
6

[2Al, 4Cl]

↓
Terminal

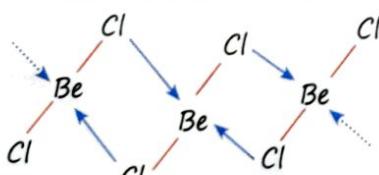
3

BeCl_2 in vapour phase → Dimer



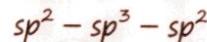
6

BeCl_2 in solid phase → Polymer



$\text{Be} \rightarrow sp^2$ (planar)

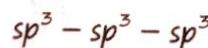
$\text{Be} - \text{Cl} \rightarrow \text{Be}$



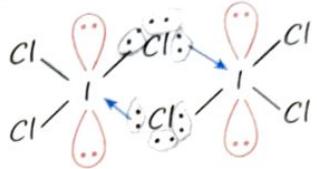
-

$\text{Be} \rightarrow sp^3$ (Tetrahedral)

$\text{Be} - \text{Cl} \rightarrow \text{Be}$



I_2Cl_6 in solid phase \rightarrow Planar molecule

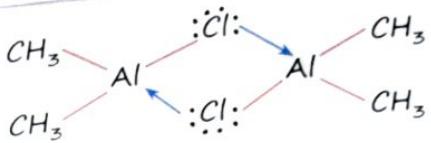


$I - Cl - I$
 $sp^3d^2 - sp^3 - sp^3d^2$

8
[2I and 6Cl]



$Al_2Cl_2(CH_3)_4$

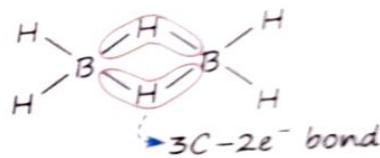


$Al - Cl \rightarrow Al$
 $sp^3 - sp^3 - sp^3$

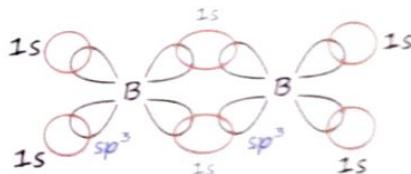
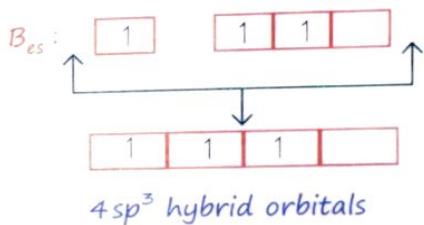
Type-2

Diborane: $[BH_3]^2 = B_2H_6$

\square $B-H-B$ bond = banana bond = $3C - 2e^-$ bond
= Electron deficient bond

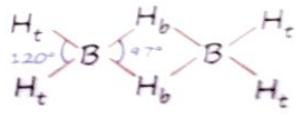


\square Hybridisation of $B \rightarrow sp^3$

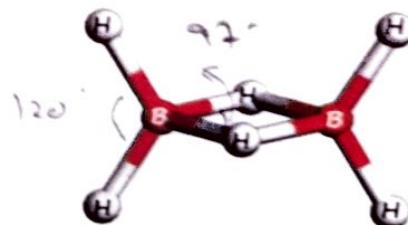


\square $B-H-B \Rightarrow sp^3 - 1s - sp^3$

$\angle H_tBH_t = 120^\circ \rightarrow \theta \uparrow : \% s\uparrow : \% p\downarrow : \text{Bond length} \downarrow$



$\angle H_bBH_b = 97^\circ \rightarrow \theta \downarrow : \% s\downarrow : \% p\uparrow : \text{Bond length} \uparrow$



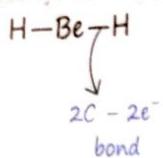
\square Terminal $B-H$ bonds have less p -character when compared to bridging bonds.

\square Bond Length: $B-H_t < B - H_b$

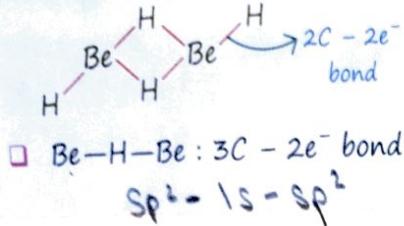
\square Bond Angle: $H_tBH_t > H_bBH_b$

\square Max. No. of atoms in same plane: $6[2B, 4H_t]$

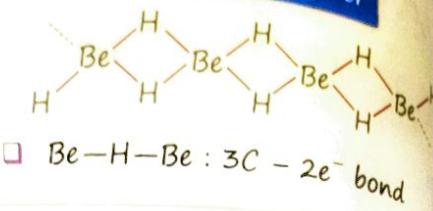
BeH_2 : Monomer



Be_2H_4 : Dimer



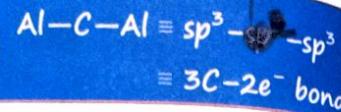
$[\text{BeH}_2]_n$: Polymer



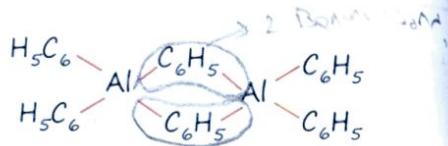
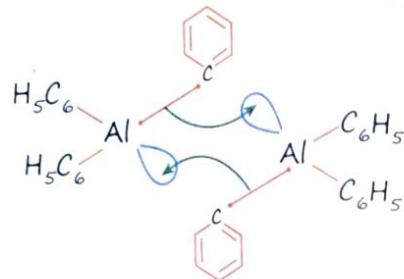
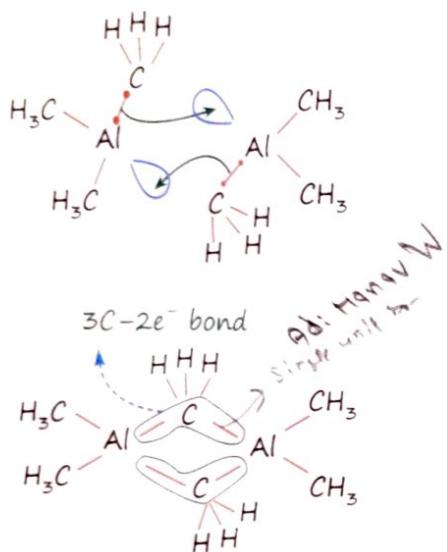
$\text{Al}_2(\text{CH}_3)_6$



$\text{Al}_2(\text{C}_6\text{H}_5)_6$

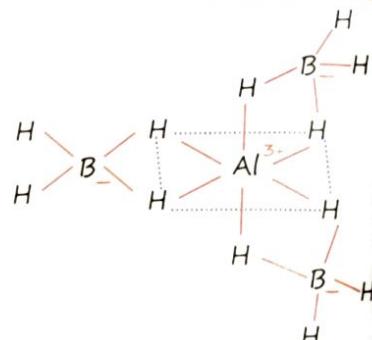


→ 8 p 2



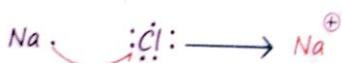
$\text{Al}(\text{BH}_4)_3$

- Number of $3\text{C} - 2\text{e}^- \text{ bond } [\text{B}-\text{H}-\text{Al}]$ in $\text{Al}(\text{BH}_4)_3 \equiv 6$
- Hybrⁿ on Al $\equiv \text{sp}^3\text{d}^2$ (Octahedral)
 $\text{B} \equiv \text{sp}^3$ (Tetrahedral)



IONIC BONDING

- The chemical bond formed between two or more atoms as a result of transfer of one or more electrons between them.



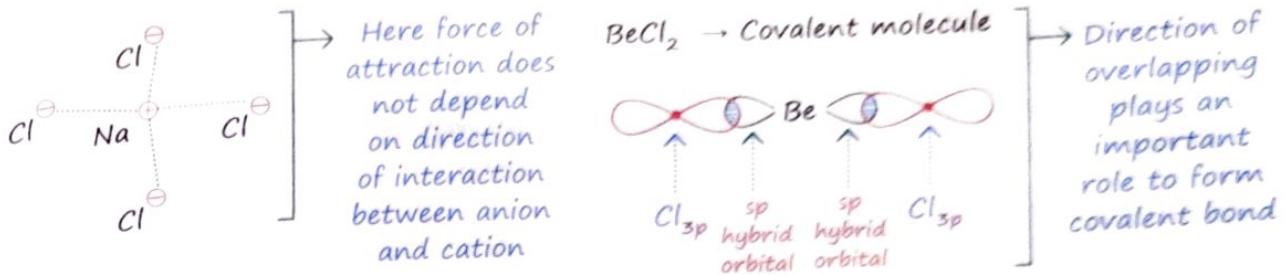
Cation



Anion

Electrostatic force of attraction between cation and anion \equiv Ionic Bond
 \equiv Electrovalent bond

- Ionic bond (electrovalent bond) is non-directional in nature but covalent bond is directional in nature



Ionic Compounds

A^+
Cation

(a) Metal (Na, Mg)

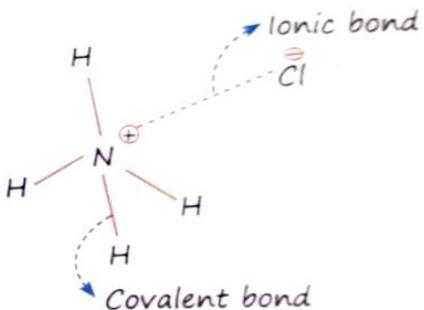
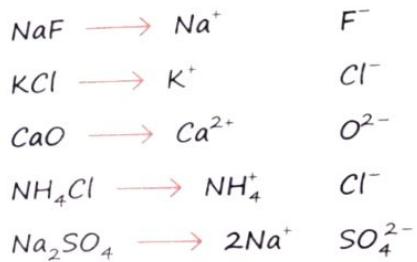
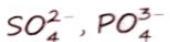
(b) Group of atoms having (+)ve charge



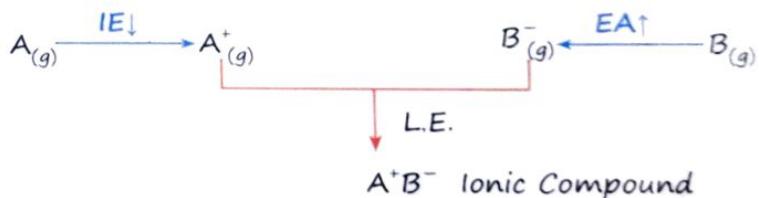
B^-
Anion

(a) Non-Metal (B, C, N, S, O, F)

(b) Group of atoms having (-)ve charge



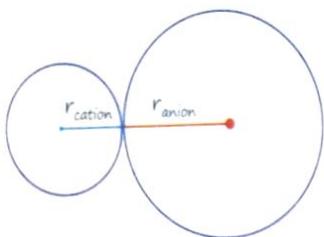
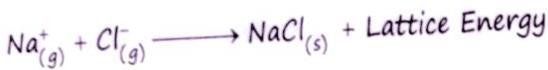
Favourable Condition for Ionic Bond



- (i) Less Ionisation Energy for A
- (ii) More Electron Affinity for B
- (iii) Energy released because of the combination of cation (A^+) and anion (B^-) should be high. This energy is also defined in terms of lattice enthalpy.

LATTICE ENERGY

- Energy which is released when the component ions (in gas phase) were brought together from infinity to make the lattice of the crystal.



$r = r_{\text{cation}} + r_{\text{anion}} \equiv \text{Internuclear Distance}$

$$\text{Lattice Energy} \propto \frac{q_1 \cdot q_2}{r}$$

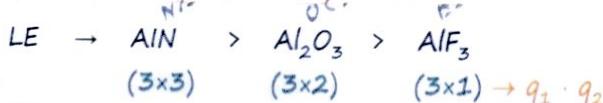
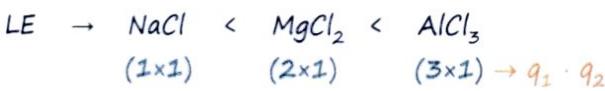
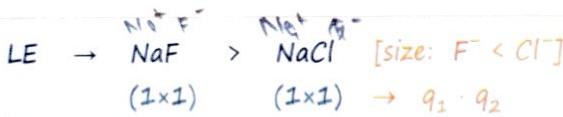
Factors Affecting LE

(i) Charge \uparrow : LE \uparrow

$$1. \text{LE} \propto q_1 \cdot q_2$$

(ii) Size \uparrow : LE \downarrow

$$2. \text{LE} \propto \frac{1}{r_{\text{cation}} + r_{\text{anion}}}$$



पहले
फिर SO_4^{2-}

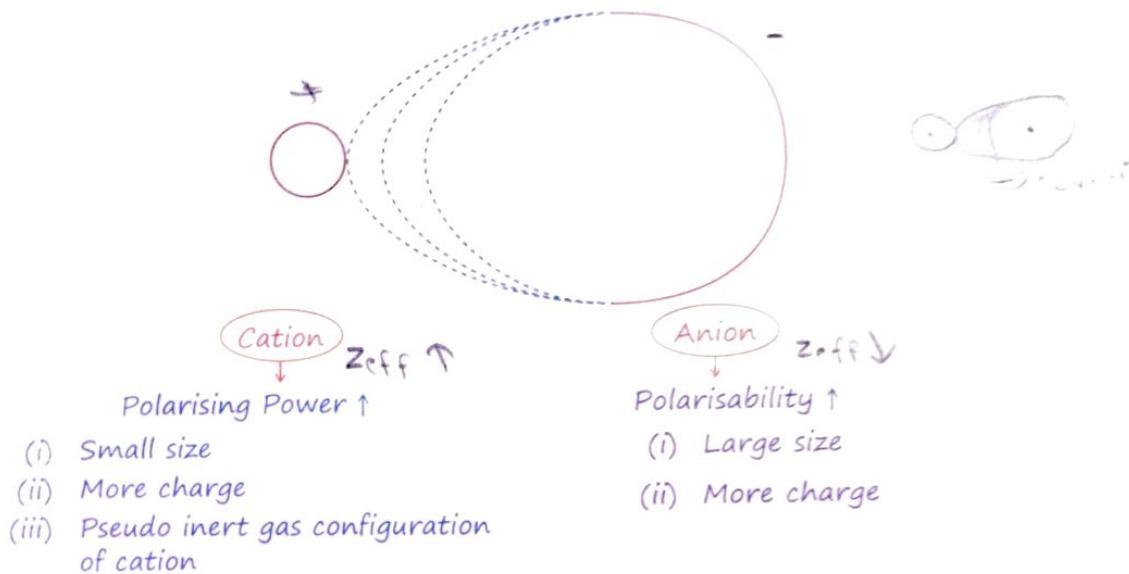
FAJAN'S RULE

Zonic - $A^+ B^-$
Cordon - $A:B$

- There is no compound which is 100% ionic.
- Covalent character in ionic compound can be explained with the help of Fajan's rule.
- The negative charge of an isolated anion is evenly distributed, but in the presence of a cation, anion's negative charge density is distorted. This distortion of e⁻ cloud is known as polarisation.

size \downarrow , charge \uparrow , charge density ($\frac{q}{r}$) \uparrow

- Polarising power** \rightarrow a cation's ability or power to distort the electron density of an anion towards itself, or to pull the electron density of an anion towards itself.
- Polarisability** \rightarrow tendency for an anion to become polarised.



Polarising power of cation \uparrow
Polarisability of anion \uparrow

Polarisation \uparrow

Covalent character \uparrow

Polarising power of cation \longrightarrow
 $\text{Li}^+ > \text{Na}^+ > \text{K}^+$
 $\bullet \text{Be}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+}$

$\bullet \text{Na}^+ < \text{Mg}^{2+}$

Polarisability of anion \longrightarrow
 $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$
 $\bullet \text{N}^{3-} > \text{O}^{2-} > \text{F}^-$

Covalent character \longrightarrow $\text{LiCl} > \text{NaCl} > \text{KCl} > \text{RbCl} > \text{CsCl}$

Size of cation \uparrow : Polarisation \downarrow : Covalent character \downarrow

BeCl_2 MgCl_2 CaCl_2 SrCl_2 BaCl_2
Size of cation \uparrow : Polarisation \downarrow : Covalent character \downarrow

LiF LiCl LiBr LiI
- Size of anion \uparrow
- Polarisation \uparrow
- Covalent character \uparrow

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

- $\text{AlF}_3 < \text{Al}_2\text{O}_3 < \text{AlN}$ – Covalent character

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

→

 - Charge on anion ↑
 - Polarisation ↑
 - Covalent Character ↑

Ionic Character

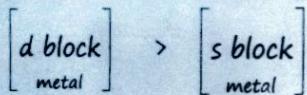
- AlN < Al_2O_3 < AlF_3 → less covalent character
more ionic character

- BeCl_2 < MgCl_2
 Covalent molecule Ionic compound ($\text{Mg}^{2+} 2\text{Cl}^-$)

- BeF_2 > BeCl_2 [BeF_2 has more ionic character than BeCl_2 but both are covalent molecules]
 $(\text{F}-\text{Be}-\text{F})$ $(\text{Cl}-\text{Be}-\text{Cl})$

Note

- ❑ Cation having pseudo-inert gas configuration, has more polarising power than other cations.

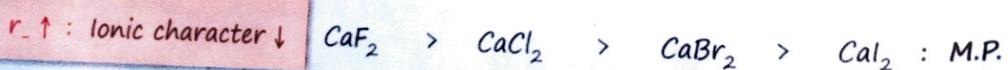


- Z_{eff} : $\begin{array}{c} \text{Cu}^+ \\ [\text{Ar}]3d^{10} \\ \downarrow \\ \text{Pseudo inert gas configuration} \end{array} > \begin{array}{c} \text{Na}^+ \\ [\text{Ne}] \\ \downarrow \\ \text{Inert gas configuration} \end{array}$

- Polarising power : $Cu^+ > Na^+$

Melting point ↑ : Ionic character ↑

- Melting point of covalent compound < melting point of ionic compound.



Colour



Energy by light to generate
F.O.P.
Copper - Barium
etc.
polar.

- The colour of some compounds can be explained on the basis of polarisation of their bigger negative anion.
- The bigger anions are more polarised and hence their electrons get excited by partial absorption of visible light.

1. AgCl is white but AgBr , Agl is yellow.

\Rightarrow Polarisation : $\text{AgCl} < \text{AgBr} < \text{Agl}$

more polarisation,
more intensity of colour

2. SnCl_2 is white but SnI_2 is red.

\Rightarrow Polarisation : $\text{SnCl}_2 < \text{SnI}_2$

3. PbCl_2 is white but PbI_2 is yellow.

\Rightarrow Polarisation : $\text{PbCl}_2 < \text{PbI}_2$

54. The number of following factors which affect the percent covalent character of the ionic bond is _____.

[8 April, 2023 (Shift-I)]

(A) Polarising power of cation

(B) Extent of distortion of anion

(C) Polarisability of the anion

(D) Polarising power of anion

Sol. [3] Acc. to Fajan's rule a compound is said to be covalent having smaller cation, larger anion and having high charge density. A, B and C are factors which affect the percent covalent character of the ionic bond according to Fajan's rule

55. Which of the following is least ionic?

(a) BaCl_2

(b) AgCl

(c) KCl

(d) CaCl_2

Sol. (b) $\text{AgCl} < \text{CaCl}_2 < \text{BaCl}_2 < \text{KCl}$ (ionic character)

Reason: Ag^+ has pseudo inert gas configuration.

56. Arrange the bonds in order of increasing ionic character in the molecules. LiF , K_2O , N_2 , SO_2 and ClF_3 .

[01 Feb, 2024 (Shift-I)]

(a) $\text{ClF}_3 < \text{N}_2 < \text{SO}_2 < \text{K}_2\text{O} < \text{LiF}$

(b) $\text{LiF} < \text{K}_2\text{O} < \text{ClF}_3 < \text{SO}_2 < \text{N}_2$

(c) $\text{N}_2 < \text{SO}_2 < \text{ClF}_3 < \text{K}_2\text{O} < \text{LiF}$

(d) $\text{N}_2 < \text{ClF}_3 < \text{SO}_2 < \text{K}_2\text{O} < \text{LiF}$

Sol. (c) Increasing order of ionic character

$\text{N}_2 < \text{SO}_2 < \text{ClF}_3 < \text{K}_2\text{O} < \text{LiF}$

The degree of ionic character in a bond depends on the difference in electronegativity, which determines the bond polarity.

57. Order of Covalent bond;

(A) $\text{KF} > \text{KI}$; $\text{LiF} > \text{KF}$

(B) $\text{KF} < \text{KI}$; $\text{LiF} > \text{KF}$

(C) $\text{SnCl}_4 > \text{SnCl}_2$; $\text{CuCl} > \text{NaCl}$

(D) $\text{LiF} > \text{KF}$; $\text{CuCl} < \text{NaCl}$

(E) $\text{KF} < \text{KI}$; $\text{CuCl} > \text{NaCl}$

(a) C, E only (b) B, C only

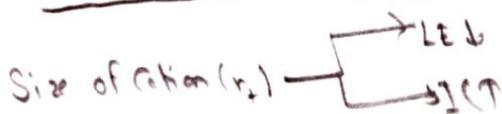
(c) B, C, E only (d) A, B only

Sol. (c)

THERMAL STABILITY

- $\text{Li}_2\text{CO}_3 \xrightarrow{\Delta} \text{Li}_2\text{O} + \text{CO}_2 \uparrow$
- $\text{Na}_2\text{CO}_3 \xrightarrow{\Delta} \text{No Reaction}$

Thermally stable \rightarrow Strong lattice \rightarrow



Monoatomic anions

\downarrow Lattice energy



Apply Lattice Energy concept to get order for thermal stability



▼



▼



▼



▼



size of cation \uparrow
Lattice Energy \downarrow
Thermal stability \downarrow



▼



▼



▼



▼



Li_2CO_3 is thermally unstable

Na_2CO_3 is thermally stable

- (i) Lattice Energy \uparrow
- (ii) Ionic Character \uparrow

More energy released during formation
more energy absorbed for dissociation

Anions

Polyatomic anions

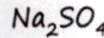
\downarrow Ionic char



Apply ionic character concept to get order for thermal stability



^



^



^



^



size of cation \uparrow
Ionic character \uparrow
Thermal stability \uparrow



^



^



^



^



▼



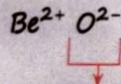
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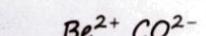


▼



Monoatomic anion

Lattice Energy \downarrow
Thermal stability \uparrow



^



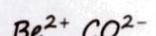
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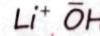
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^

Polyatomic anion

Ionic character \uparrow
Thermal stability \uparrow



Polyatomic anion



^



^



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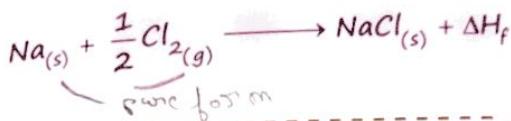


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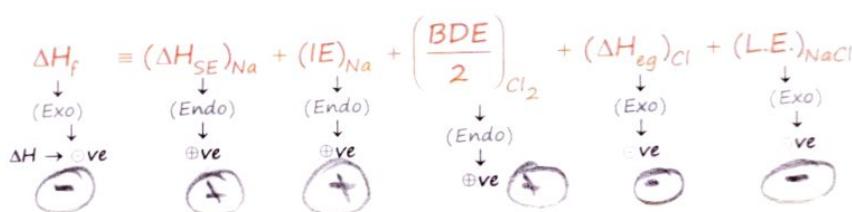
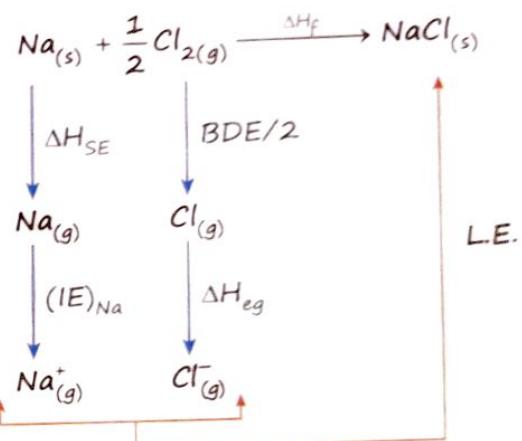
HEAT OF FORMATION

Amount of heat released when **1 mole of substance** is formed by its elements in pure and stable state.

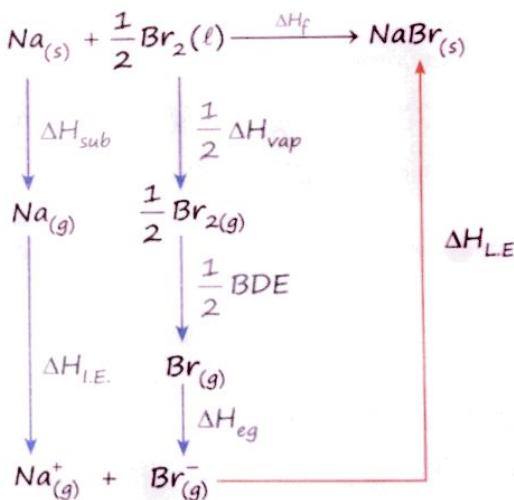


BORN-HABER CYCLE

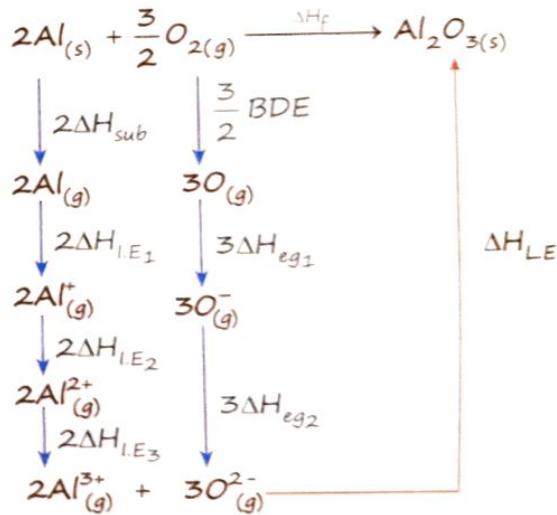
- ΔH_f → Heat of formation of NaCl
- $[\Delta H_{SE}]_{\text{Na}}$ → Sublimation energy of Na
- BDE → Bond dissociation energy of 1 mole Cl_2 molecule
- ΔH_{eg} → Electron gain enthalpy of $\text{Cl}_{(g)}$
- ΔH_{IE} → Ionisation Energy
- ΔH_{LE} → Lattice Energy



Born Haber Cycle for NaBr

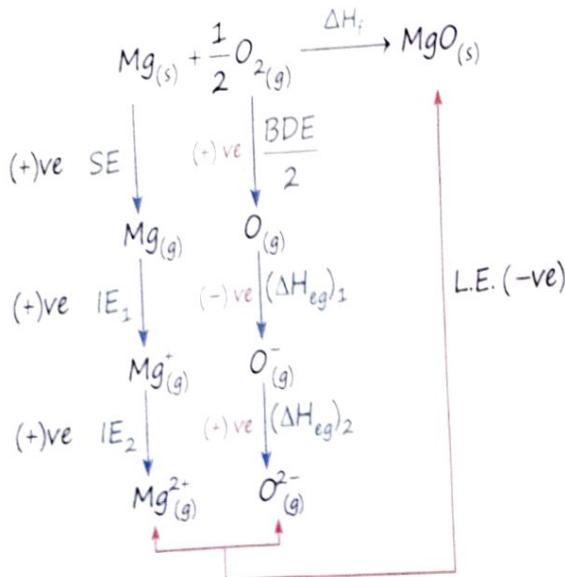


Born Haber Cycle for $\text{Al}_2\text{O}_{3(s)}$



$$\begin{aligned} \Delta H_f &= 2\Delta H_{sub} + 2\Delta H_{IE_1} + 2\Delta H_{IE_2} + 2\Delta H_{IE_3} \\ &\quad + \frac{3}{2} \text{BDE} + 3\Delta H_{eg_1} + 3\Delta H_{eg_2} + \Delta H_{LE} \end{aligned}$$

Born Haber Cycle for MgO



58. Arrange the following in the increasing order of their covalent character.

- (a) NaF , Na_3N and Na_2O (b) $NaCl$, $MgCl_2$, $AlCl_3$, $SiCl_4$ and PCl_5

Sol. (a) $NaF < Na_2O < Na_3N$

(b) $NaCl < MgCl_2 < AlCl_3 < SiCl_4 < PCl_5$: Covalent character

$[Na^+ < Mg^{2+} < Al^{3+} < Si^{4+} < P^{5+}$: Charge]

59. $SnCl_4$ has melting point $-15^\circ C$ whereas $SnCl_2$ has melting point $535^\circ C$. Why?

Sol. Covalent character : $SnCl_4 > SnCl_2$

[Charge : $Sn^{+4} > Sn^{+2}$]

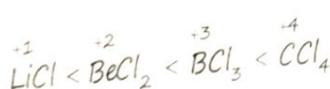
According to Fajan's rule, as charge on cation increases, its polarising power increases resulting in the greater polarisation of anion. Thus, covalent character increases and melting point decreases.

60. Which of the following is in order of increasing covalent character?

- (a) $CCl_4 < BeCl_2 < BC_3 < LiCl$
 (c) $LiCl < BeCl_2 < BC_3 < CCl_4$

- (b) $LiCl < CCl_4 < BeCl_2 < BC_3$
 (d) $LiCl < BeCl_2 < CCl_4 < BC_3$

Sol. (c) As charge on cations increases, their polarising power increases and thus covalent character increases.



61. Which of the following combination of ion will have highest polarisation?

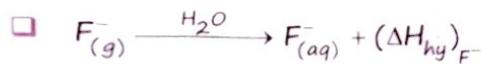
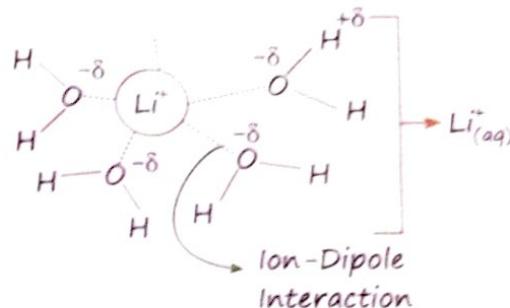
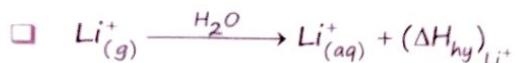
- (a) Fe^{2+}, Br^- (b) Ni^{4+}, Br^-

- (c) Ni^{2+}, Br^- (d) Fe^{3+}, Br^-

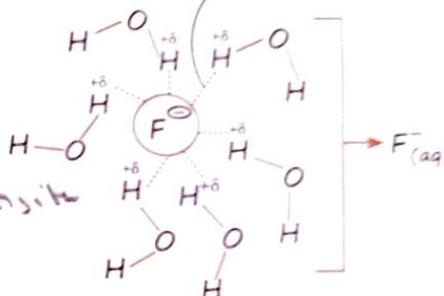
Sol. (b) Increase in oxidation state (Ni^{4+}) increases the polarising power of cation and thus increases the polarisation of Br^- ions.

HYDRATION ENERGY

Hydration energy is the amount of energy released when one mole of ions undergoes hydration.



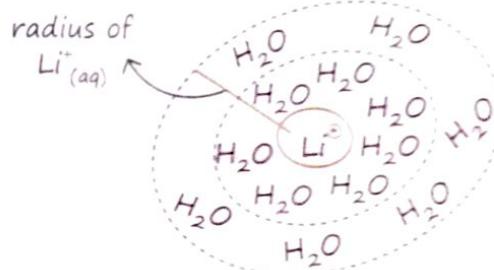
Hydration Energy $\propto \frac{\text{charge (q)}}{\text{size (r)}}$ *(charge density)*



Radius_(g) : $Li^{+} < Na^{+}$

Radius_(aq) : $Li^{+}_{(aq)} > Na^{+}_{(aq)}$

Mobility : $Li^{+}_{(aq)} < Na^{+}_{(aq)}$



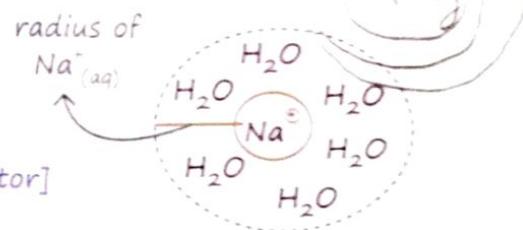
Ion Dipole Interaction : $Li^{+} > Na^{+}$

Hydration Energy : $Li^{+} > Na^{+}$

Hydration Energy : $Li^{+} > Na^{+} > K^{+} > Rb^{+} > Cs^{+}$ [Size factor]

: $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ [Size factor]

: $Na^{+} < Mg^{2+}$ [Charge factor]

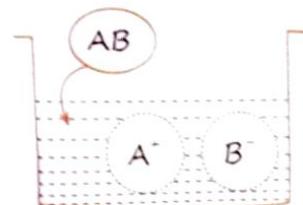
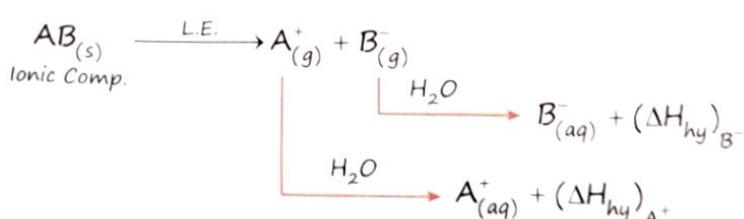


Solubility in Water

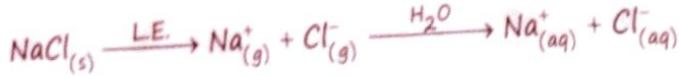
2 factors are responsible:

(i) Lattice energy of ionic compounds

(ii) Hydration energy of component ions

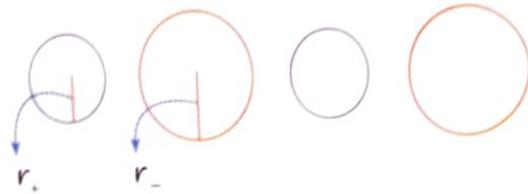


- Ionic Compound is soluble: $LE < [(\Delta H_{hy})_{A^+} + (\Delta H_{hy})_{B^-}]$
- Ionic Compound is insoluble: $LE > [(\Delta H_{hy})_{A^+} + (\Delta H_{hy})_{B^-}]$
- High solubility of NaCl $\rightarrow (LE)_{NaCl} < [(\Delta H_{hy})_{Na^+} + (\Delta H_{hy})_{Cl^-}]$



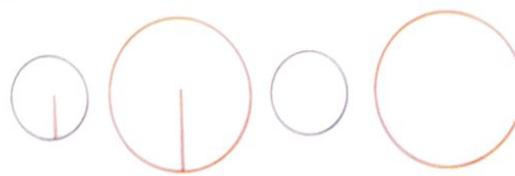
□ Perfect lattice: $r_+ \approx r_-$

→ Solubility \downarrow



□ Imperfect lattice: $r_+ < r_-$

→ Solubility \uparrow



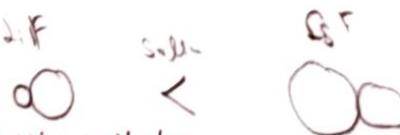
□ Extent of solubility $\propto |r_- - r_+|$

□ Solubility: LiF < CsF

Low solubility of LiF is due to its high lattice enthalpy

□ Solubility: LiI > CsI

Low solubility of CsI is due to smaller hydration enthalpy of its two ions (Cs^+ , I^-)



Small size

F^-, OH^-, O^{2-}

Anion

Large size

$I^-, Br^-, SO_4^{2-}, NO_3^-, NO_2^-, CO_3^{2-}$

$Li^+ F^- / OH^- \rightarrow r_+ \approx r_- \rightarrow \text{less soluble}$

$Cs^+ I^-, Br^-, NO_3^-, NO_2^- \rightarrow r_+ \approx r_- \rightarrow \text{less soluble}$

Basic nature of hydroxide \rightarrow ionic

□ $LiOH < NaOH < KOH < RbOH < CsOH$

□ $Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2 <$

$Be(OH)_2$

Be compounds are generally more soluble than others due to high hydration Be^{2+} ion.



Solubility \downarrow

$2Cs^+ CO_3^{2-}/SO_4^{2-} \rightarrow 2r_+ > r_-$

Solubility \uparrow

□ $Li_2SO_4 < Na_2SO_4 < K_2SO_4 < Rb_2SO_4 < Cs_2SO_4$

□ $Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$

- LiHCO₃ < NaHCO₃ < KHCO₃ < RbHCO₃ < CsHCO₃

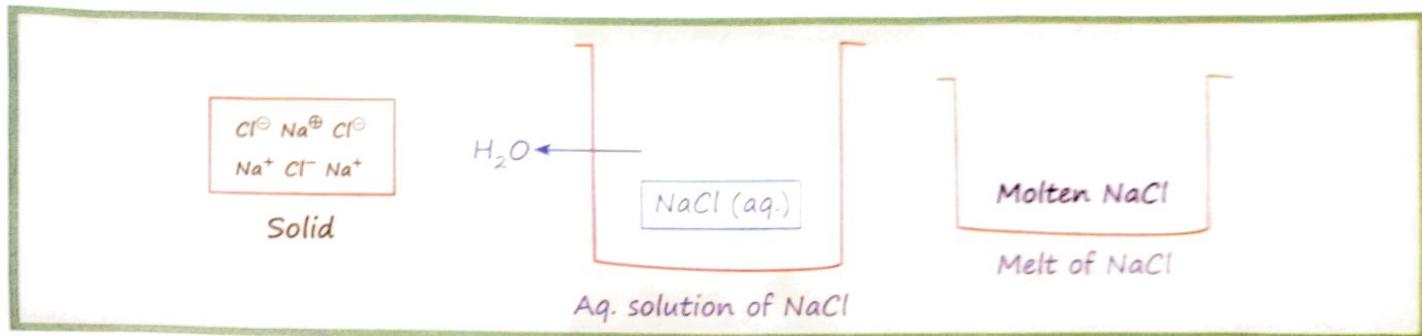
Same order for: CO₃²⁻ = HCO₃⁻



- BeCO₃ > MgCO₃ > CaCO₃ > SrCO₃ > BaCO₃
- BeSO₄ > MgSO₄ > CaSO₄ > SrSO₄ > BaSO₄

Properties of Ionic Compound

- Physical state:** At room temperature, ionic compounds exist either in solid state or in solution phase but not in gaseous state.



- Electrical conductivity:** Ionic solids are almost non-conductors. All ionic solids are good conductors in molten state & in aqueous solutions because their ions are free to move.
- Solubility of ionic compounds:** Soluble in polar solvents like water which have high dielectric constant (like H₂O, C₂H₅OH)

ISOMORPHISM

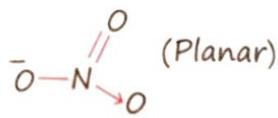
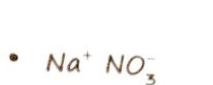
- Crystals of different ionic compounds having similar crystal structures are known to be isomorphs to each other and the phenomenon is known as isomorphism.

Example: FeSO₄·7H₂O & MgSO₄·7H₂O are isomorphs.

Crystals having same shape of anion are isomorphs

- BaSO₄ & KMnO₄ → isomorphs
→ Both anions SO₄²⁻ and MnO₄⁻ are tetrahedral in shape.
- NaNO₃ & NaClO₃ → not isomorphs
→ Because anions have different shape.

anion depen^t of shape



INTER MOLECULAR FORCE OF ATTRACTION



1. Interaction between Polar molecules

Dipole - dipole attraction

2. Interaction between Polar & non polar molecules

Dipole - induced dipole attraction

3. Interaction between non-polar molecules

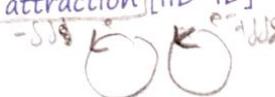
Instantaneous induced dipole - induced dipole attraction [IID-ID]

Dispersion force

London force

Vander Waal force of attraction includes 1st, 2nd and 3rd interactions.

Induced = non polar



Order of Inter-molecular Forces

(a) Ion - ion attraction



▼

(b) Ion - dipole attraction



▼

(c) Dipole - dipole attraction



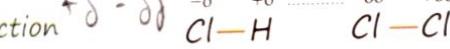
▼

(d) Ion-induced dipole attraction



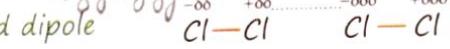
▼

(e) Dipole-induced dipole attraction



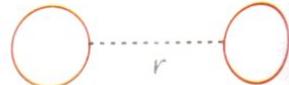
▼

(f) Ins. Induced dipole - induced dipole



Energy & Distance Relationship between 2 Interacting Particles

1. Ion-ion attraction $E \propto \frac{1}{r}$



2. Ion-dipole attraction $E \propto \frac{1}{r^2}$

3. Dipole-dipole attraction $E \propto \frac{1}{r^3}$

4. Ion-induced dipole attraction $E \propto \frac{1}{r^4}$

5. Dipole - induced dipole attraction

$$\rightarrow E \propto \frac{1}{r^6}$$

6. Ins. Induced dipole - induced dipole

These forces are always attractive and interaction energy is inversely proportional to the sixth power of the distance between two interacting particles ($1/r^6$ where r is the distance between two particles)

62. Identify type of interaction present between following species
- (1) Xe and H₂O
 - (2) Na⁺ and Br₂
 - (3) Br₂ and Br₂
 - (4) CO₂ and CO₂
 - (5) CCl₄ and CCl₄
 - (6) K⁺ and Cl⁻
 - (7) Li⁺ and H₂O
 - (8) H₂S and H₂S
 - (9) Ne and Ne
 - (10) I⁻ and I₂

Sol. 1. Xe, H₂O → Dipole-induced dipole
[non polar-polar]

2. Na⁺, Br₂ → Ion-induced dipole
[ion-nonpolar]

3. Br₂, Br₂ → London force/IID-ID
[nonpolar - nonpolar]

4. CO₂, CO₂ → IID-ID
[nonpolar - nonpolar]

5. CCl₄, CCl₄ → IID-ID
[nonpolar - nonpolar]

6. K⁺, Cl⁻ → Ion-ion attraction
[ion - ion]

7. Li⁺, H₂O → Ion-dipole attraction
[ion - polar molecule]

8. H₂S, H₂S → Dipole-dipole attraction
[polar - polar molecule]

9. Ne, Ne → London force
[nonpolar - nonpolar]

10. I⁻, I₂ → Ion-induced dipole
attraction
 $I^{\ominus} + I^{\delta} - I^{\delta} \Rightarrow I_3^-$ ion

63. The interaction energy of London forces between two particles is proportional to r^x, where r is the distance between the particles. The value of x is:

(a) -3

(b) -6

(c) 6

(d) 3

[26 Aug, 2021 (Shift-II)]

Sol. (b) $E \propto r^{-6}$ where E is the interaction energy of London forces.

Thus, x = -6.

Vander Waal Force of Attraction

Molecular mass ↑: Vander Waal force ↑
Boiling Point ↑

Order of Boiling Point

PH ₃ ^	H ₂ S ^	HCl
ASH ₃ ^	H ₂ Se ^	HBr
SbH ₃	H ₂ Te	HI

Size of the atom ↑: Vander Waal force ↑: BP ↑
He < Ne < Ar < Kr < Xe : BP/MP

Lowest B.P.
(4.2 K) of any known substance



	Boiling Point (K)	Melting Point (K)
He	4.216	0.95
Ne	27.1	24.7
Ar	87.29	83.6
Kr	120.85	115.8
Xe	166.1	161.7
Rn	211.5	202.2

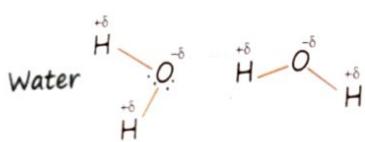
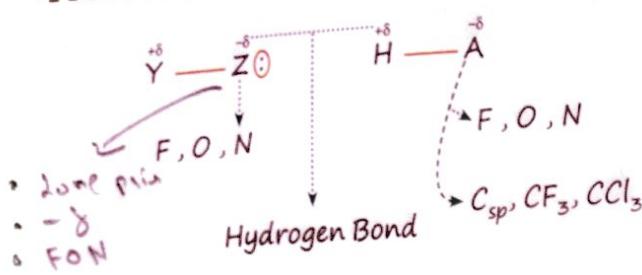
Not to draw value

893 → boiling P (generally) less than 0°C.

Chemical Bonding and Molecular Structure

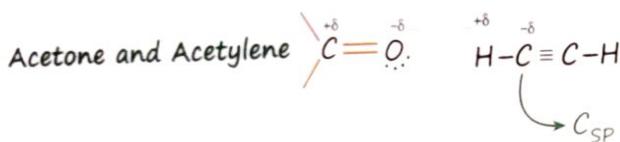
HYDROGEN BONDING

(very V.V. simple)

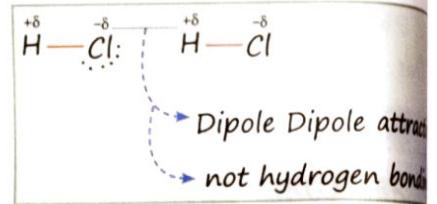
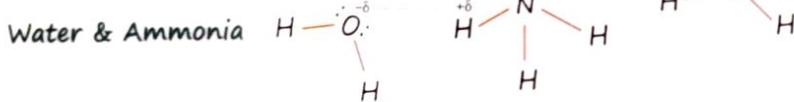
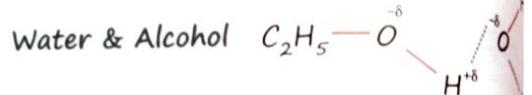
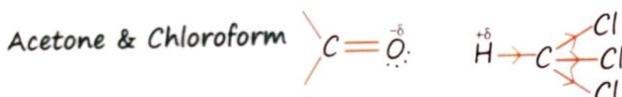
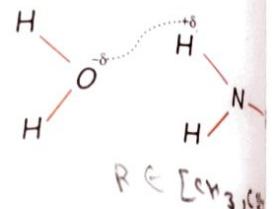


Force of attraction : H-bonding

Van der Waals force of attraction



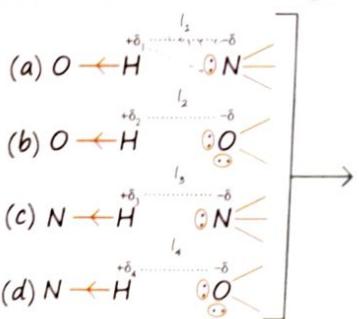
Water & Amine



Extent of H-bonding

Extent of H-bonding ↑ : (i) Partial (+)ve charge on H ↑ n.h.e. more e- in H due to less off

(ii) Electron density on Z ↑

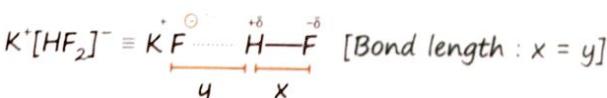


Extent of H-bonding : $a > b > c > d$

Bond length : $l_1 < l_2 < l_3 < l_4$

Order for partial charge : $(\delta_1 = \delta_2) > (\delta_3 = \delta_4)$

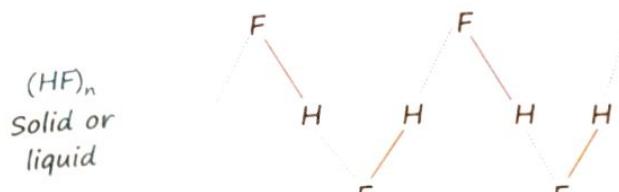
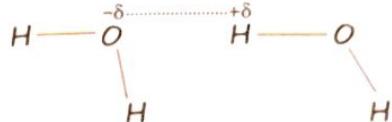
□ $K[HF_2^-]$



Types of Hydrogen Bonding

Inter-molecular H-bonding

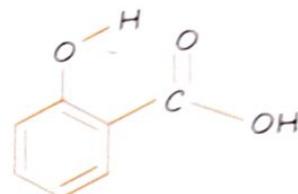
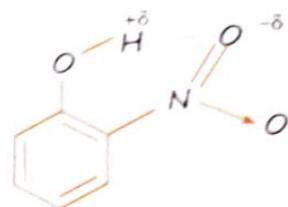
H-bonding between molecules



- The hydrogen bonds in HF link the F atom of one molecule with the H-atom of another molecule, thus forming a zig-zag chain $(\text{HF})_n$ in both the solid and also in the liquid.

Intra-molecular H-bonding

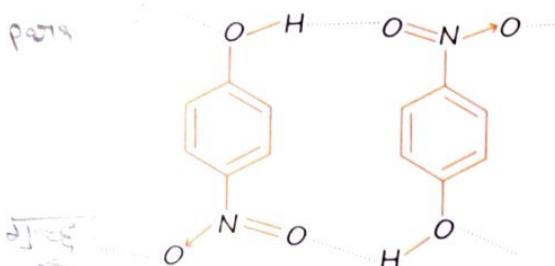
H-bonding within a molecule



Formation of ring

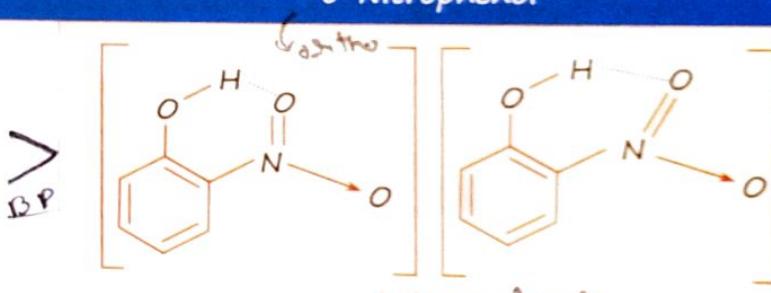
Boiling Point

p-Nitrophenol



- Association of molecules due to inter-molecular H-bonding $\Rightarrow \text{BP} \uparrow$
- The intermolecular hydrogen bonding in *p*-nitrophenol requires more energy to break the intermolecular forces, resulting in a higher boiling point.

o-Nitrophenol



- It exists as discrete molecules which are held together by weak van der waals forces of attraction. A small amount of energy is required to break these forces of attraction. So, less boiling point.

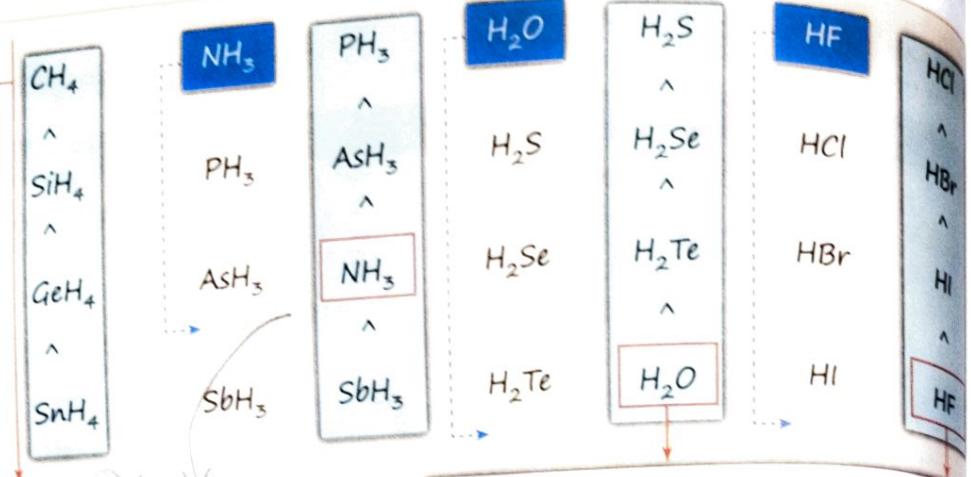
Order of Boiling Point

$\text{NH}_3, \text{H}_2\text{O}$ and $\text{HF} \rightarrow$ Inter-molecular hydrogen bonding $\Rightarrow \text{BP} \uparrow$

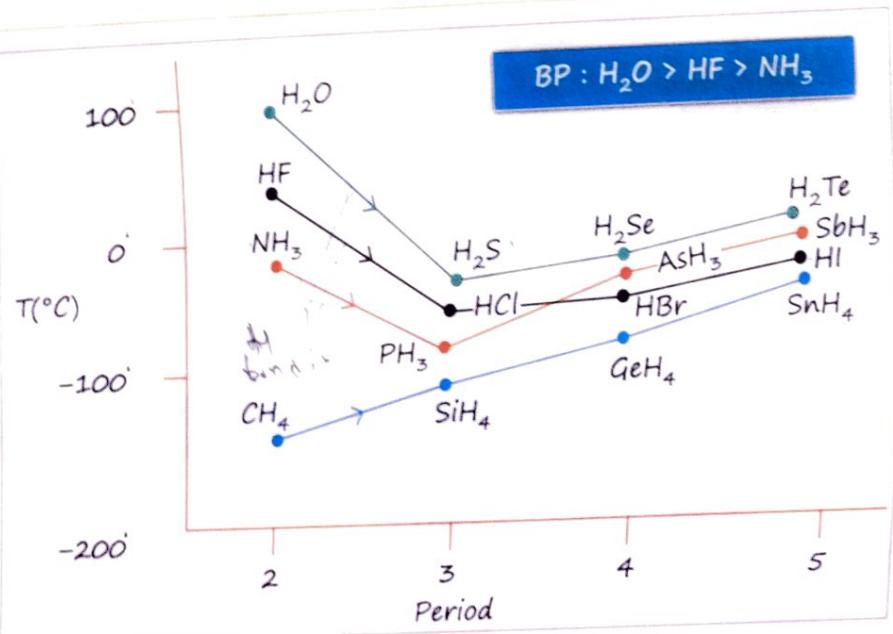
Chemical Bonding and Molecular Structure

Top → Bottom

- Molecular Mass ↑
- Vander Waal Force of attraction ↑
- BP ↑



It has stronger intermolecular force attraction (H-bonding) than others (having vander Waal force of attraction).

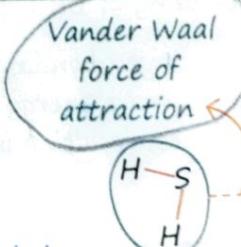
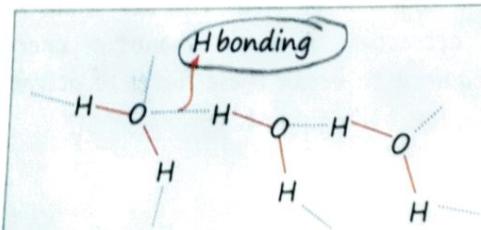


□ Sudden increase in boiling point of H_2O and HF is due to hydrogen bonding
(BP): $H_2O > HF > NH_3$

$H_2O > HF > NH_3$
Liquid

Physical State

(i) H_2O is liquid but H_2S is gas at room temperature.



There is extensive hydrogen bonding in H_2O , which is absent in H_2S . Molecules of H_2S are held together only by weak van der Waal's forces of attraction.

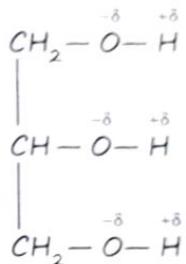
Hence, H_2O exists as a liquid while H_2S as a gas.

(ii) HF is liquid but HCl is gas. Think why?

B.P. & Viscosity

Honey has more viscosity than water which is on a slope or hill.

→ No. of Hydrogen bonds per molecule ↑ : viscosity ↑ or Mol. wt ↑: BP ↑



Mol. wt

WATER

□ No. of water molecules attached to 1 H_2O molecule = 4

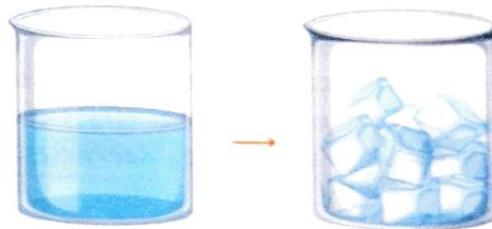
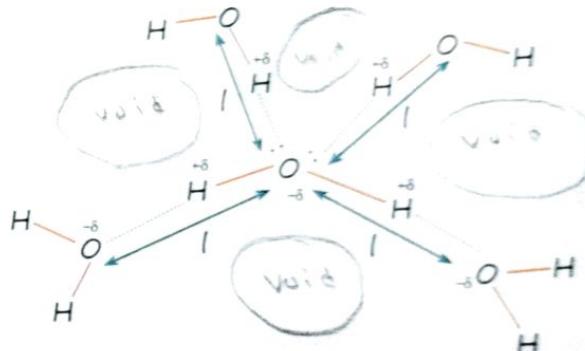
in ice

in water molecules

□ Tetrahedrally bonded to a water molecule in solid state.

Density : $\text{H}_2\text{O}_{(s)} < \text{H}_2\text{O}_{(l)}$

Volume : $\text{H}_2\text{O}_{(s)} > \text{H}_2\text{O}_{(l)}$

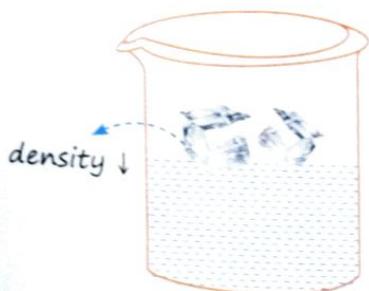


□ Volume of ice is more because of open cage like crystal structure, form by association of water molecules with the help of hydrogen bond.

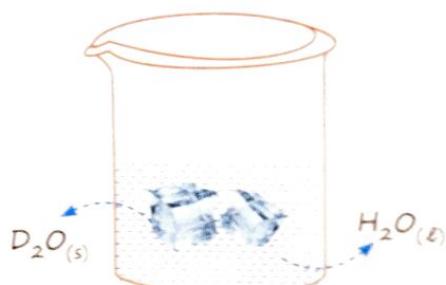
$\text{H}_2\text{O}_{(s)}$ in $\text{H}_2\text{O}_{(l)}$

$\text{D}_2\text{O}_{(s)}$ in $\text{H}_2\text{O}_{(l)}$

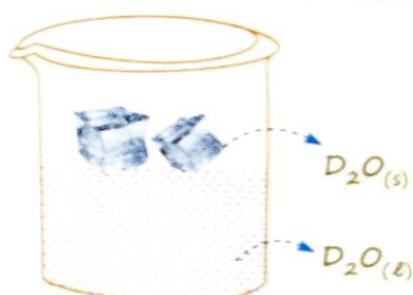
$\text{D}_2\text{O}_{(s)}$ in $\text{D}_2\text{O}_{(l)}$



Ice [$\text{H}_2\text{O}_{(s)}$] Floats on water



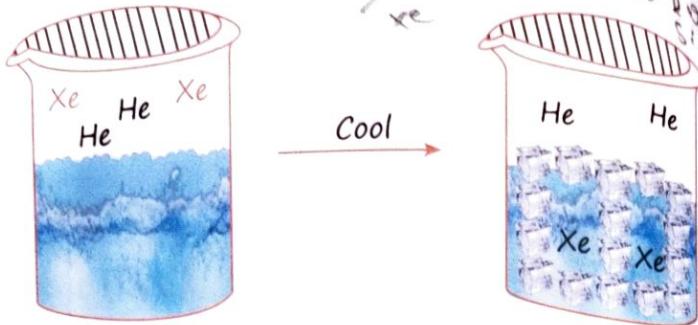
$\text{D}_2\text{O}_{(s)}$ sinks into water



$\text{D}_2\text{O}_{(s)}$ floats on heavy water

due to small size
trapped to cage
get trapped to cage
Clathrates compounds

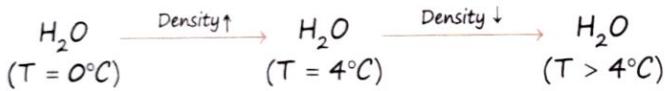
Clathrates compounds
Cage like compounds



- Due to open structure, ice is capable of forming Clathrates.
- Noble gas hydrate (clathrate compound):** Ar, Kr, Xe can form clathrate compounds but He, Ne due to their smaller size.

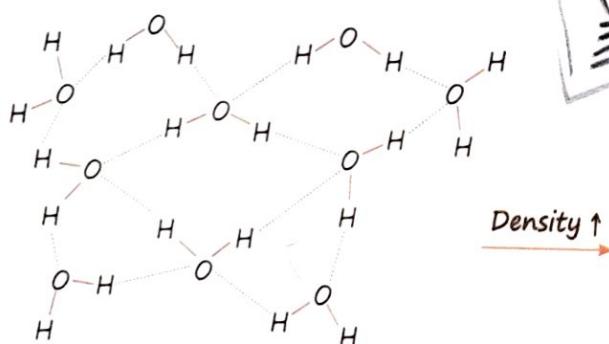
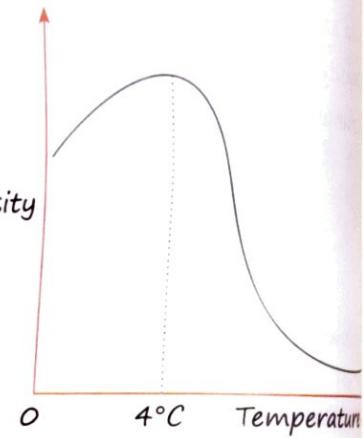
$\text{Xe} \cdot 6\text{H}_2\text{O}$	formed only where
$\text{Ar} \cdot 6\text{H}_2\text{O}$	water freezes at high
$\text{Kr} \cdot 6\text{H}_2\text{O}$	pressure together with noble gas

Variation of Density with Temperature

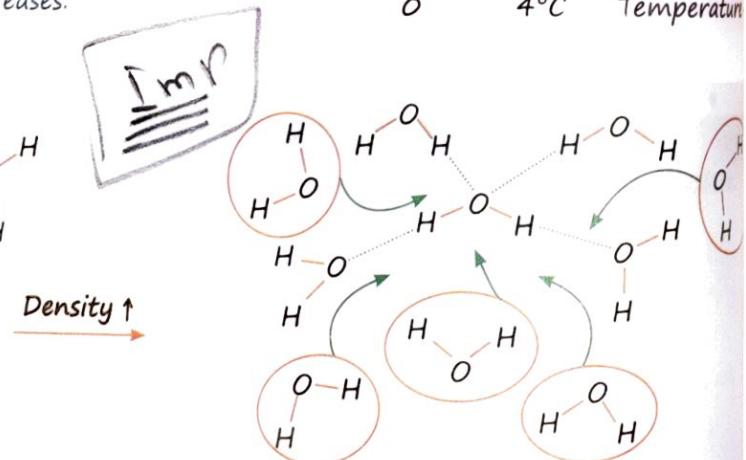


- In this temperature region (0°C to 4°C), some of the ice melts and hence some H_2O molecule go into the cages of remaining ice structure.

So, volume decreases, density increases becoming max at 4°C but beyond this temp thermal effects become dominating volume increases then density decreases.



$\text{H}_2\text{O}(s)$
 $T = 0^\circ\text{C}$



(IIT JEE 2000)

64. Amongst H_2O , H_2S , H_2Se and H_2Te , the one with the highest boiling point is

- (a) H_2O because of hydrogen bonding
- (b) H_2Te because of higher molecular weight
- (c) H_2S because of hydrogen bonding
- (d) H_2Te because of lower molecular weight

Sol. (a) H_2O displays higher boiling point (in spite of lower molecular weight) on account of strong hydrogen bonding, while H_2S , H_2Se and H_2Te do not display H-bonding.

65. The correct statement/s about Hydrogen bonding is/are :

[04 April, 2024 (Shift-I)]

- A. Hydrogen bonding exists when H is covalently bonded to the highly electronegative atom.
- B. Intermolecular H bonding is present in o-nitrophenol
- C. Intramolecular Hs bonding is present in HF.
- D. The magnitude of H bonding depends on the physical state of the compound.
- E. H-bonding has powerful effect on the structure and properties of compounds.

Choose the correct answer from the options given below:

- (a) A only
- (b) A, D, E only
- (c) A, B, D only
- (d) A, B, C only

Sol. (b)

66. If the boiling point of H_2O is 373 K, the boiling point of H_2S will be: [3 Sept, 2020 (Shift-I)]

- (a) more than 373 K
- (b) less than 300 K
- (c) greater than 300 K but less than 373 K
- (d) equal to 373 K

Sol. (b) Boiling point of H_2S is 213K.

"Chalo, NEET ke PYQs
practice karte hain,
QR code scan karo aur
apni preparation ko
boost karo!"

