Chemical Bond?

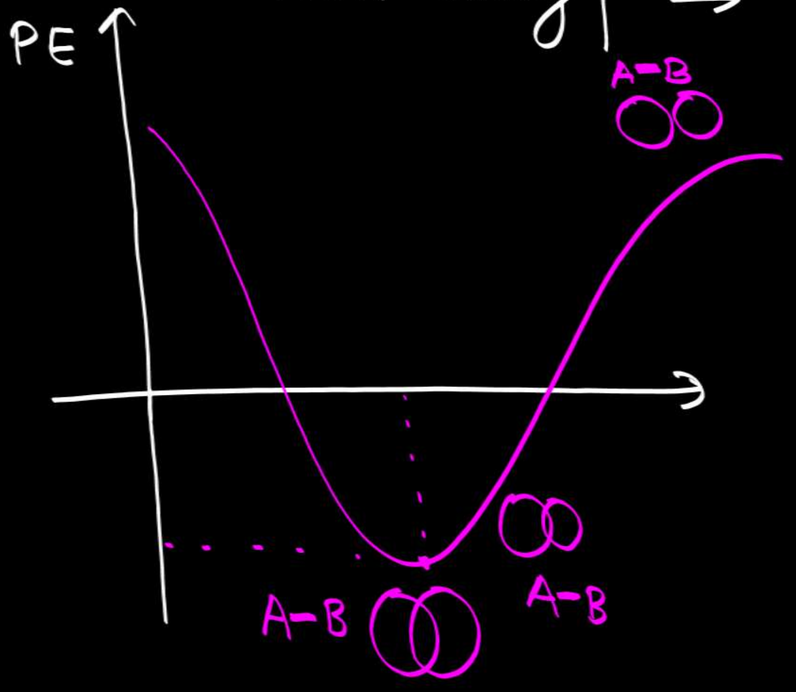
Force of attraction that holds atom / ions / molecule together.

Chem. Bond is formed to achieve stability

More Bonding ⟹ more stability
- → Exothermic Process
- → least energy ⟹ strongest Bond
  - ⇓ Bond length Small
    - ⇓ (Stiff Bond)
  - ⇑ (High Bond energy / enthalpy)
    - ⇑ energy req. to Break Bond

ex H^+ , H_2 , H^-

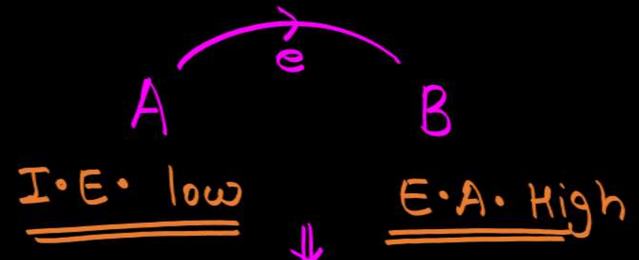
(most stable)



Ionic Bond

- The electrostatic attraction between the positive and negative ions is called ionic or electrovalent bond.
- Electrovalence = No. of unit charge is on the ion.

1) Form by transfer of charge



$A^+ :::: B^-$

2) Ionic bond is non-directional

3) It is due to electrostatic force of attraction

4) favourable cond^n : metal (Low IE)
Non-metal (High EA)

5) conductor in molten / aq. state

6) Soluble in water

7) Isomorphism : Similar structure but diff chem Prop.

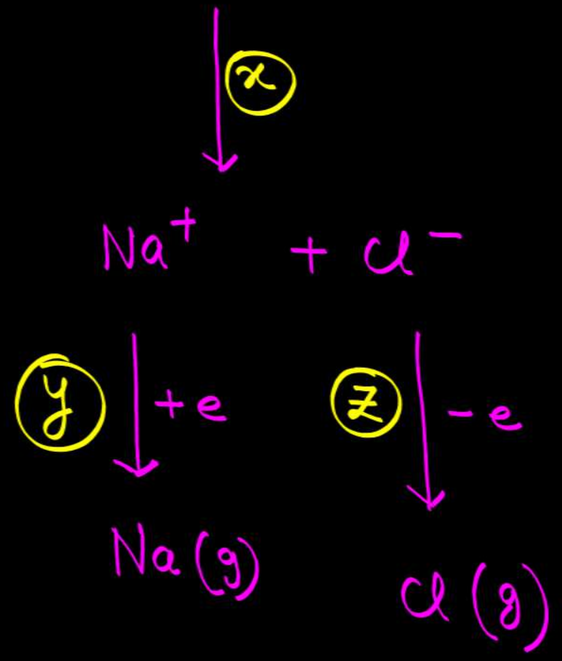
8) High M.P. & High lattice enthalpy

9) strongest Bond

Lattice Energy

Is defined as energy evolved when one gram molecule of the crystal is formed from Isolated gaseous ions:

Ex NaCl



$\Delta H_{lattice} = x + y + z$

$\Delta H_{lattice} \propto$ charge on Cation / anion

$\propto \frac{1}{size}$

+1 +2 +3

$NaCl$ $MgCl_2$ $AlCl_3$

Charge ↑ $\Delta H_{lattice}$ ↑

$LiCl$, $NaCl$, KCl, $RbCl$, $CsCl$

Size ↑ $\Delta H_{lattice}$ ↓

Hydration Energy

Energy released when 1 mole of ionic compd is completely hydrated

$$NaCl(s) \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq)$$

ΔH_{hyd}

$NaCl \quad MgCl_2 \quad AlCl_3$

Charge ↑ ΔH_{hyd} ↑

$LiCl, \quad NaCl, \quad KCl, \quad RbCl, \quad CsCl$

Size ↑ ΔH_{hyd} ↓

$\Delta H_{hyd} \propto$ Charge on cation / anion

$\propto \frac{1}{\text{Size}}$

Applications of Hydration Energy

ΔH_{hyd} more

- Solubility ↑
- Hydrated radius ↑
- Mobility in aq. med ↓
- Conductivity ↓

ex $Li^+ < Na^+$ (size)

ex $Li^+(aq) > Na^+(aq)$ (size)

ex Conductivity / mobility

$Na^+(aq) > Li^+(aq)$

Applications of Hydration Energy

(a) Size of the hydrated ions: Greater the hydration of the ion greater will be its hydrated radii.

$$Li^+(aq) > Na^+(aq) > K^+(aq) > Rb^+(aq) > Cs^+(aq)$$

(b) Mobility of the ion: more is the hydration smaller will be the mobility of the ions

$$Li^+(aq) < Na^+(aq) < K^+(aq) < Rb^+(aq) < Cs^+(aq)$$

(c) Electrical conductance: is related to mobility so follows the same order.

$$Li^+(aq) < Na^+(aq) < K^+(aq) < Rb^+(aq) < Cs^+(aq)$$

Solubility depends on $(\Delta H_{Lattice} + \Delta H_{hyd})$ = - ve

less — more

⇓

ionic compd ⇒ soluble in water

↳ ⇒ more Ionic ⇒ more soluble

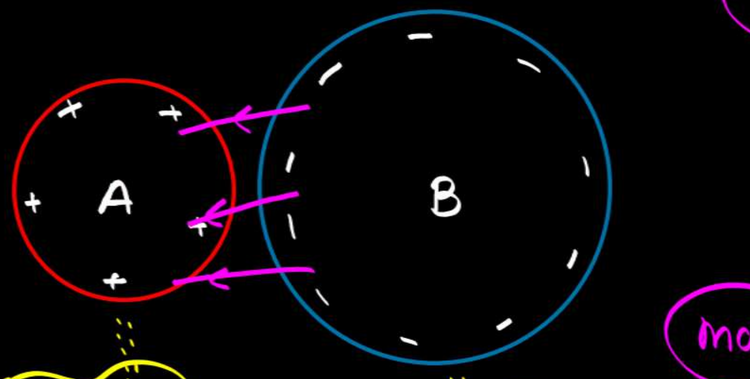
(Covalent compds are less soluble)

(Fajan's Rule) (Covalent nature in ionic bond) :

Polarisation Power: The ability of cation to polarize a nearby anion

Polarizabilty

Polarisation ∝ Covalent character



Polarisation Power of Cation

Polarizability of anion

more

Polarization ∝ charge more

∝ Small Cation

∝ Big anion

Covalent more

Ionic character ↓

example : Covalent character

NaCl < $MgCl_2$

NaCl > KCl

NaCl > NaF

Polarisation more WHEN :

1. Small cation
2. Bigger anion
3. Greater Charge on ion
4. Non-inert gas configuration

inert Gas configuration

Cu^{+}, Ag^{+}, Zn^{+2}

- - - .

most Covalent

Polarisation more $\rightarrow$ *covalent character more*

$\rightarrow$ *ionic character less*

$\rightarrow$ *M. P. less*

$\rightarrow$ *SOLUBILITY less*

Solubility of ionic Compounds

Solubility depends on so many factors :

$\propto \frac{1}{\text{lattice energy'}}$

$\propto$ hydration energy,

$\propto \frac{1}{\text{polarization'}}$

packing pattern, entropy, etc.

Such combination is more soluble

For single cations/anions [Metal]

Chhota

Bada

For Poly anions

Chhota

OH^-

CO_3^{2-} , HCO_3^-
FOR 1st group

$C_2O_4^{2-}$

Bada

ClO_4^- , NO_3^- ,SO_4^{2-}

CO_3^{2-} , HCO_3^-
FOR 2ND group

Covalent Bond

Lewis Theory: No. of e- shared by each atom is equal to no. of e- required to complete the octate = Valency

⇓

Bond formed by sharing of e-

⇓

$A \cdot \times B \Rightarrow A-B$

$A :: \times\times B \Rightarrow A=B$

$A ::: \times\times\times B \Rightarrow A \equiv B$

Valence e-

	1	2	3	4	5	6	7	8
Valency	1	2	3	4	3	2	1	0
No. of bond = Valency	Li°	Be	B	C	N	O	F	Ne
No. of bonds max = Valence	Mg	Al	Si°	P	S	Cl	Ar	
e-				As		Br		

Molecule

→ Central atom (CA) ← least in number, less E.N.

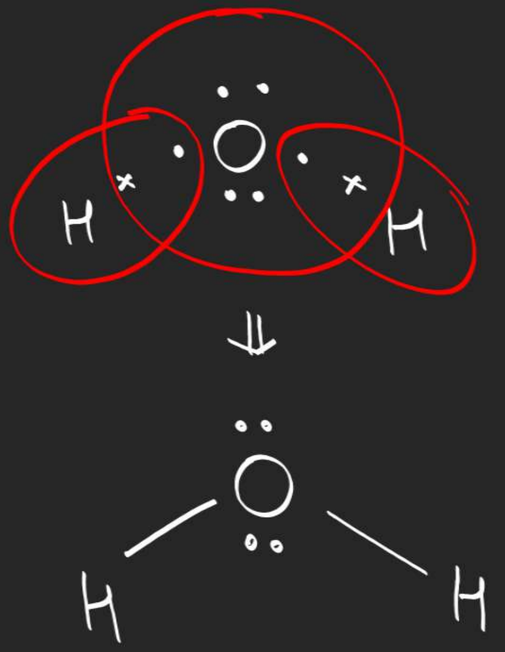
→ Surrounding atom (SA)

⇓

			At max
H, Li, F, Cl	1 bond	OH^-, CN^-	
O, CO_3^{2-}	2 bond	SO_4^{2-}	
			N ⇒ 3,4 bond; C ⇒ 4 bond

Draw Lewis Dot structure

1) H_2O

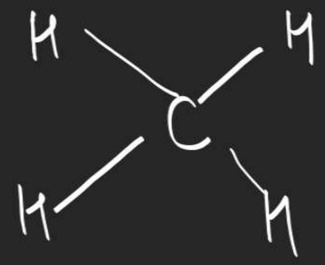


2) CO_2

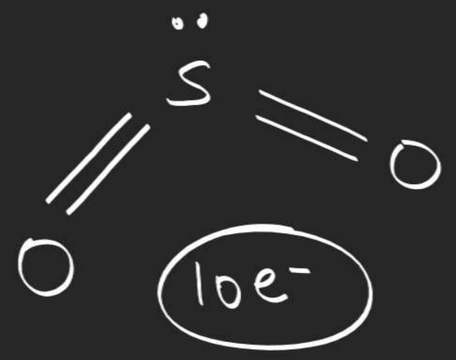
3) HCl

4) NH_3

5) CH_4

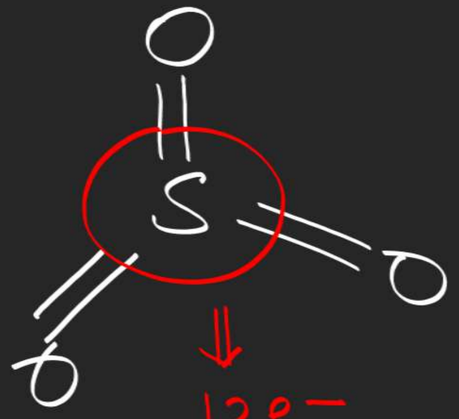


SO_2



10 e⁻

SO_3

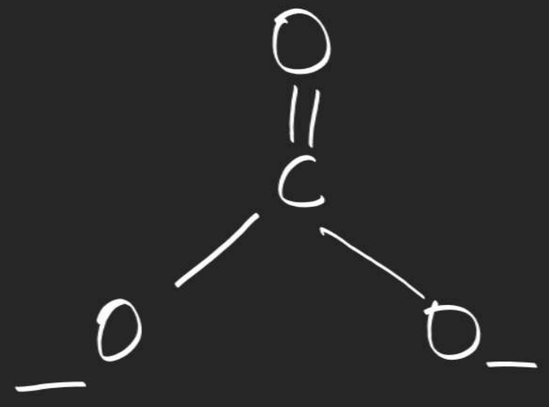


12 e⁻

Hypervalent (e > 8)

(expanded octate)

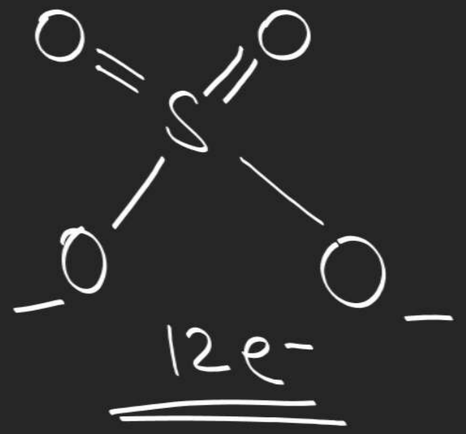
CO_3^{2-}



NO_2

odd e⁻ molecule

SO_4^{2-}



12 e⁻

$BeCl_2$

$AlCl_3$

BCl_3

e- deficient molecule

(e < 8)

No. of bonds > Valency then hypervalent / Expanded octate / Super octate

Li, Be, B
Mg, Al

↓

Always e- defient

C	N	O	F
Si	P	S	Cl

→ Valency = no. of bond
Complete octate

Valency : 4, 3, 2, 1

ispe zaada bond

↓

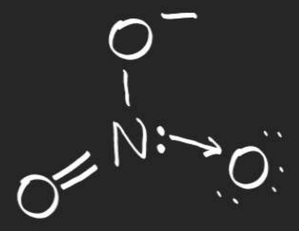
super octate

odd e−

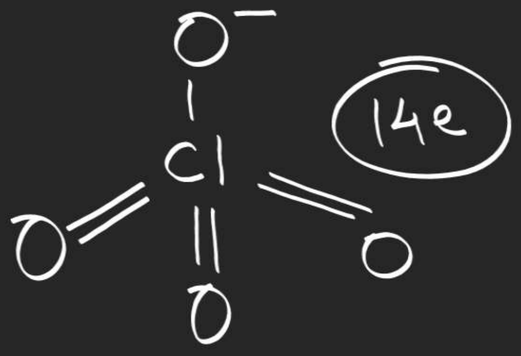
NO_2

NO

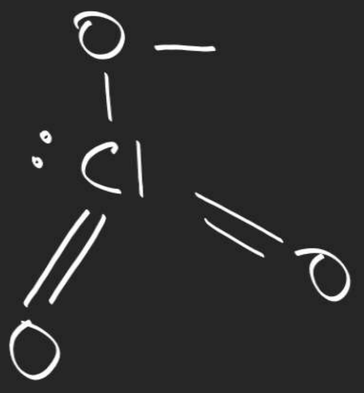
NO_3^-



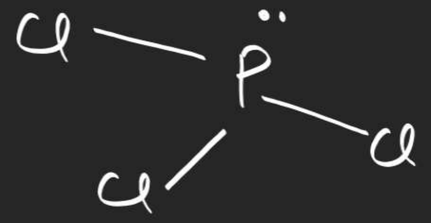
ClO_4^-



ClO_3^-

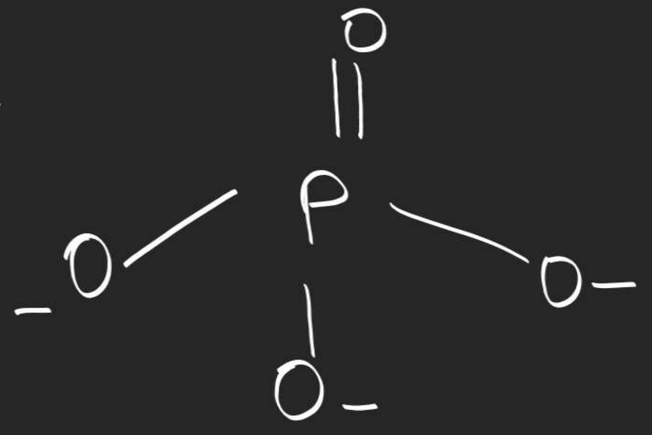


PCl_3



O_3

PO_4^{3-}



NO_2^+

Limitations of Octet Rule : Lewis Theory

1. Incomplete octet of central atom. Ex: $BeCl_2$, BCl_3, $AlCl_3$
2. Odd electron molecules. NO, NO_2
3. Expanded octet. SF_4 , SF_6 , PCl_5 etc.
4. Octet rule is based on the chemical inertness of noble gases, however some noble gases do form compounds. eg: XeF_4, XeO_2F_2
5. Doesn’t account for the shape of the molecules.
6. Doesn't explain the relative stability of molecules or energy of a molecule.

Bond Order

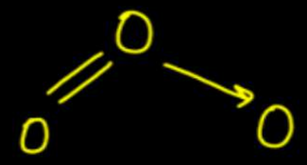
Effective no. of bonds b/w CA with each SA

Ex

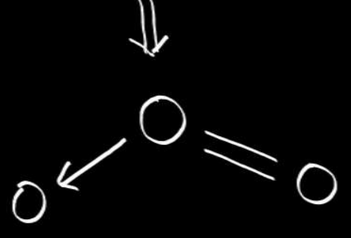
Molecule	(B.O.)
A – B	1
A = B	2
A ≡ B	3

B.O. more → Bond length ↓, Bond strength ↑, Bond enthalpy ↑

Ex



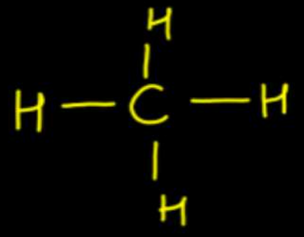
$\Rightarrow BO = \frac{\text{Total bonds}}{\text{Total SA}}$



$= \frac{3}{2}$

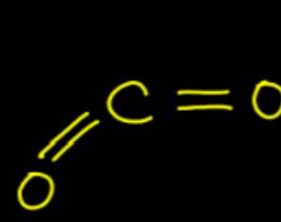
$= (1.5)$

Ex $CH_4 \Rightarrow$



$\Rightarrow BO = 1$

$CO_2 \Rightarrow$

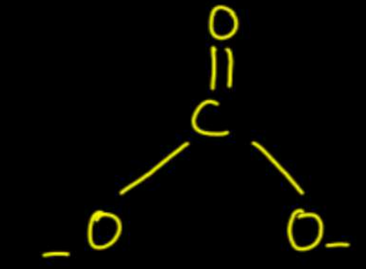


$\Rightarrow BO = 2$

$CO \Rightarrow$

$\Rightarrow BO = 3$

Ex CO_3^{2-}

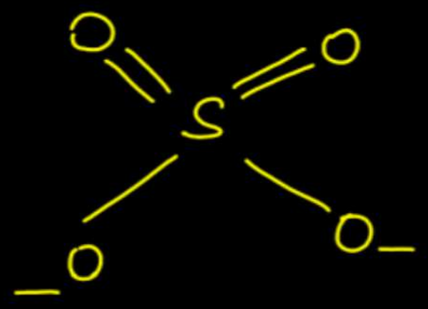


$BO = \frac{4}{3} = 1.33$

Bond Order

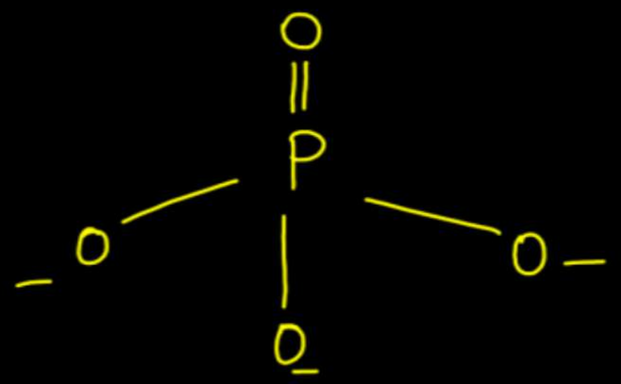
$(B.O.) \propto$ Bond strength
$\propto$ Bond energy
$\propto \frac{1}{(\text{Bond length})}$

SO_4^{2-}



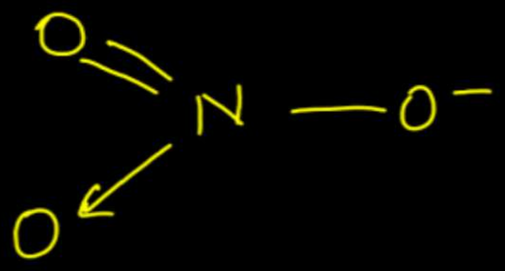
$$BO = \frac{6}{4} = (1.5)$$

PO_4^{3-}



$$BO = \frac{5}{4} = 1.25$$

NO_3^-



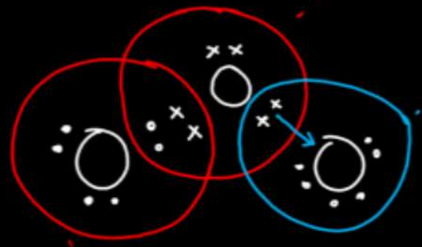
$$BO = \frac{4}{3} = 1.33$$

Formal Charge

Formal charge (F.C.) on an atom in a Lewis structure = **total valence electrons in the free atom** − **(lone pair) electrons** − $\frac{1}{2}$ [number of bonding] (no. of bonds)

(+1, −1, 0)

1. O_3

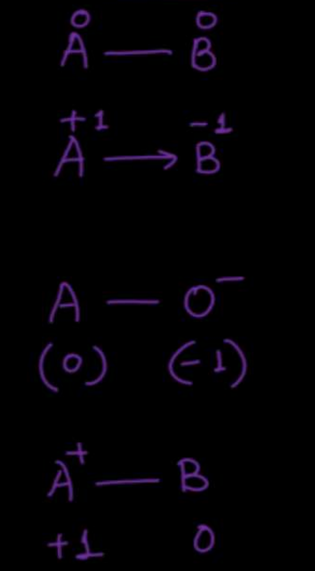


$\rightarrow 6 - 2 - \frac{1}{2}(6) = +1$

$\rightarrow 6 - 6 - \frac{1}{2}(2) = -1$

$\rightarrow 6 - 4 - \frac{1}{2}(4) = 0$

Ninja Tech



Avg F.C. of oxygen

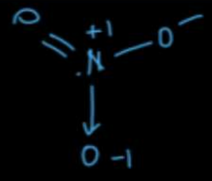
Trick

CO_3^{2-} ⇓ $\frac{(-2)}{3}$

PO_4^{3-} ⇓ $\left(\frac{-3}{4}\right)$

SO_4^{2-} ⇓ $\left(\frac{-2}{4}\right)$

(*) NO_3^- ⇒



formal charge = $-\frac{2}{3}$

$O_3 \Rightarrow$

$6 - 2 - 3 = (1)$

Valence e⁻ − Lone Pair e − Bonds

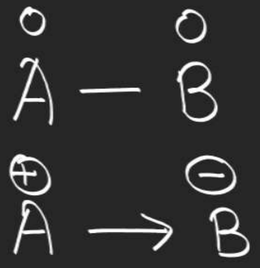
$6 - 4 - 2 = 0$

$6 - 6 - 1 = -1$

$\Rightarrow$ Individual $= (1, 0, -1)$

avg $= \frac{-1+0}{2}$

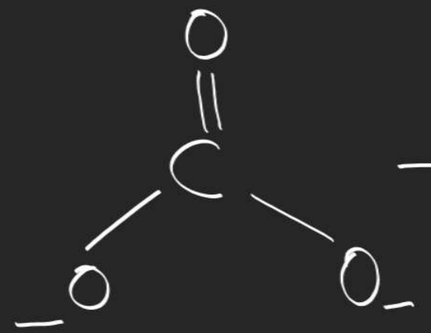
Trick :



$\overset{\oplus}{A} \rightarrow \overset{\ominus}{B}$

Anion | Cation : formal charge = charge on atom

$CO_3^{2-} \Rightarrow$



$(0, -1, -1)$

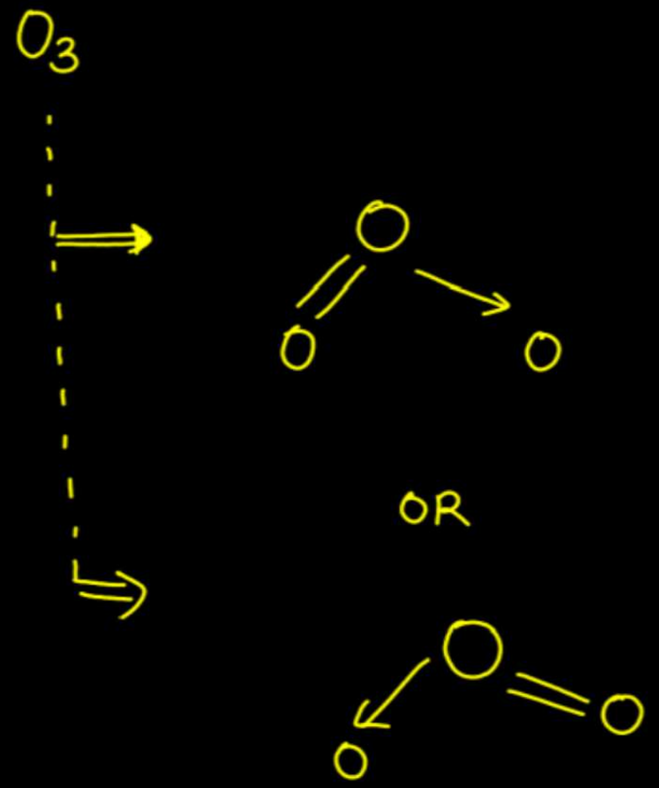
Individual

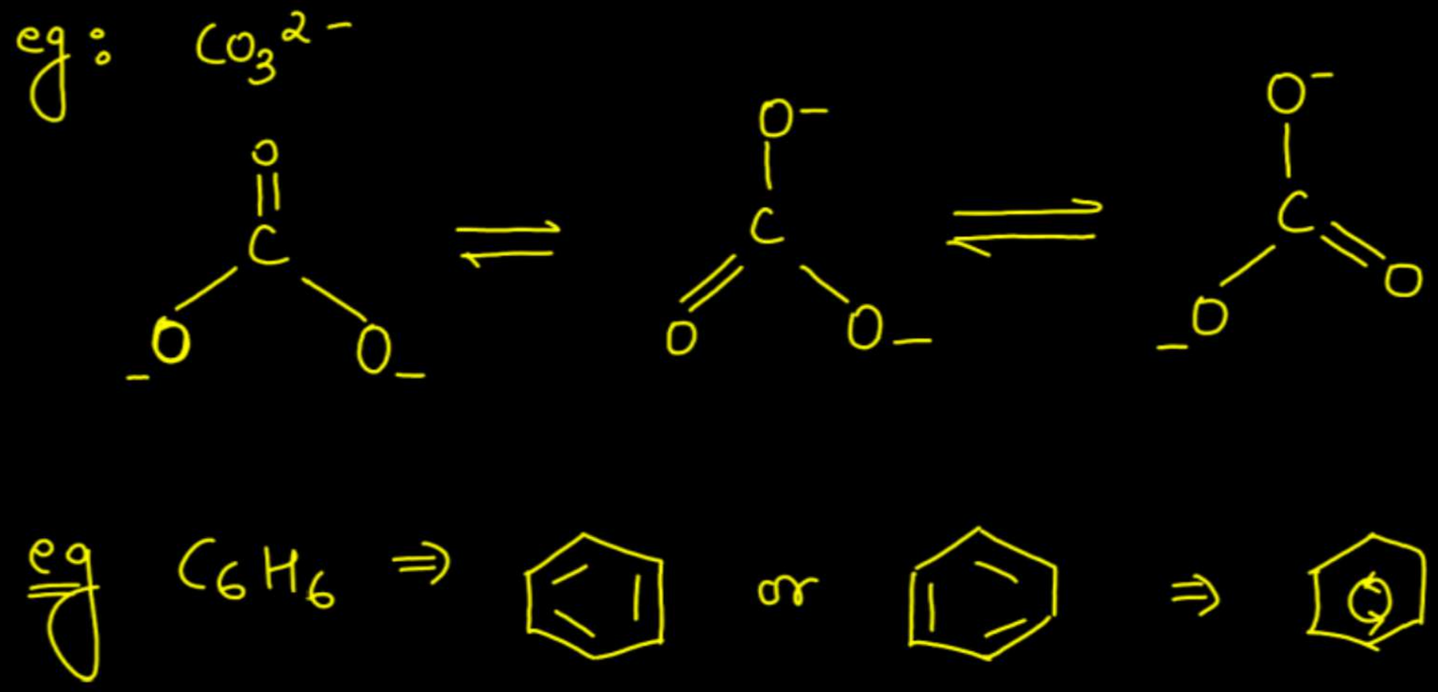
avg F.C.

$-2/3$

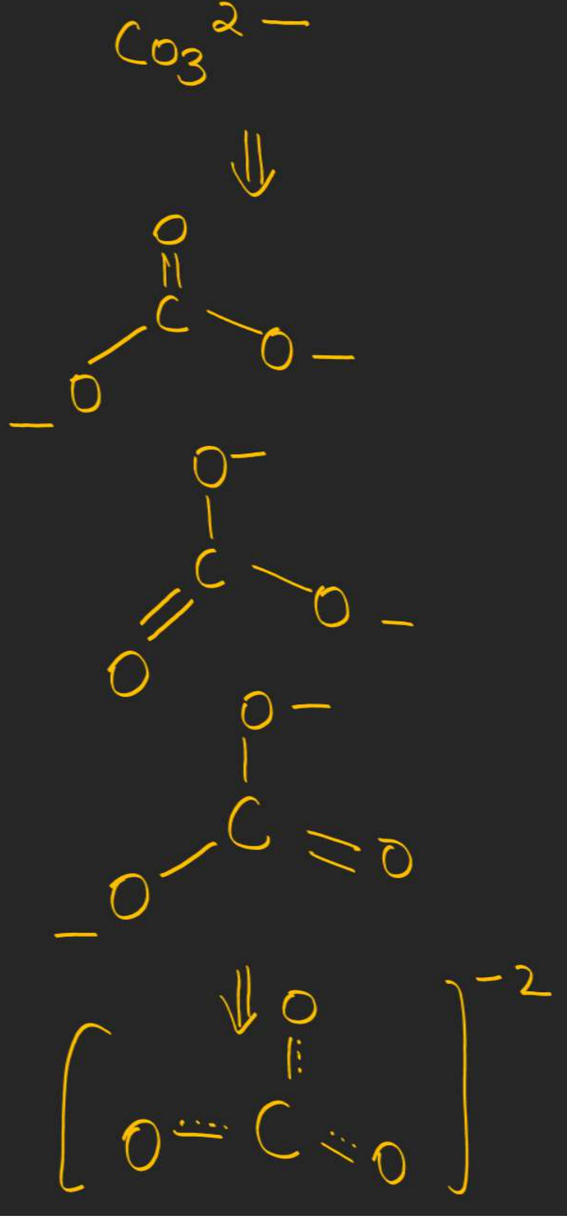
Resonance Structure

for a molecule or polyatomic ion with double bonds next to single bonds, we can write more than one Lewis structure and all are said to be correct





Resonance structure : Hypothetical equivalent structure



Valence Bond Theory

a) Bond is formed by overlapping of orbitals with opp. spin

b) Greater extent of overlapping $\Longrightarrow$ stronger bond

c) Two type of bond forms

- sigma (σ)
- Pi (π)

1st sigma bond forms & then (π) bond.

(σ) bond is stronger than (π) bond.

of z-axis is internuclear axis

(i) $s + s$

(ii) $s + p_z$

(iii) $s + d_{z^2}$

} Always form (σ) bond

(iv) $s + p_x$

$s + p_y$

$s + d_{xy}$

$+ d_{yz}$

$+ \ldots$

} no bond forms

(v) $p_z + p_z$ ..... (σ) bond

(vi) $p_x + p_x$

(vii) $p_y + p_y$

} π- bond

(viii) $p_x + p_y$ or $p_x + p_z$ or $p_y + p_z$

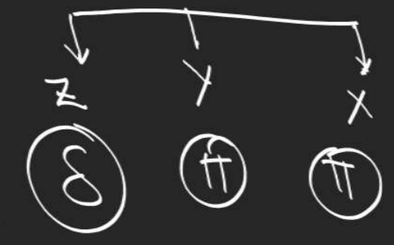
no bond formn

(ix) $p_x + d_{xy} = \pi$ bond

$p_y + d_{xy} = \pi$ bond

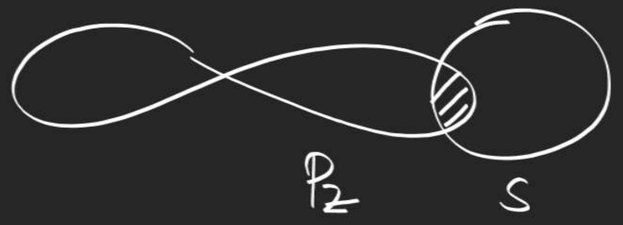
$p_z + d_{xy} =$ no bond

(x) $d_{xy} + d_{xy}$

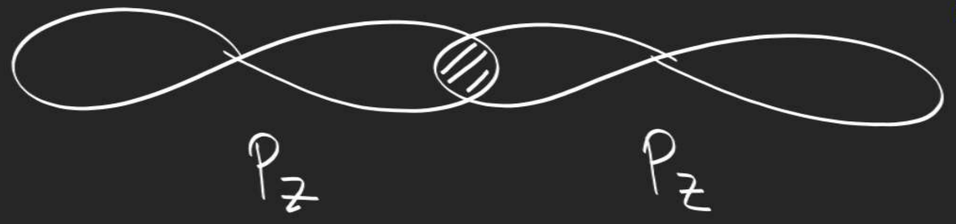


Along the axis

S S

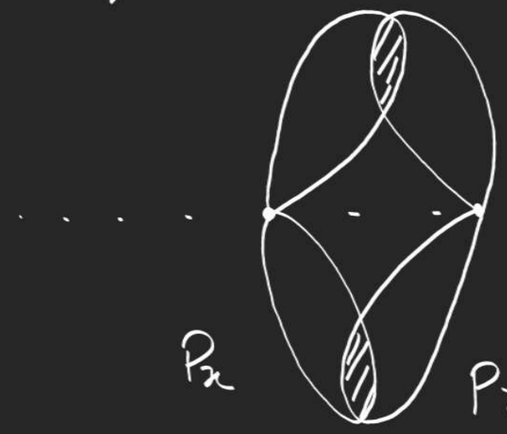


P_z S



P_z P_z

Lateral / br overlapping



P_x P_x z-axis

π- bond formn

Valance Bond Theory

(iv) Two type of Bond Forms due to overlapping of orbitals

(a)If the overlapping is along the molecular axis (z-axis) then bond will be sigma (σ)

(b)If the overlapping is in the perpendicular direction (x, y), it will be pi(π) bond. (s orbital never forms π - bond)

Assuming z-axis as molecular axis

σ - bond

- s - s (always)
- s - p_z
- p_z - p_z
- s - d_{z^2}
- p_z - d_{z^2}

(π - bond)

(Linear axis never →/←)

- p_x - p_x
- p_y - p_y
- p_x - p_y (never forms bond)
- p_x - d_{xy} or p_x - d_{xz}
- d_{xy} - d_{xy} or d_{yz} - d_{yz}

❖ Who is Stronger Sigma or pi Bond??

Ans: Sigma bcs extent of overlapping is more in sigma

Q. Count the π & σ bonds in **N ≡ C – C ≡ C –C ≡ N**

σ bond = 5

π bond = 6

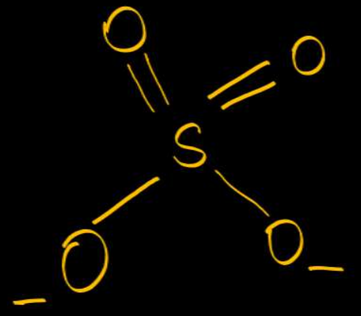
ex

σ = 12

π = 3

For no cyclic structure

SO_4^{2-} [σ = 4, π = 2]



Hybridisation

According to him the atomic orbitals combine to form new set of equivalent orbitals known as **hybrid orbitals** and this phenomenon is known as **Hybridisation**

Types of Hybridisation

Sp

Sp^2

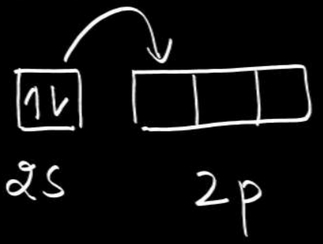
Sp^3

Sp^{3}d

Sp^{3}d^2

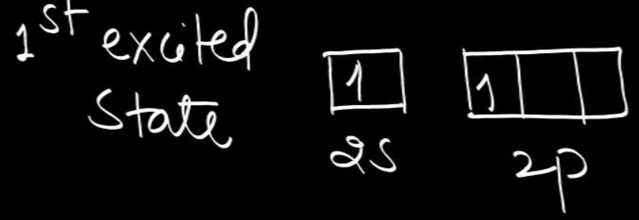
Sp^{3}d^3

BeF_2 ----> Be = $1s^2 2s^2$



NH_3

$N = 1s^2 2s^2 2p^3$



H_2O

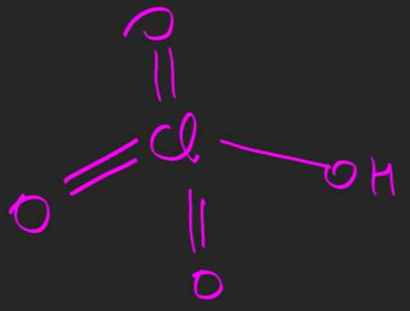
HF

sp Hyb.

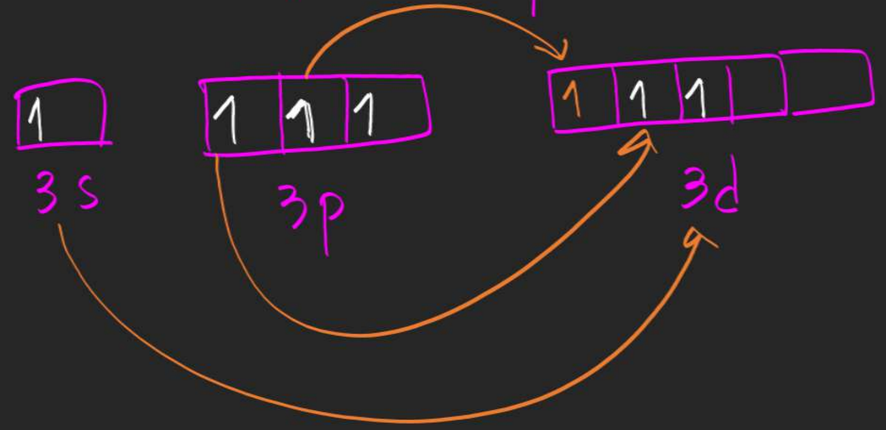
$BeCl_2$
BF_3
CH_4
} 1st excited state

NH_3 , PCl_3
H_2O , H_2S
HF , HCl
} Ground state

$HClO_4$ ⇒



Cl ⇒ $1s^2 2s^2 2p^6 \underline{3s^2 3p^5 3d^0}$



SO_2 (1st) SO_3 (2nd) SO_4^{2-} (2nd) H_2SO_4 (2nd)
PCl_5 (1st) H_3PO_4 (1st) H_3PO_3 (1st) - -
$HClO_3$ (2nd), $HClO_4$ (3rd), - - -
} excited state

% S - Character in Hybride orbital

$sp = \frac{1}{2} \times 100 = 50\%$

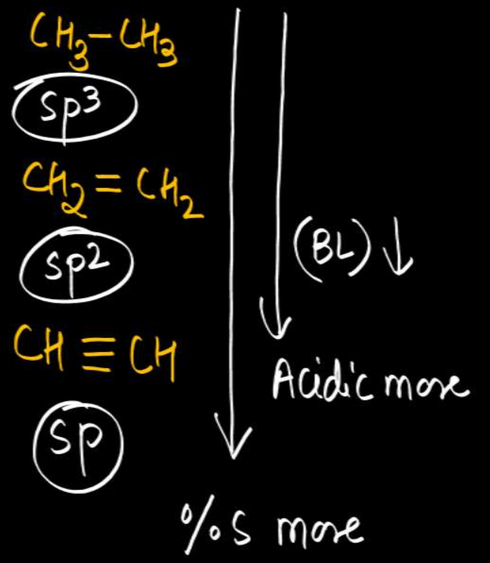
$sp^2 = \frac{1}{3} \times 100 = 33.3\%$

$sp^3 = \frac{1}{4} \times 100 = 25\%$

$sp^3d = \frac{1}{5} \times 100 = 20\%$

$sp \quad sp^2 \quad sp^3 \quad sp^3d \ldots$

(% S) more
Electronegativity ↑
Bond length ↓
Bond strength / enthalpy ↑
Acidic nature more



In the context of carbon, which of the following is arranged in the correct order of electronegativity.

(a) $sp > sp^2 > sp^3$
(b) $sp^3 > sp^2 > sp$
(c) $sp^2 > sp > sp^3$
(d) $sp^3 > sp > sp^2$

Strength of Overlapping

(i) small $(n_1 + n_2)$ ex $1s - 1s > 1s - 2s$

(ii) of $(n_1 + n_2)$ same ex $2s - 3p > 3s - 4p$

$\Downarrow$

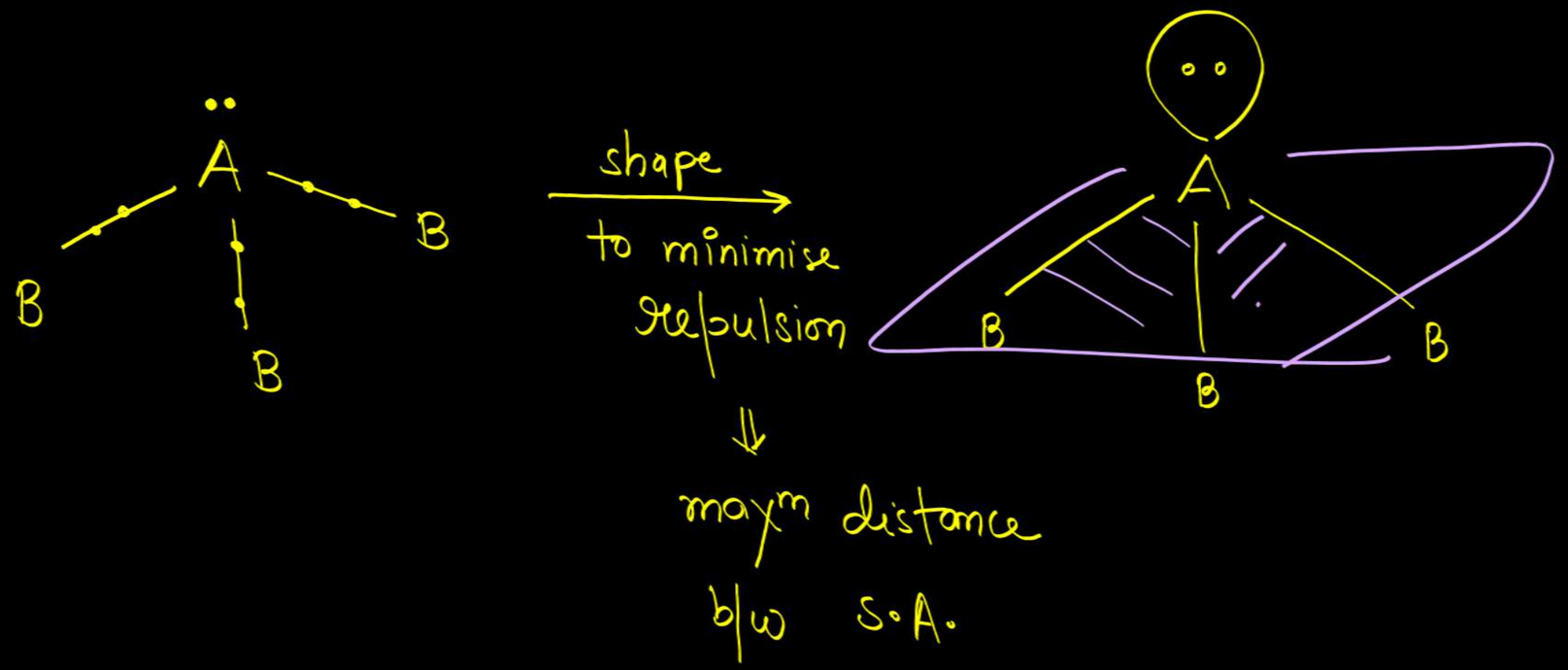
$d > p > s$ ex $3s - 3p < 3p - 3p$

← B/c of more directional nature

VSEPR THEORY

This theory provides a simple procedure to predict the shapes of covalent molecules

1. Shape of a molecule depends upon the number of valence shell electron pairs [bonded or nonbonded) around the central atom.



VSEPR THEORY

- Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.

$$(lp - lp) > (lp - bp) > (bp - bp)$$

- These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.

VSEPR THEORY

- The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.

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

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

Ninja Tech

SA bonds : $-H$, $-X$, $=O$, $-OH$, $\equiv N$,

1. No. of Bond pairs (except oxyacids) = Surr. atoms

ex ≡ BeF_2 CH_4 CO_2 CO_3^{2-} SO_4^{2-} NH_3 H_2O PCl_3 $XeOF_6$

B.P. (2) (4) (2) (3) (4) (3) (2) (3) (7)

2-2 ⇒ 0 | 4-4 ⇒ 0 | 4-4 ⇒ 0 | 6-6 ⇒ 0 | 8-8 ⇒ 0 | 5-3 ⇒ (1) | 6-2 ⇒ (2) | 5-3 ⇒ (1) | 8-8 ⇒ 0

lone Pair ⇓

Valence e⁻ → (Subtract no. of bonds) then do Half ≡ lone pair

Keeping in mind ⊕ / ⊖ charge ⇒

i) (Valence e⁻) − (+ve Charge) ⇒ NH_4^+ ⇒ (N) ⇒ 5e − e ⇒ (4e)

ii) (Valence e⁻) + (−ve Charge) ⇒ PO_4^{3-} ⇒ (P) ⇒ 5e + 3e ⇒ (8e)

Valence e⁻

H → 1

Be → 2

B, Al → 3

C, Si → 4

N, P → 5

O, S → 6

Halogens → 7

Xe → 8

Bond Form

—H

=O

—O—

C—

C=

C≡

N—

N=

N≡

(Halogen)—

Central Atom (CA)

→ Present in less no

Ex $\underline{C}H_4$, $\underline{S}O_3$, $\underline{C}O_2$, $H_2\underline{O}$

→ less E·N· atom

→ H never central atom

→ F " " except (H) with

Ex $H\underline{Cl}$, $\underline{O}F_2$, $\underline{C}O$

$\underline{N}O$

Other atoms are called Surrounding Atom (SA)

	Central atom
H_2SO_4	(S)
CO_2	(C)
NH_3	(N)
$XeOF_2$	(Xe)
SF_4	(S)
HF	(F)
OF_2	(O)
$HCHO$	(C)

Calculation lone Pair & Bond Pair

Concept

→ BP = (SA) except oxyacids where (OH) is counted together

Lone Pair

Remaining Pair of e^-

Ex H_2O → BP = 2

→ $lp = 6-2 = \frac{4}{2} = 2$ pair

Counting of lone Pairs

① NH_3 → BP = 3
→ lp = 5 − 3 = $\frac{2}{2}$ = 1 pair

② SO_2 → BP = 2
→ lp = 6 − 4 = $\frac{2}{2}$ = 1 pair

③ SO_3 → BP = 3
→ lp = 6 − 6 = 0 lp

④ PCl_3 → BP = 3
→ lp = 5 − 3 = $\frac{2}{2}$ = 1 pair

⑤ XeF_2 → BP = 2
→ lp = 8 − 2 = $\frac{6}{2}$
lp = 3

⑥ $XeOF_2$ → BP = 3
→ lp = 8 − 4 = $\frac{4}{2}$
lp = ②

⑦ XeO_2F_2 → BP = 4
→ lp = 8 − 6 = $\frac{2}{2}$ = ①

⑧ ICl_3 → Bp = 3 lp = ①
→ lp = 7 − 3 = $\frac{4}{2}$ = 2 pair

SO_4^{2-} $\xrightarrow[=8e]{S=6+2}$ BP = 4, lp = 8 − 8 = 0

CO_3^{2-} $\xrightarrow{C=4+2=6}$ BP = 3, lp = 6 − 6 = 0

NO_3^- $\xrightarrow[(6e)]{N=5+1}$ BP = 3, lp = 6 − 6 = 0

PO_4^{3-} $\xrightarrow[(8e)]{P=5+3}$ BP = 4, lp = 8 − 8 = 0

NH_4^+ $\xrightarrow[=4e]{N=5-1}$ BP = 4, lp = 4 − 4 = 0

Structure
- ⊕ CA
- ⊖ SA

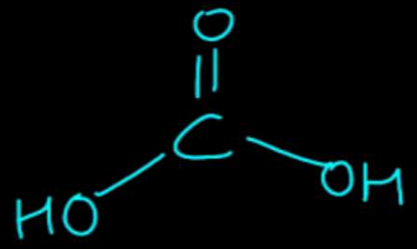
While Calculating
↓
Give ⊕ ⊖ both to CA

Ex CO_3^{2-}

→ Valence e⁻ of Carbon = 4 + 2 = 6

OXy Acid

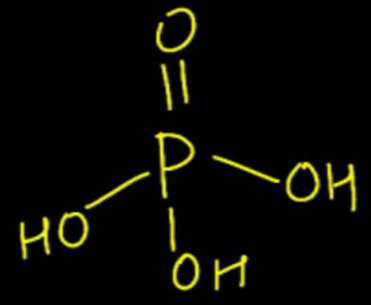
$H_2CO_3 \longrightarrow (HO)_2CO \longrightarrow BP = 3$



$HNO_2 \longrightarrow (HO)NO \longrightarrow BP = 2$

$HNO_3 \longrightarrow (HO)NO_2 \longrightarrow BP = 3$

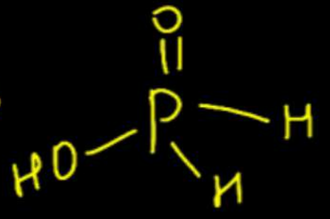
$H_3PO_4 \longrightarrow (HO)_3PO \longrightarrow BP = 4$



Except

$H_3PO_3 \longrightarrow (HO)_2POH \longrightarrow BP = 4$

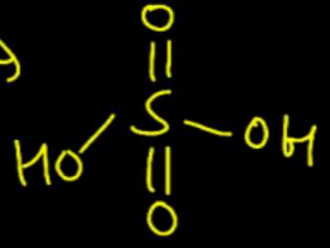
$H_3PO_2 \longrightarrow (HO)_1POH_2 \Rightarrow BP = 4$



$H_2SO_4 \longrightarrow (HO)_2SO_2 \Rightarrow BP = 4$

$H_2SO_3 \longrightarrow (HO)_2SO \Rightarrow BP = 3$

$\Rightarrow \text{Up} = 1$



eg $HNO_2 = (HO)NO$

$BP = 2$

$\text{Up} = \frac{5-3}{2} = 1$

eg $HClO_3$

Ans $(HO)ClO_2$

$BP = 3$

$\text{Up} = \frac{7-5}{2}$

$= 1 \text{ Up}$

lp + bp = steric no.

2 ⇒ sp Hybridisation

3 ⇒ sp^2 —, —

4 ⇒ sp^3 —, —

5 ⇒ sp^3d —, —

6 ⇒ sp^3d^2 —, —

7 ⇒ sp^3d^3 —, —

1) H_2O → BP = (2)
→ $lp = \frac{6-2}{2} = (2)$

BP + lp = 2 + 2 = (4) ≡ (sp^3)

2) NH_3 → BP = 3
→ $lp = \frac{5-3}{2} = 1$
} (4) sp^3

3) SO_2 → BP = 2
→ $lp = \frac{6-4}{2} = 1$
} (3) sp^2

4) $XeOF_2$ → BP = 3
→ $lp = \frac{8-4}{2} = (2)$
} (5) sp^3d

Trick

$sp^3 \Leftarrow 4 \Leftarrow \frac{(6+2)}{2} \leftarrow SO_4^{2-}$

$sp^3 \Leftarrow 4 \Leftarrow (6+2)/2 \leftarrow SO_3^{2-}$

$sp^2 \Leftarrow 3 \Leftarrow (4+2)/2 \leftarrow CO_3^{2-}$

$sp^2 \Leftarrow 3 \Leftarrow \frac{5+1}{2} \leftarrow NO_3^-$

$sp^3 \Leftarrow 4 \Leftarrow \frac{5-1+4}{2} \hookleftarrow NH_4^+$

$sp^3 \Leftarrow 4 \Leftarrow \frac{5+3}{2} \hookleftarrow PO_4^{3-}$

Species

SO_4^{2-}

SO_3^{2-}

CO_3^{2-}

NO_3^-

NH_4^+

PO_4^{3-}

Concept

$SO_4^{2-} \rightarrow (BP = 4, lp = 0) \Rightarrow 4 \Rightarrow sp^3$

$SO_3^{2-} \rightarrow (BP = 3, lp = 1) \Rightarrow 4 \Rightarrow sp^3$

$CO_3^{2-} \rightarrow (BP = 3, lp = 0) \Rightarrow 3 \Rightarrow sp^2$

$NO_3^- \rightarrow (BP = 3, lp = 0) \Rightarrow 3 \Rightarrow sp^2$

$NH_4^+ \rightarrow (BP = 4, lp = 0) \Rightarrow 4 \Rightarrow sp^3$

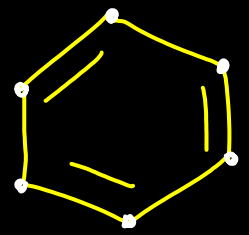
$PO_4^{3-} \rightarrow (BP = 4, lp = 0) \Rightarrow 4 \Rightarrow sp^3$

(*) $-\overset{|}{\underset{|}{C}}-$ sp^3

$-C=C-$ sp^2 sp^2

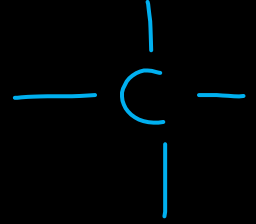
$\equiv C =$ sp

$-C \equiv$ sp

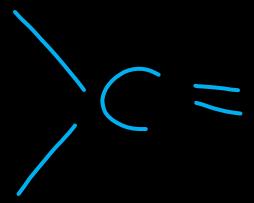


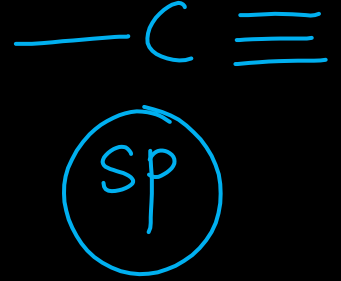
$\Rightarrow$ each (C) $= sp^2$

Alkane (C) $\rightarrow sp^3$

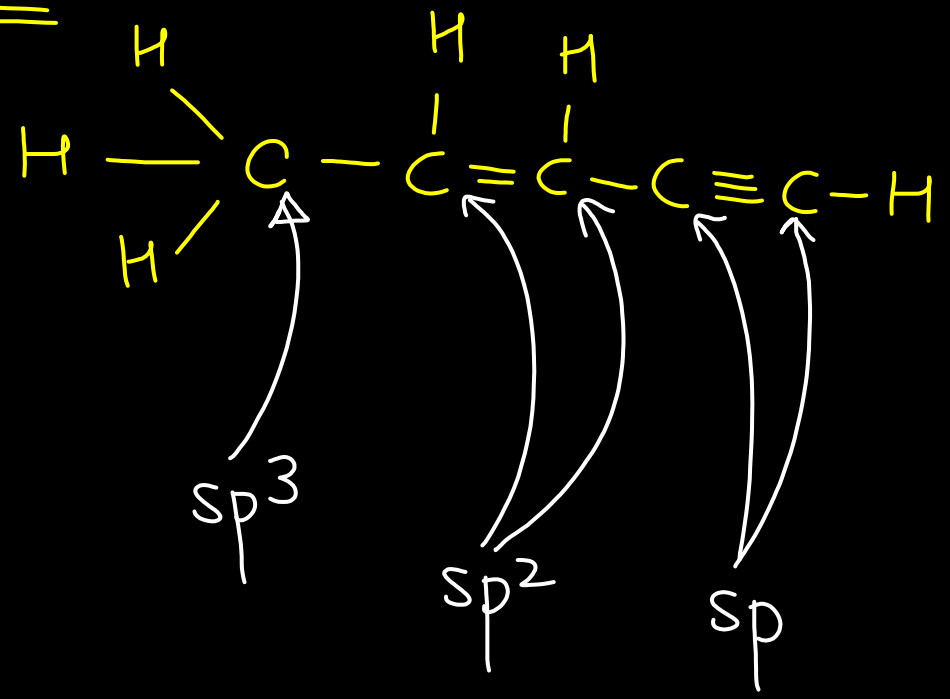


Alkene (C) $\rightarrow sp^2$



Alkyne 

Ex



Oxyacids

- $\longrightarrow$ 2nd Period $\longrightarrow$ sp^2
- $\longrightarrow$ Rest all $\longrightarrow$ sp^3

H_2CO_3, HNO_2, HNO_3, H_3BO_3 $\Longrightarrow$ sp^2

$Si(OH)_4$, H_3PO_4, H_3PO_3, H_3PO_2, $H_4P_2O_7$, $H_4P_2O_6$ ⋮

H_2SO_4, H_2SO_3, $H_2S_2O_7$, $H_2S_2O_6$ ⋮

$HClO_4$, $HClO_3$, $HClO_2$, $HClO$, HIO_3 ⋮

$\Longrightarrow$ sp^3

SP Hybridization

when : BP + lp = 2

Molecule

A : Central atom

B : Bond Pair

L : lone Pair

(i) AB_2 $\Rightarrow$ B — A — B (180°) Linear shape

(ii) AB_1L_1 (doesn't exist)

Ex : $BeCl_2$ < BP = 2, lp = 0 } sp Hybo. Cl — Be — Cl Linear shape

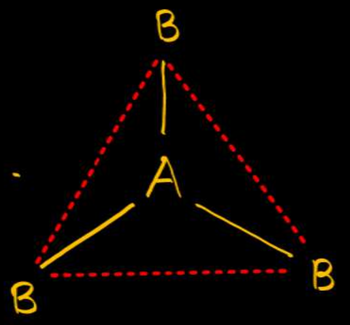
Ex CO_2 $\Longrightarrow$ O = C = O

CO_2 < BP = 2, lp = 0 Linear

Ex. $BeCl_2$, CO_2

SP^2 Hybridization

Case - I AB_3

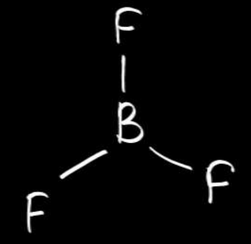


Trigonal Planar

* Each angle (120°)

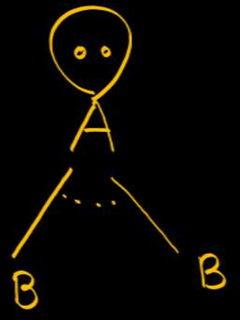
Ex BF_3 — BP = 3, lp = 0 } sp^2

Ans : Trigonal planar



Case - II AB_2L_1

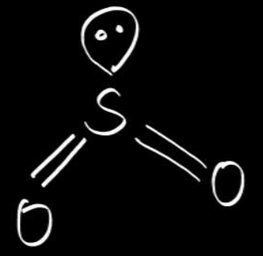
Angle $< 120^\circ$



Bent shape

(inverted V-shape)

Ex : SO_2 — BP = 2, lp = 1 } sp^2

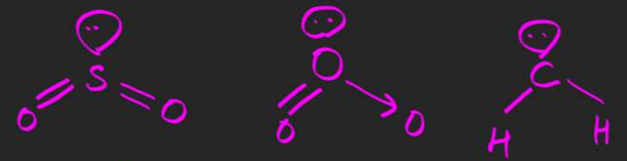


Bent shape

(NO_3^-) $(H_2CO_3, HNO_3, H_3BO_3)$ ⇒ (AB_3) type ⇒ sp^2 (trigonal planar)

Ex. BF_3, SO_3, CH_3^+, CO_3^{2-}, All oxyacides of period-2

Note: SO_2 , O_3 , CH_2 , HNO_2 ----> (AB_2L_1) ⟹ Bent shape

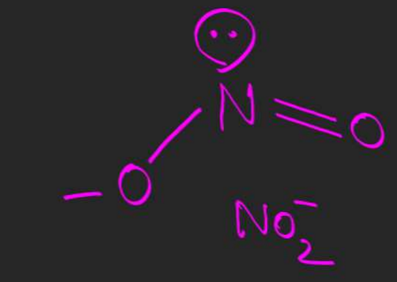


Structure

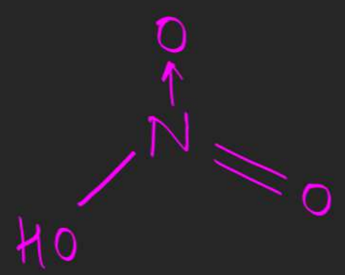
Bent

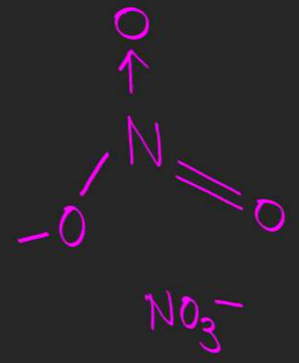
Trigonal planar

HNO_2

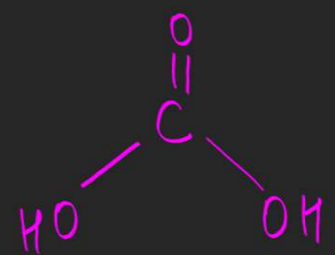


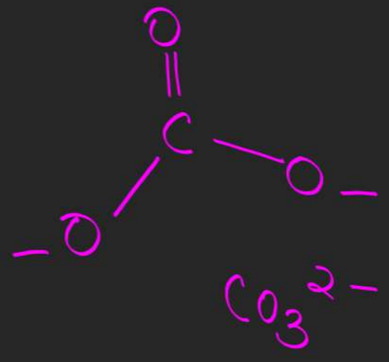
HNO_3



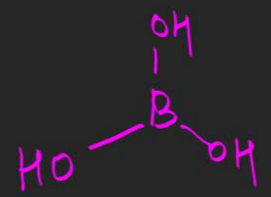


H_2CO_3



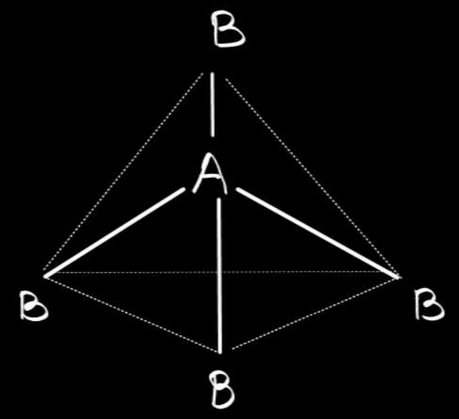


H_3BO_3 ⟶ $B(OH)_3$



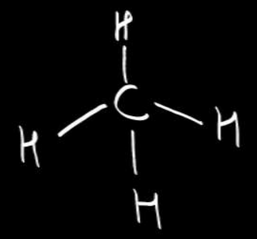
SP^3 Hybridization

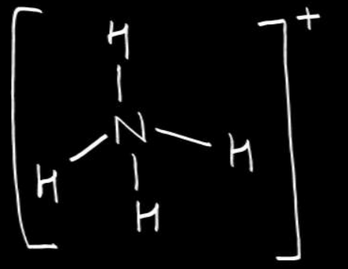
Case-I : AB_4 . . . . . .

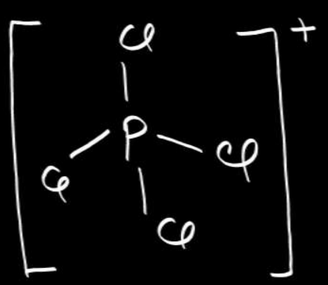


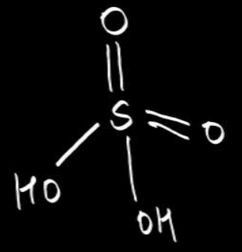
Tetrahedral $\left(\angle BAB \cong 109^\circ\right)$

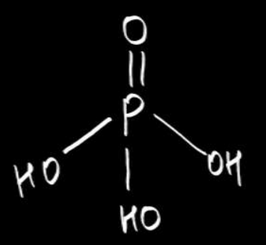
Example

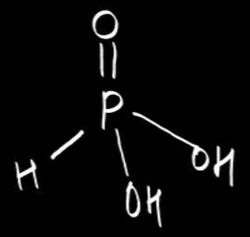
CH_4 

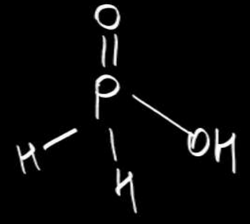
NH_4^+ 

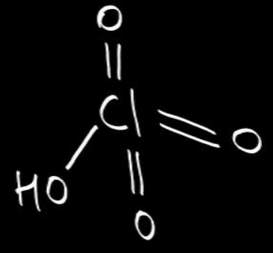
PCl_4^+ 

H_2SO_4 

H_3PO_4 

H_3PO_3 

H_3PO_2 

$HClO_4 \Rightarrow$ 

All have [BP = 4 , lp = 0]

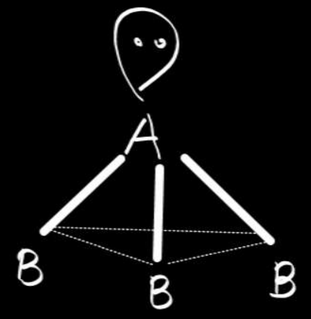
$\Downarrow$ SO_4^{2-}

$\Downarrow$ PO_4^{3-}

Ex. CH_4 , NH_4^+ , CCl_4 , PCl_4^+ , SO_4^{2-} , PO_4^{3-}, All oxyacid of Period-3

SP^3 Hybridization

Case-II : AB_3L_1 ------

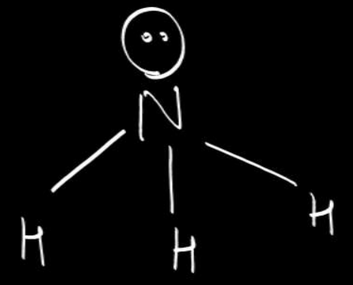


Pyramidal

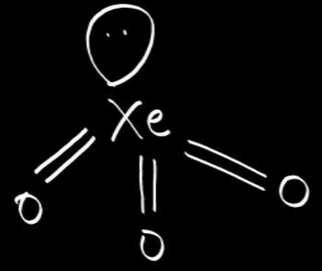
$\angle BAB < 109^\circ$

Examples

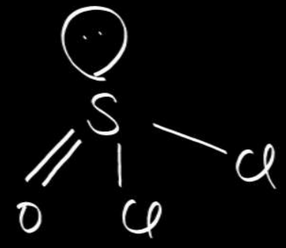
NH_3



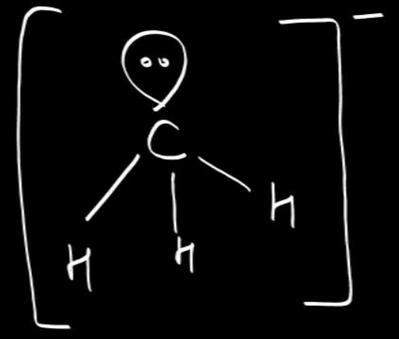
XeO_3



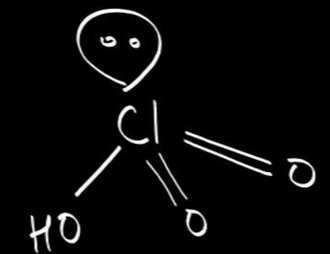
$SOCl_2$



CH_3^-



$HClO_3$



⇓

ClO_3^-

All have $\begin{cases} bp = 3 \\ lp = 1 \end{cases}$

Ex. NH_3 , PH_3 , PCl_3 , XeO_3 , $SOCl_2$, CH_3^- , ClO_3^-

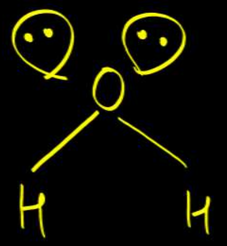
SP^3 Hybridization

Case-III AB_2L_2 - - - - -

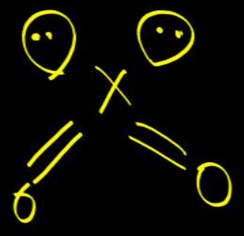
Bent shape

$\angle BAB << 109°$

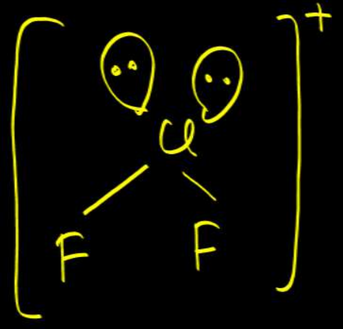
H_2O



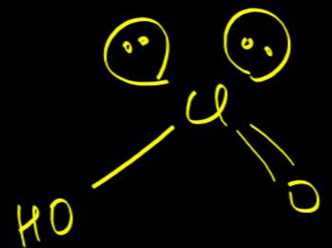
XeO_2



ClF_2^+



$HClO_2$



⇓

ClO_2^-

All Have
- BP = 2
- lp = 2

Ex. H_2O, SF_2, OF_2, H_2S, ClF_2^+, XeO_2, ClO_2^-

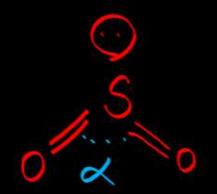
Note

Bent

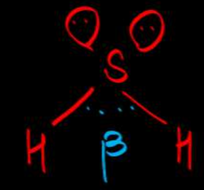
- sp^2 (AB_2L_1) $\angle BAB < 120°$
- sp^3 (AB_2L_2) $\angle BAB << 109°$

example :

SO_2



H_2S



sp^2 sp^3

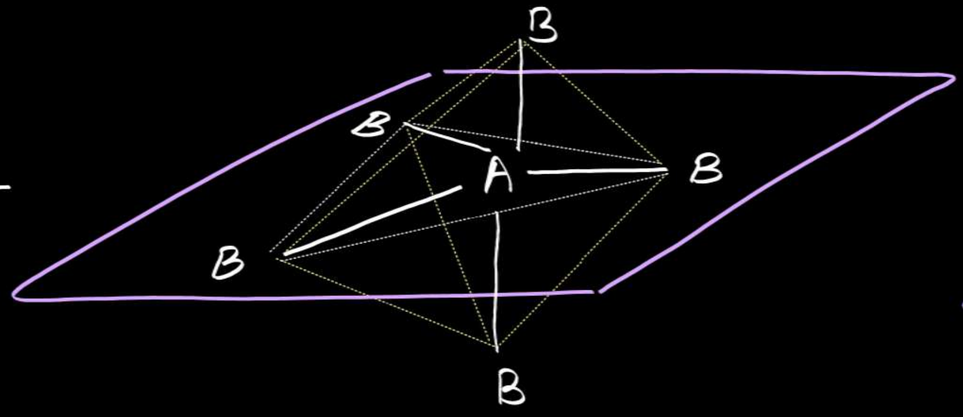
⇒ Hyb : diff

⇒ Isostructural

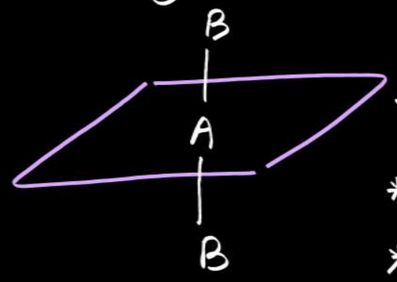
⇒ $\alpha > \beta$

SP^3d Hybridization

Case-I : AB_5 - - - - - -



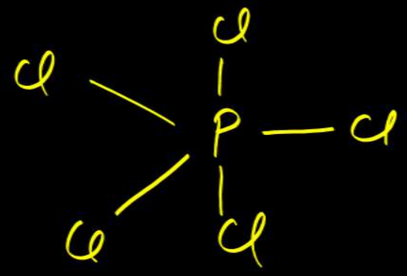
Trigonal bipyramidal (TBP)



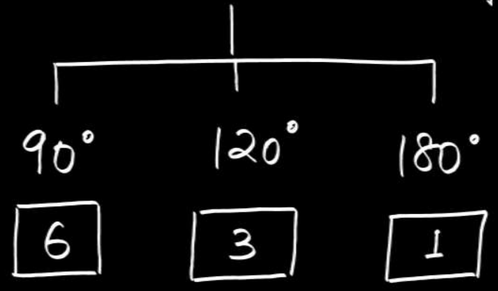
Two axial bonds

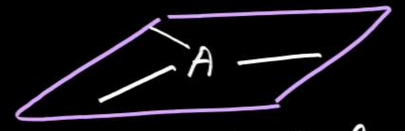
* max Repulsion
* Occupied by more E.N. atom to minimise the Repulsion

example : PCl_5



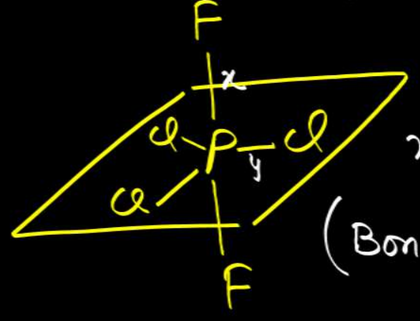
In whole Geometry





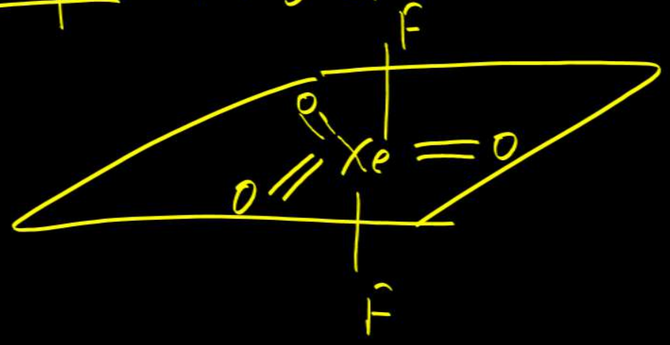
* Three Equitorial Bonds at 120°
* Equal Bond length
* Bond length is more as compare to Equitorial

example PCl_3F_2



$x > y$ (Bond length)

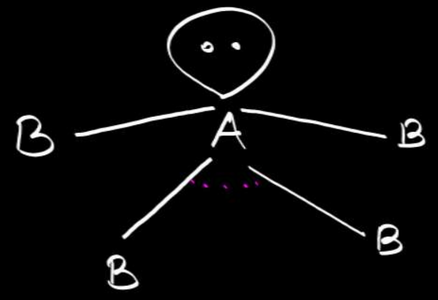
example XeO_3F_2



Ex. PCl_5, PF_5, $SOCl_4$, XeO_3F_2

SP^3d Hybridization

Case - II AB_4L_1 - - - -



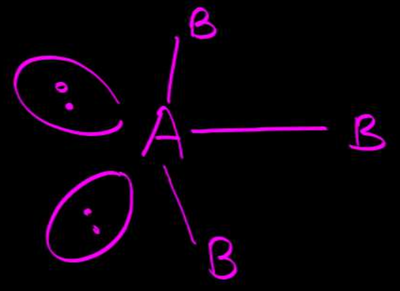
See Saw

angles $< 90°$ (axial)

$< 120°$ (equitorial)

Examples SF_4, PCl_4^-, XeO_2F_2 . . .

Case - III AB_3L_2



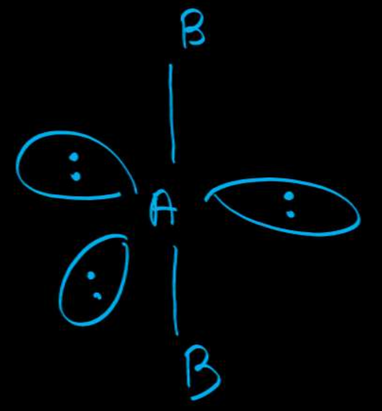
T-shape

Example: $XeOF_2$, ClF_3

Case - IV AB_2L_3

Example: XeF_2, I_3^-

ICl_2^-



Linear shape

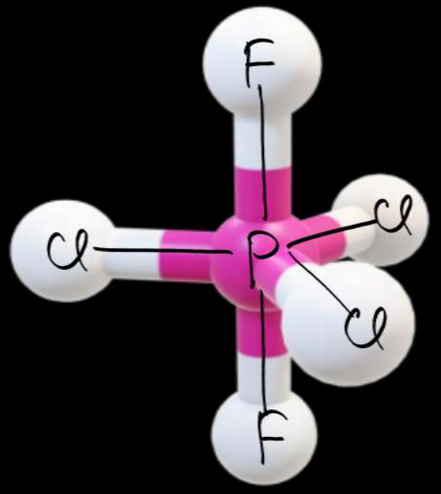
SP^3d Hybridization

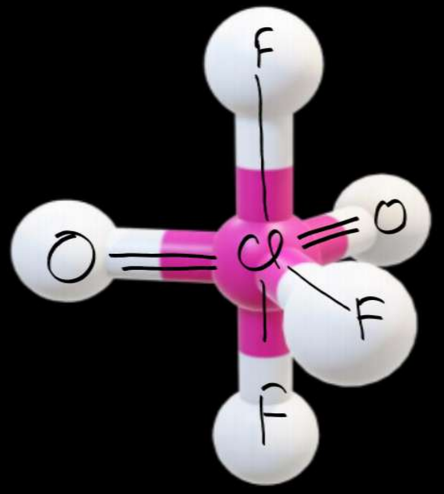
More E.N. Occupy axial position

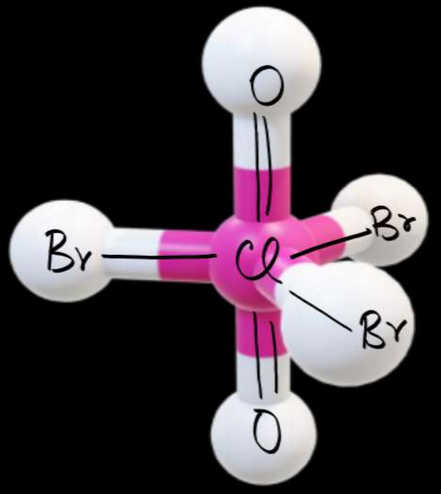
Ex. PCl_3F_2

Ex. ClO_2F_3

Ex. ClO_2Br_3

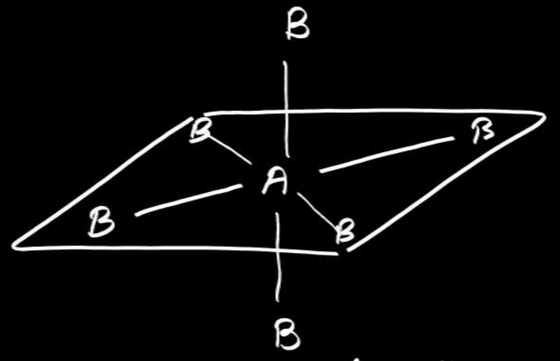






SP^3d^2 Hybridization

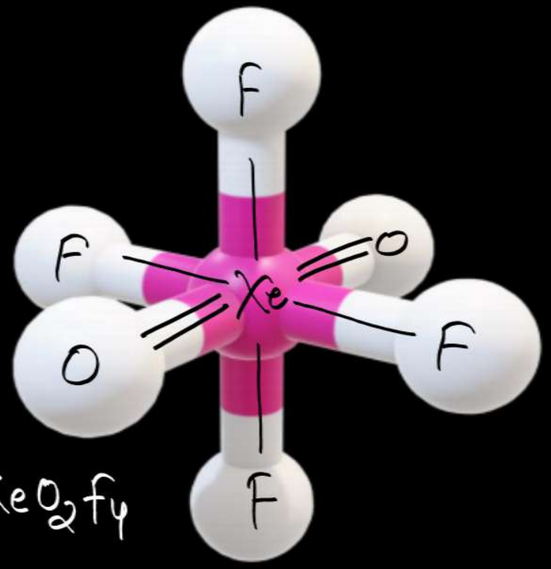
Case – I : AB_6 ----



square bipyramidal (octahedral)

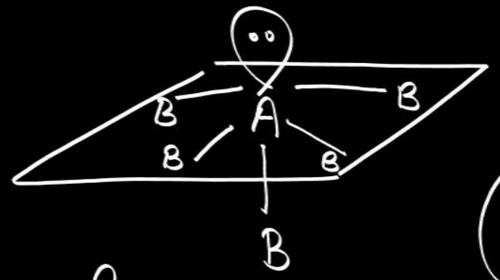
ex PCl_6^-, SF_6, $ClOF_5$

Angle — [90° (12) ; 180° (3)]



Ex : XeO_2F_4

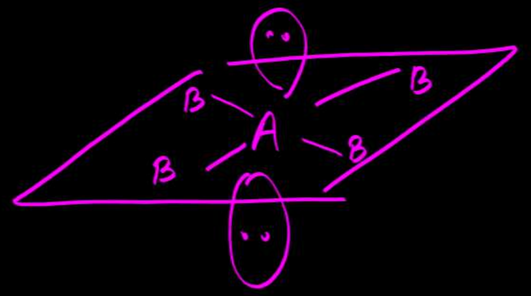
Case-II AB_5L_1



Distorted octahedral (sq. pyramidal)

angle < 90°

Case – III : AB_4L_2

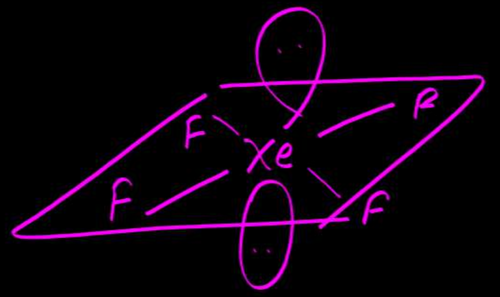


Square Planar

examples

ICl_4^-

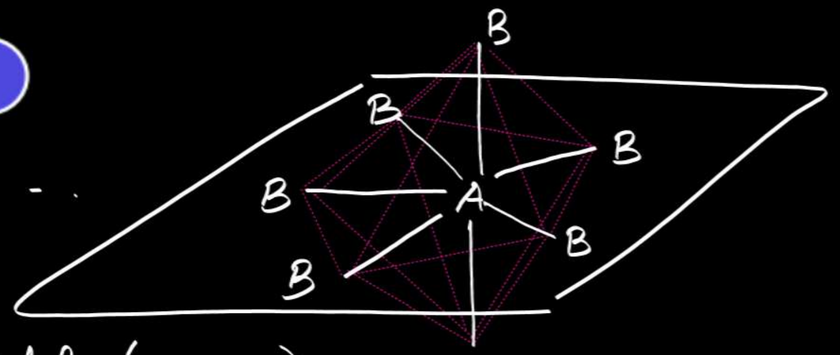
XeF_4



Ex. ICl_5, BrF_5, $XeOF_4$, $ClOF_4^-$

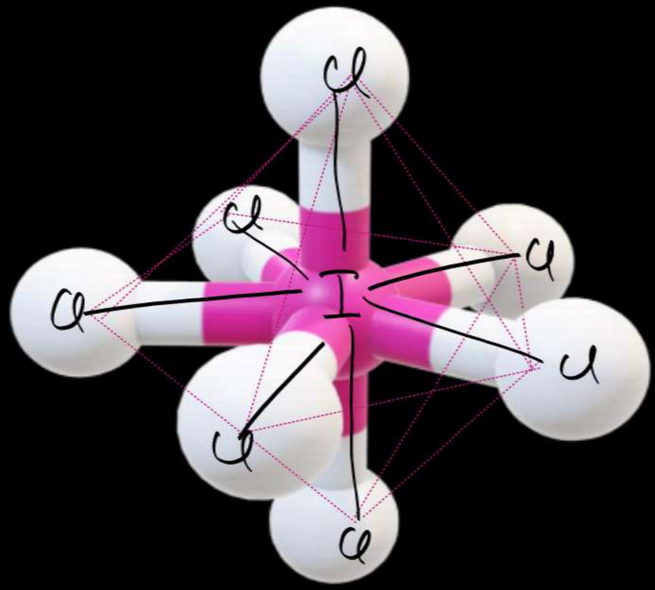
SP^3d^3 Hybridization

Case-I AB_7

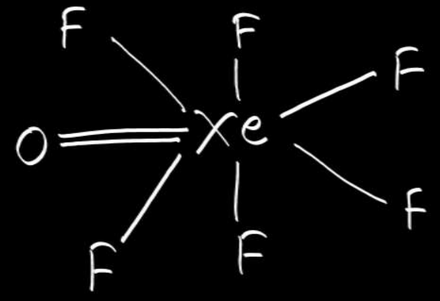


Pentagonal bipyramidal (PBP)

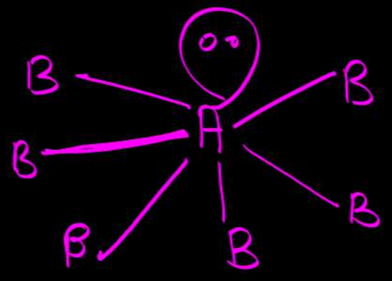
ex : ICl_7



example ; $XeOF_4$



Case-II AB_6L_1

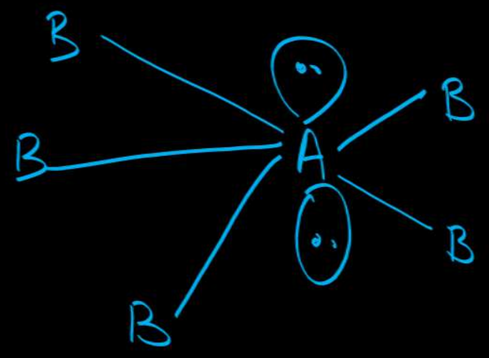


distorted Pentagonal Pyramidal

ex: XeF_6

ICl_6^-

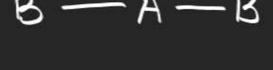
Case-III AB_5L_2 ⟹ Pentagonal planar



ex XeF_5^-

Summary [Highlighted ones are planer shape] Other's non planer

1) sp → **Linear** (180°)



2) sp^2
- **AB_3** ⇒ Trigonal planar (120°)

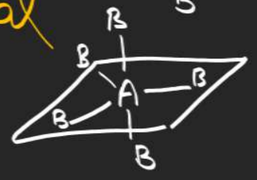
- **AB_2L** ⇒ Bent (< 120°)

3) sp^3
- AB_4 ⇒ Tetrahedral (≈ 109°)

- AB_3L ⇒ Pyramidal (< 109°)

- **AB_2L_2** ⇒ Bent (<< 109°)

4) sp^3d
- AB_5 ⇒ Trigonal bipyramidal



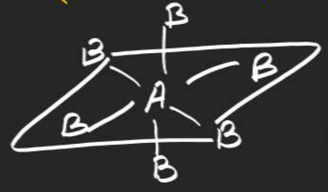
- AB_4L_1 ⇒ See saw

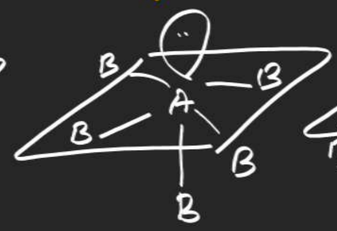
- **AB_3L_2** ⇒ T-shape

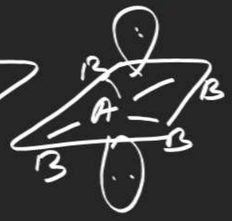
- **AB_2L_3** ⇒ linear

5) sp^3d^2

AB_6	**AB_5L**	**AB_4L_2**
Sq. Bipyramidal (12 → 90°)	distorted Sq. Pyramid	square Planer







6) sp^3d^3

AB_7	**AB_6L**	**AB_5L_2**
(PBP)	distorted (P.P.)	Pentagonal Planer

Drawbacks of VBT

1. Couldn't explain Paramagnetic Behaviour of O_2
2. Couldn't explain Existence of odd electron species
3. Couldn't explain why Fractional Bond order exist
4. Couldn't explain why C_2, B_2 have only pi-bond
5. According to VBT Sigma is stronger than pi but in N_2, O_2 SIGMA is weaker than pi
6. Bond order of CO is 3 but couldn't explain why CO > 3
7. Couldn't explain why halogens are colored.

2 JEE Main 2019 (Online) 9th April Evening Slot MCQ Single Answer

The correct statements among I to III are :
(I) Valence bond theory cannot explain the color exhibited by transition metal complexes.
(II) Valence bond theory can predict quantitatively the magnetic properties of transtition metal complexes.
(III) Valence bond theory cannot distinguish ligands as weak and strong field ones.

A (II) and (III) only

B (I) and (II) only

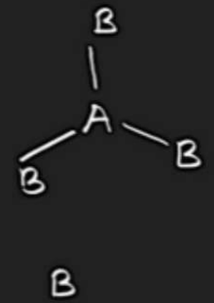
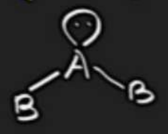
C (I), (II) and (III)

D (I) and (III) only

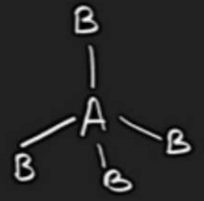
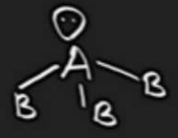
Summary [Highlighted ones are planer shape] other's non planer

1) sp → Linear (180°) B — A — B

2) sp^2
- AB_3 ⇒ Trigonal planarr (120°)
- AB_2L ⇒ Bent (< 120°)

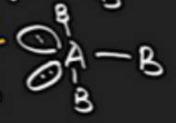



3) sp^3
- AB_4 ⇒ Tetrahedral (≈ 109°)
- AB_3L ⇒ Pyramidal (< 109°)
- AB_2L_2 ⇒ Bent (<< 109°)

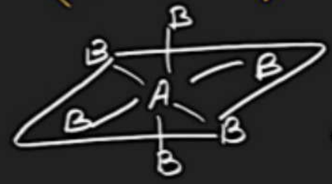
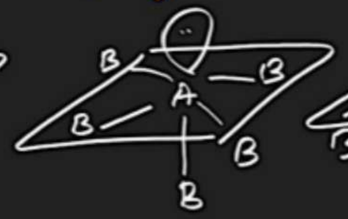
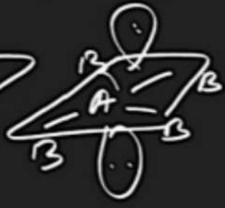

4) sp^3d
- AB_5 ⇒ Trigonal bipyramidal
- AB_4L_1 ⇒ See saw
- AB_3L_2 ⇒ T-shape
- AB_2L_3 ⇒ Linear






5) sp^3d^2

AB_6	AB_5L	AB_4L_2
Sq. Bipyramidal (12 → 90°)	distorted Sq. Pyramid	square Planer

6) sp^3d^3

AB_7	AB_6L	AB_5L_2
(PBP)	distorted (P.P.)	Pentagonal Planer

a) Isostructural : Same shape < BP Same / lp Same

b) CH_3^+ $CH_3^\cdot$ $CH_3^\ominus$

Carbocation
sp^2
Trigonal planar
$< 120^\circ$

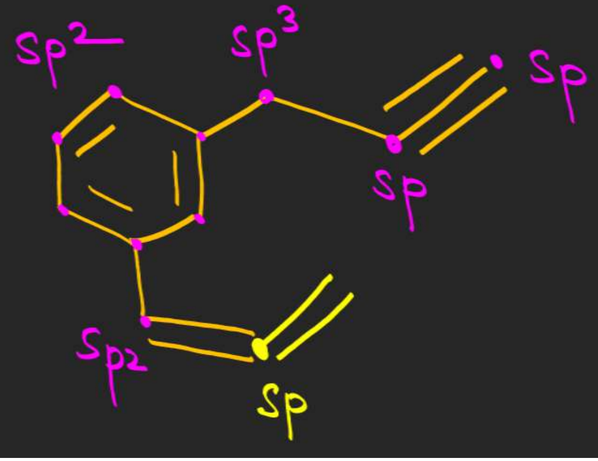
Free radical
sp^2

Carbanion
sp^3 $(lp = 1)$
Pyramidal (N.P.)
angle $< 109^\circ$

sp^3
Tetrahedral

sp^2
Trigonal Planar

ex



ex

- Diamond : sp^3 Tetrahed
- Graphite, C-60 } sp^2

sp
Linear

sp
Linear

Bond Parameters

1. Bond angle
2. Bond order
3. Bond Length
4. Bond Energy (enthalpy)

1) Bond angle (BAB)

a) Check Hyb : $sp > sp^2 > sp^3 > \cdots$

(% s ↓) ⟹ Bond angle dec.

ex $BeCl_2$ > BF_3 > CH_4 > PCl_5

sp sp^2 sp^3 sp^3d

b) If Hyb same : Check lone Pairs

More lone pair ⟹ Bond angle ↓

H_3O^+	>	H_2O
sp^3		sp^3
$lp = 1$		$lp = 2$

CH_4	>	NH_3	>	H_2O
sp^3		sp^3		sp^3
$lp = 0$		$lp = 1$		$lp = 2$

③ If Hyb & lp is same

Check Central atom

↳ Small ⟹ Angle more

ex $H_2\ddot{O}: > H_2\ddot{S}:$

ex $\ddot{N}H_3 > \ddot{P}H_3$

H_2O | NH_3 | CH_4

H_2S | PH_3 | SiH_4

SeH_2 | AsH_3 | ⋮

TeH_2 ↓

(Angle) dec.

④ If Hyb, lp, CA same

Check Surrounding atom

↳ Big → Angle more

$NH_3 < NF_3$

$PF_3 < PCl_3$

⑤ Check Geometry Also

$XeF_2 > CH_4$

sp^3d (linear)

sp^3 (Tetrahedral)

Bond Angle

Depends on following factors

1. Hybridization → $Sp > Sp^2 > Sp^3 > Sp^3d$ ….
2. No. of lone Pairs → Bond angle decreases as lone pair increases
3. Size of C.A. → Bond angle MORE for small C.A.
4. Size of S.A. → Bond angle MORE for bigger S.A.
5. Tip: Bigger molecules do check shape also

Ex. XeF_2

Drago's Rule

In Period no. (3, 4, 5 ...)

Period (2) →	H_2O	NH_3
" — (3) →	H_2S	PH_3
" — (4) →	H_2Se	AsH_3
" — (5) →	TeH_2	⋮

Repulsion more ↓

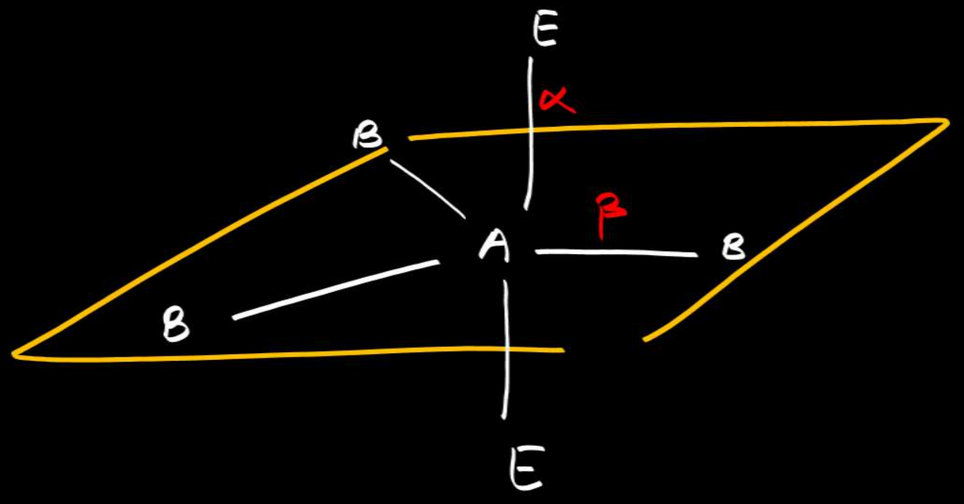
Angle dec. sharply ↓

lone Pair : (S) orbital

% S character = 100 %

Bent's Rule

In sp^3d Geometry



1) (E) more E.N.
2) More repulsion in axial
3) $\alpha > \beta$ in (BL)

4) Axial orbital : P_z , d_{z^2}

equitorial : s , P_x , P_y

Bond Order

- Bond strength
- Bond energy (enthalpy)

1. Number of bonds b/w two atoms or number of electron pair shared b/w two atoms
2. Theoretical concept
3. Can be integer fraction
4. It is calculated for two atoms not molecule.

F_2 ⇒ F – F

O_2 ⇒ O = O

N_2 ⇒ N ≡ N

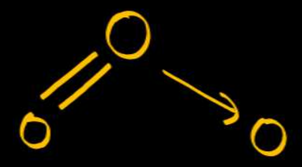
CO_2 ⇒ O = C = O

SO_2 ⇒ 

HCN ⇒ H — C ≡ N

Organic Compound

$CH_3 — CH = CH — C \equiv CH$

ex ⇒ 

O = O

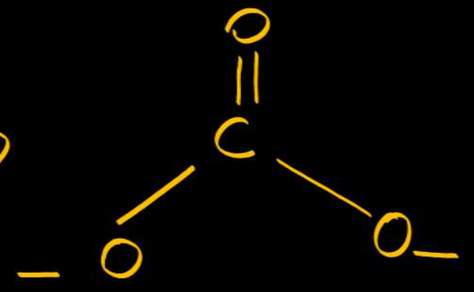
(Bond order) ⇒ (1.5)

(2)

Bond Order

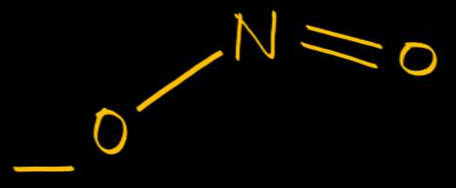
1. Effect due to Resonance

CO_3^{2-} ⇒



Bond order = (4/3)

NO_2^-

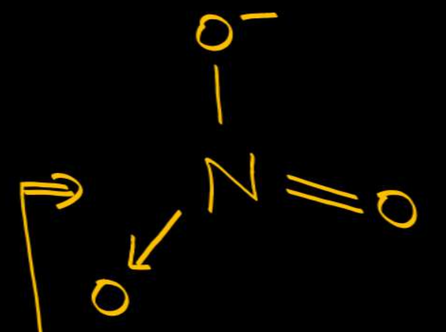


Bond order = (3/2)

SO_4^{2-} ⇒ 6/4

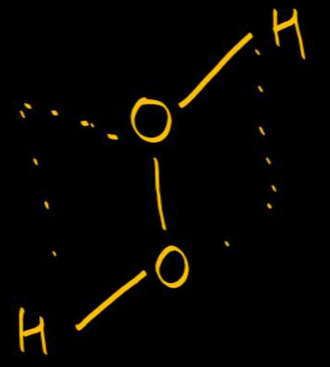
PO_4^{3-} ⇒ 5/4

NO_3^-



BO = (4/3)

ex H_2O and H_2O_2



Bond length : **Check – 1** : Bond order more $\Rightarrow$ (B.L.) $\downarrow$

ex $HC \equiv CH$ (sp) $\quad H_2C = CH_2$ (sp^2) $\quad CH_4 - CH_4$ (sp^3)

$\longrightarrow$

C–H, C–C bond length more

C–H changes by %s and $\oplus$ $\ominus$ charge

more $\Rightarrow$ (BL) $\downarrow$

(BL) $\downarrow$

$\ominus$ charge $\Rightarrow$ BL $\uparrow$

ex $\overset{\ominus}{C}H_3 \quad CH_4 \quad \overset{\oplus}{C}H_3$

$\longleftarrow$

BL more

ex $O=O$ 

$\longrightarrow$ more BL

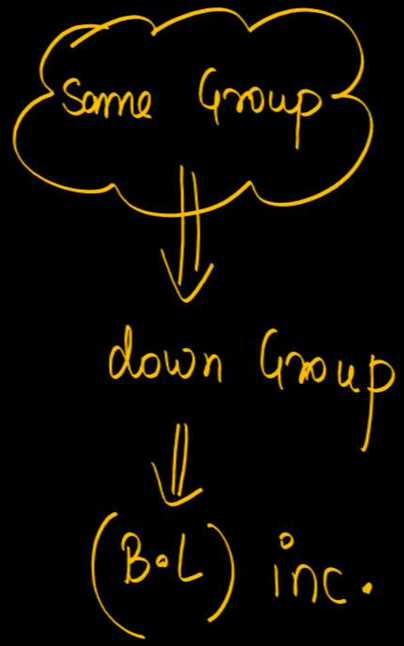
Bond Length

Depends on following factors

1. Bond Order
2. Size of atoms — more ⇒ BL more
3. %S character/ E.N. Difference
4. Inter electronic Repulsion

1. HF HCl HBr HI →

NH_3 PH_3 AsH_3 →



2. H_2O H_2S H_2Se →

CH_4 SiH_4 GeH_4 →

Bond Length

Depends on following factors

1. Bond Order
2. Size of atoms
3. %S character/ E.N. Difference
4. Inter electronic Repulsion

CH_4 NH_3 H_2O HF

←

(BL) more

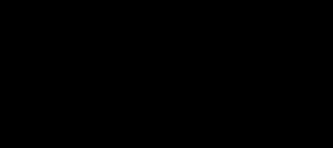
C-C N-N O-O F-F

←

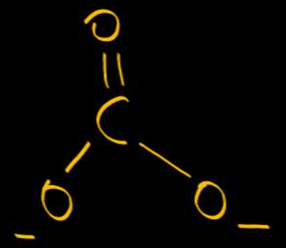
O_2 O_3

Doub

CO_2 CO_3^{2-} CO $\Rightarrow$ $CO_3^{2-} > CO_2 > CO$



BO = 2



BO = 4/3

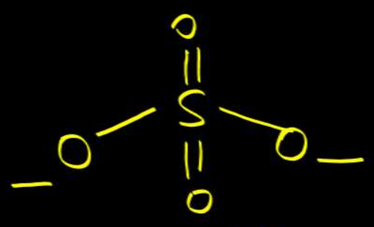
MOT (BO = 3)

Bond Length

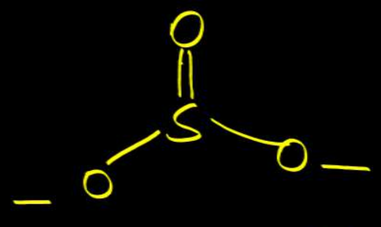
Depends on following factors

1. Bond Order
2. Size of atoms
3. %S character/ E.N. Difference
4. Inter electronic Repulsion

SO_4^{2-} < SO_3^{2-}



BO = 6/4



BO = 4/3

C_2H_2 C_2H_4 C_2H_6

Double

CH_3^+ CH_3^- CH_4

$\overset{\ominus}{C}H_3 > CH_4 > \overset{\oplus}{C}H_3$

Molecular Orbital Theory

Features of this theory are :

1. As electrons in an atom present in atomic orbitals, in molecule electron is present in molecular orbital.

2. Just as the electron finding probability in an atom is given by an atomic orbital, the electron finding probability in a molecule is given by a molecular orbital.

3. In atomic orbital electron is influenced by one nucleus while in molecular orbital, it is influenced by two or more nuclei. Hence called as Polycentric

4. Molecular orbitals are formed when atomic orbitals of comparable energies and proper symmetry are available. Atomic orbitals doesn't exist in molecule.

5. The number of molecular orbital formed is equal to the number of combining atomic orbitals.

6. When two atomic orbitals combine, two molecular orbitals are formed.
   One is known as bonding molecular orbital while the other is called antibonding molecular orbital.

7. The BMO has lower energy and hence greater stability than the corresponding ABMO

8. The molecular orbitals like atomic orbitals are filled in accordance with the aufbau principle obeying the Pauli's exclusion principle and the Hund's rule.

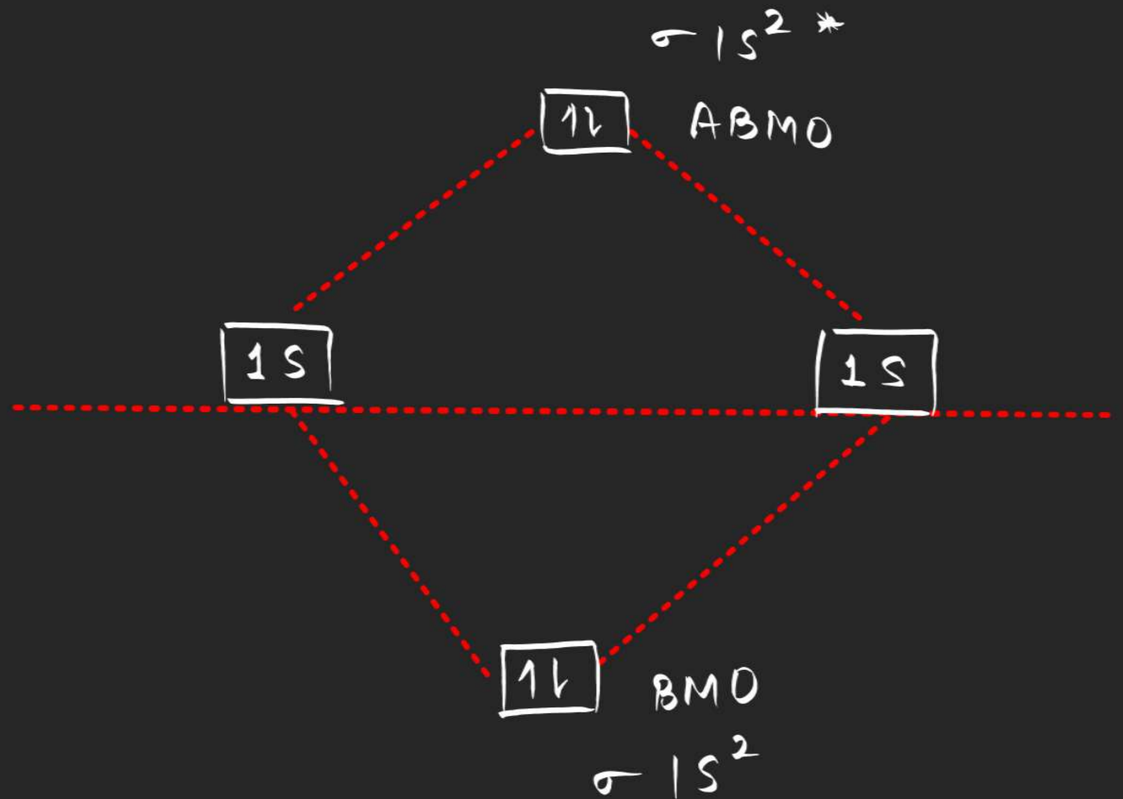
MOT : Molecular orbital theory ⟶ syllabus (e ≤ 20)

BMO ABMO

$\Psi_A + \Psi_B$ $\Psi_A - \Psi_B$

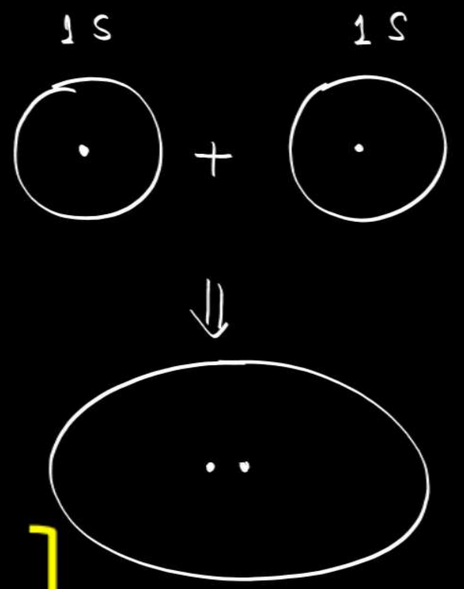
More stable less stable

Less energy More energy



Type of bond (σ, π)

Linear Combination of Atomic Orbitals



Conditions for the combination of atomic orbitals:

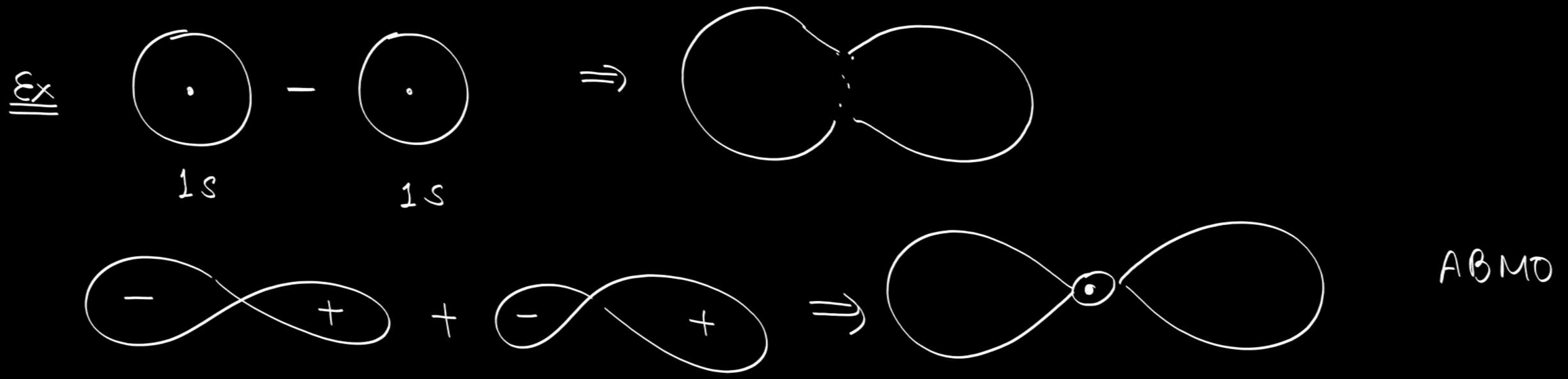
- The combining atomic orbitals must have the same or nearly the same energy.
- The combining atomic orbitals must have the same symmetry about the internuclear axis.
- The combining atomic orbitals must overlap to the maximum extent.
- The probability of finding the electron in the internuclear region of the BMO is greater than that of combining atomic orbitals.
- The electrons present in the BMO result in the attraction between the two atoms.
- They have lower energy as a result of attraction and hence has greater stability than that of the combining atomic orbitals.

They are formed by the additive effect of the atomic orbitals so that the amplitude of the new wave is given by $\Phi = \Psi_A + \Psi_B$

Linear Combination of Atomic Orbitals

- The probability of finding the electron in the internuclear region decreases in the ABMO.
- The electrons present in the ABMO result in the repulsion between the two atoms.
- They have higher energy because of the repulsive forces and lower stability.
- They are formed by the subtractive effect of the atomic orbitals. The amplitude of the new wave is given by $\Phi' = \Psi_A - \Psi_B$

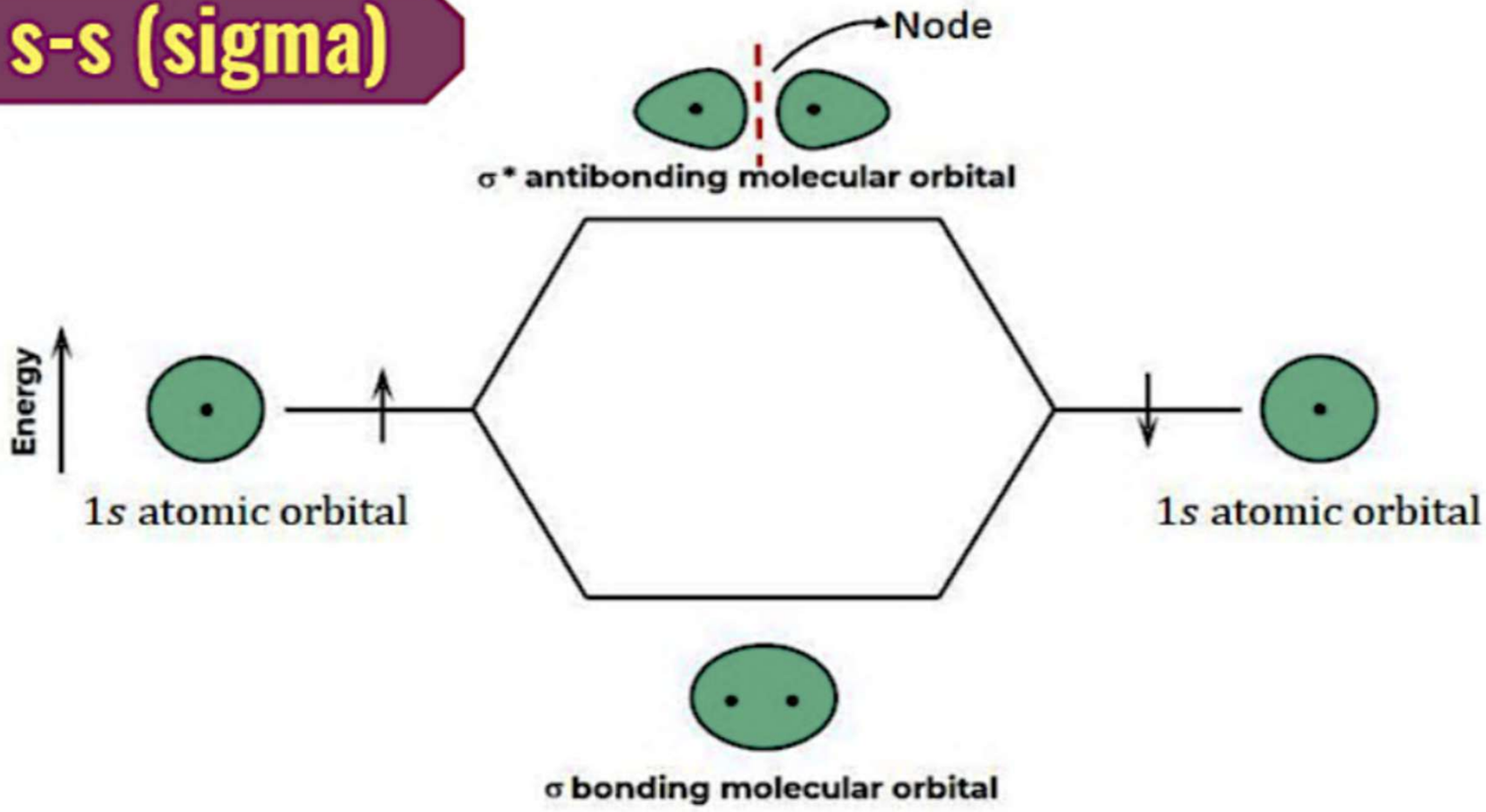
ABMO



Type of Molecular Orbitals

Molecular Orbital Theory

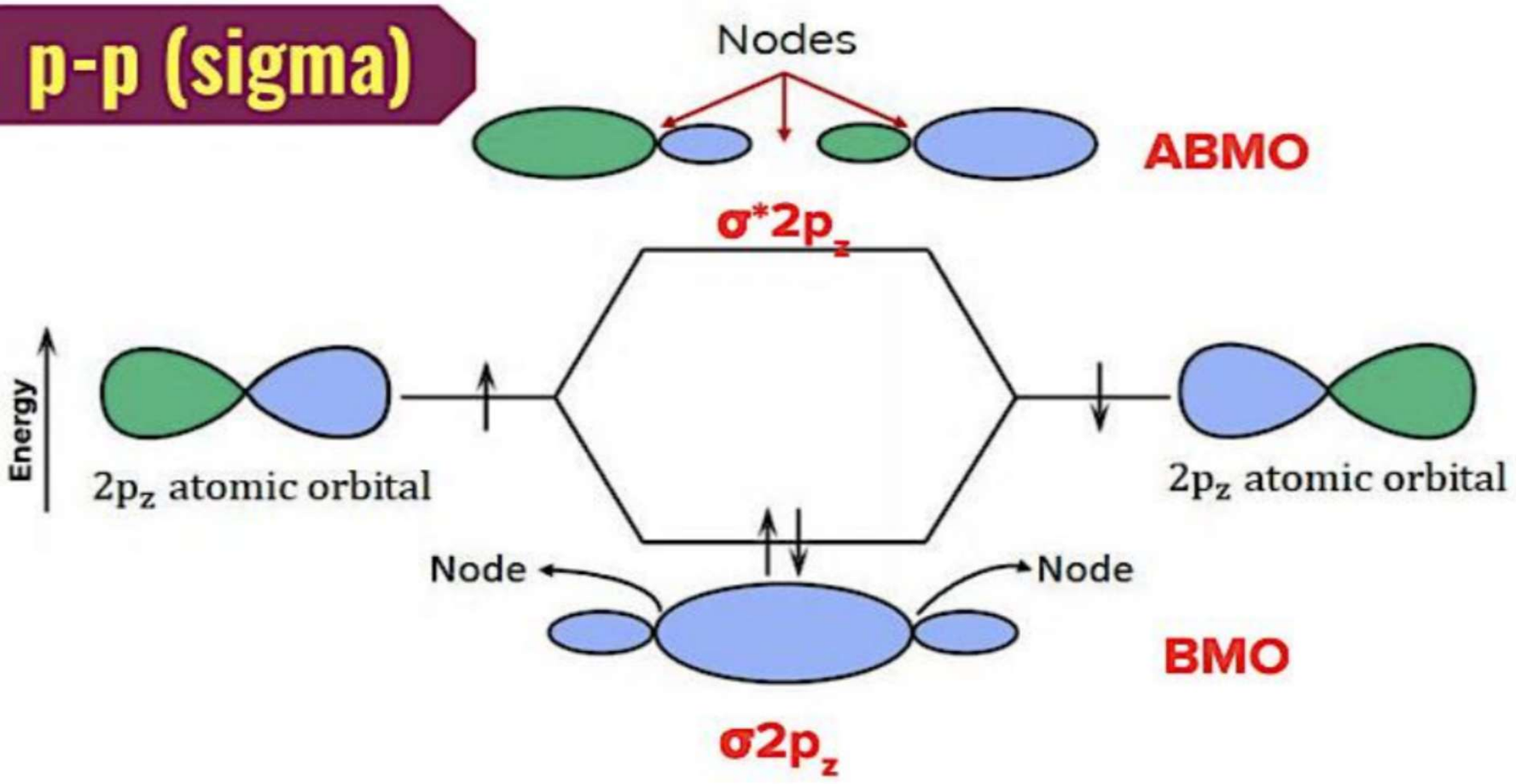
s-s (sigma)



Type of Molecular Orbitals

Molecular Orbital Theory

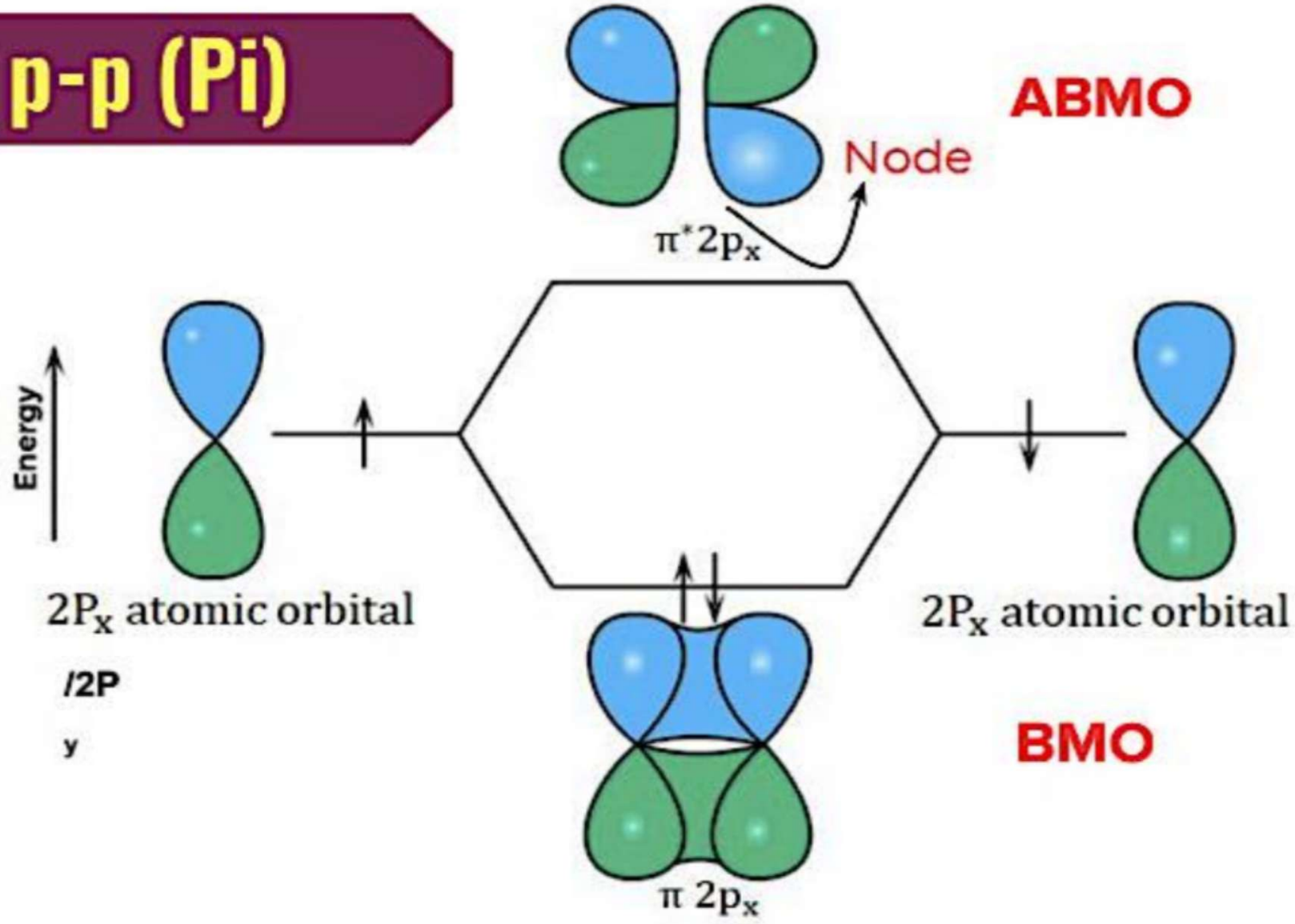
p-p (sigma)



Features of this theory are :

Molecular Orbital Theory

p-p (Pi)



Energy Level digm

$e \leq 14$ NO (S) & (P) mixing

$\sigma 1s^2 \quad \sigma 1s^{2*} \quad \sigma 2s^2 \quad \sigma 2s^{2*}$

$\left(\pi 2p_x^2 = \pi 2p_y^2\right) \sigma p_z^2 \quad \left(\pi 2p_x^{*} = \pi 2p_y^{*}\right) \sigma 2p_z^{*}$

Example C_2^- $\Rightarrow$ 13e

$\sigma 1s^2 \; \sigma 1s^{2*} \; \sigma 2s^2 \; \sigma 2s^{2*} \left(\pi 2p_x^2 = \pi 2p_y^2\right) \sigma 2p_z^1$

i) No. of BMO e$^-$ = (9)

ii) ——//—— ABMO = (4)

iii) Unpaired (e) = 1

No. of σ bond = 2.5

——//—— π bond = 2

$e > 14$ (S and P) mixing

$\sigma 1s^2 \; \sigma 1s^{2*} \; \sigma 2s^2 \; \sigma 2s^{2*}$

$\sigma 2p_z^2 \left(\pi 2p_x^2 = \pi 2p_y^2\right) \left(\pi 2p_x^{2*} = \pi 2p_y^{2*}\right) \sigma 2p_z^{2*}$

iv) HOMO $\longrightarrow$ Highest occupied M.O.

LUMO $\longrightarrow$ lowest unoccupied M.O.

$$\#\ \text{Bond order} = \frac{1}{2}\left(N_B - N_A\right) = 5/2$$

Application of Bond order

i) Calculation of Bond order

ii) Stability $\propto$ B.O.

iii) Strength (Bond energy) $\propto$ B.O.

iv) Bond length $\propto \frac{1}{\text{B.O.}}$

Exam : N_2 O_2^+ O_2

Ans : (B.O) 3 2.5 2

(B.L.) $N_2 < O_2^+ < O_2$

SMART APPROACH FOR BOND ORDER

10e	11e	12e	13e	14e	15e	16e	17e	18e	19e	20e
1	1.5	2	2.5	3	2.5	2	1.5	1	0.5	0

1e	2e	3e	4e	5e	6e	7e	8e	9e	10e
0.5	1	0.5	0	0.5	1	0.5	0	0.5	1

↓

Molecule doesn't exist

Ex : O_2 , O_2^+ , O_2^- , O_2^{2-}

B.O. : 2 , 2.5 , 1.5 , 1

i) Arrange in dec. order wrt BO, BL, Stability

BO : $O_2^+ > O_2 > O_2^- > O_2^{2-}$

Stability
strength
Bond energy
} ← same Ans

Bond length $O_2^+ < O_2 < O_2^- < O_2^{2-}$

If Bond order same

a) more Anti Bonding e⁻
less stability

Trick : (More e⁻) with same B.O. ⇒ less stable

b) more π e⁻
less B.L.

Paramagnetic : Having unpaired e⁻

All odd no. of e⁻ and (10, 16) } $n = 1$ for all except (10, 16) ⇓ $n = 2$

$B.M. = \sqrt{n(n+2)}$

Diamagnetic : No unpaired e⁻

All even no. except (10, 16) } unpaired e = 0

BM = 0

$B_2^+ \Rightarrow 9e = \sigma 1s^2 \; \sigma 1s^{2*} \; \sigma 2s^2 \; \sigma 2s^{2*} \left(\pi 2p_x^1 = \pi 2p_y\right)$

i) Unpaired e = 1

ii) Paramagnetic

iii) $BM = \sqrt{1(3)} = \sqrt{3}$

iv) $B.O = 1/2$

v) $N_B = 5$

vi) $N_A = 4$

$F_2 = 18e \Rightarrow \sigma 1s^2 \; \sigma 1s^{2*} \; \sigma 2s^2 \; \sigma 2s^{2*} \; \sigma 2p_z^2 \; (\pi 2p_x^2 = \pi 2p_y^2) \; (\pi 2p_x^{2*} = \pi 2p_y^{2*})$

$\sigma 2p_z^{2*}$

i) B.O. = 1

ii) Diamagnetic $(n=0)$

iii) Mag. moment $= 0$

iv) $N_B = 10$, $N_A = 8$

v) HOMO $\Rightarrow$ $\pi 2p_x^*$ or $\pi 2p_y^*$

vi) LUMO $\Rightarrow$ $\sigma 2p_z^*$

Nature of oxides (Para / dia)

O^{2-}	O_2^{2-}	O_2^-
oxide	Peroxide	super oxide
(dia)	(dia)	(Para)

Bond Polarity : Due to E.N. difference b/w bonded atoms, there is partial shift of bonded e- towards more E.N.

ex $H \rightarrow\!\!\!\!\rightarrow Cl \Rightarrow \overset{\delta+}{H} — \overset{\delta-}{Cl}$ (+ →) $\Rightarrow$ leads to the formation of dipole

Dipole moment : (μ) = Partial charge × Bond length

$= (\delta)(B.L.)$

- → Vector quantity
- → direction towards more E.N.
- → **SI unit** : Debye = C·m
- → **Significance** : extent of polarity

Application of Dipole Moment

a) Molecule — Non Polar $(\mu = 0)$
Polar $(\mu \neq 0)$

b) Extent of Polarity

c) (B.P., solubility) ↑ if (μ) ↑

d) Organic < Cis $(\mu \neq 0)$
Trans $(\mu = 0)$

Identification of Non-Polar molecule

a) Homoatomic molecule (H_2, O_2, Cl_2 etc.)

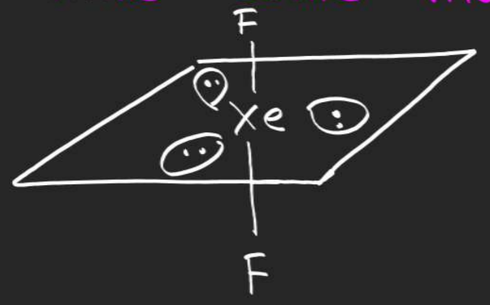
b) Molecule with (SA) same & no lone Pair

ex: $BeCl_2$, BF_3, CH_4, $\overset{+}{C}H_3$, CO_2, SO_3, PCl_5, SF_6 etc.

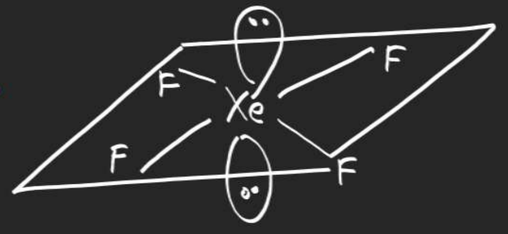
Alkane, alkene, Alkyne, Benzene, CCl_4, CS_2 etc.

c) Even with lone pair sometime some molecule are non polar

$XeF_2 \rightarrow sp^3d \rightarrow$ linear

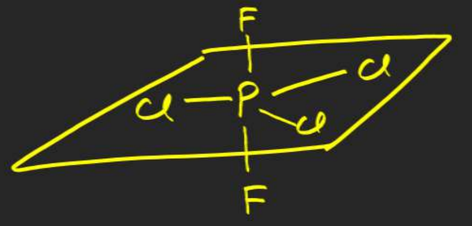


$XeF_4 \rightarrow sp^3d^2 \rightarrow$ Sq. Planar

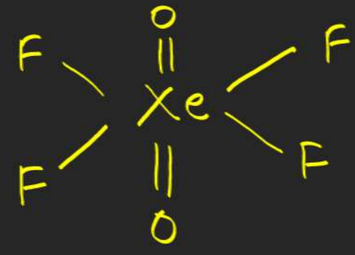


d) even with diff SA atoms some molecule non Polar

ex PCl_3F_2



ex XeO_2F_4



Examples of Polar

HCl, NH_3, O_3, H_2O, SO_2, H_2S

PH_3, PCl_3, SF_2, All oxyacids & their anion

XeO_3, XeO_2,

Haloalkane, Alcohol, ether, Aldehyde, etc.

Extent of Polarity

(i) More dipole moment

Ex $HF > HCl > HBr$

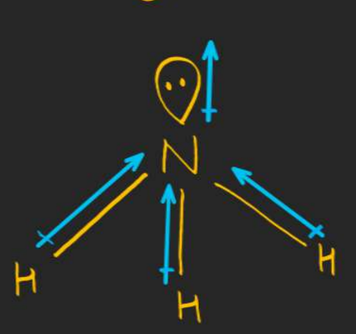
ex $CH_4 < NH_3 < H_2O < HF$

order of Bond Polarity

ex $NH_3 > PH_3$, $H_2O > H_2S$

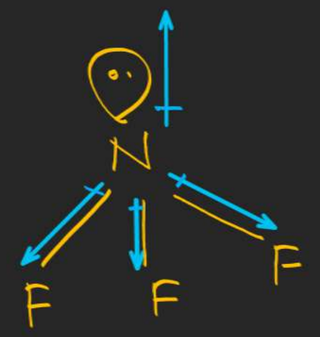
(ii) using arrow digm $(d > c > a > b)$

a) NH_3 b) NF_3 c) H_2O d) HF



All dipole moment vector sum up to increase overall Dipole moment

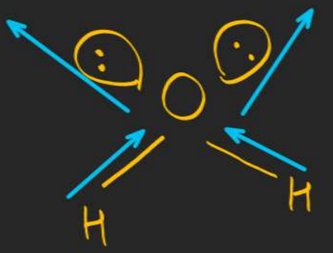
$\mu_{NH_3} =$ ↑



Dipole moment of B.P. is opp. to that of lp.

$\Rightarrow (D.M.)_{net}$ dec

$\Rightarrow \mu = \uparrow$ μ_{NF_3}



$\mu_{H_2O} =$ ↑

Hydrogen Bonding

It is electrostatic force of attraction between covalently bonded **H -** atom of one molecule and the most electronegative element [F,O,N] of another molecule.

Hydrogen bond and is weaker than the covalent bond

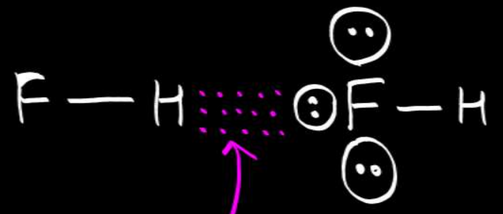
Its dipole - dipole attraction

(H) attached with

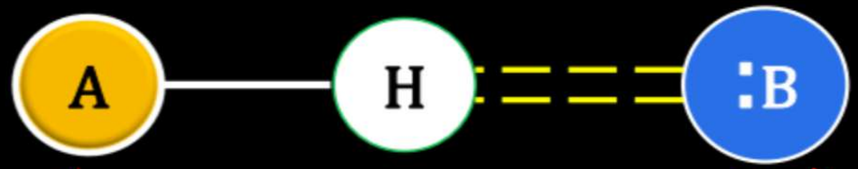
(F, O, N, $-C_{sp}$, $-CCl_3$, $-CF_3$)

⇓

with other F, O, N $-CCl_3$, $-CF_3$ having lone Pair



(H-bond)



(F > O > N)

(1st check)

with lone Pair

(N > O > F)

(2nd check)

Molecules that exhibit H-bonding

i) HF

ii) NH_3

iii) Amines

iv) H_2O , Alcohol

v) All oxyacids

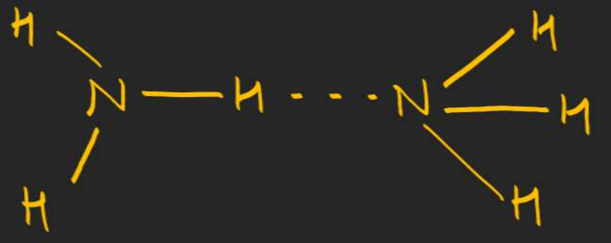
vi) Carboxylic acid

vii) Biomolecules

ex $H-F\cdots H-F$

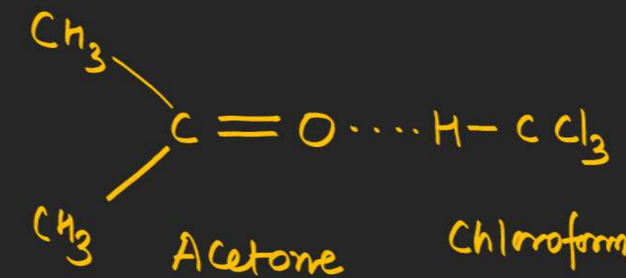
ex $H-F\cdots OH_2$

ex $H-F\cdots NH_3$

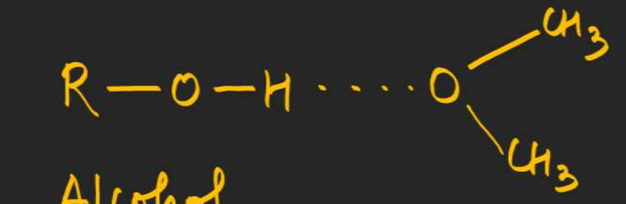
ex 

ex $H-F\cdots HC\equiv CH$

ex $CH\equiv C^{-}\cdots HF$ (H)

ex 

Acetone Chloroform

ex 

Alcohol ether

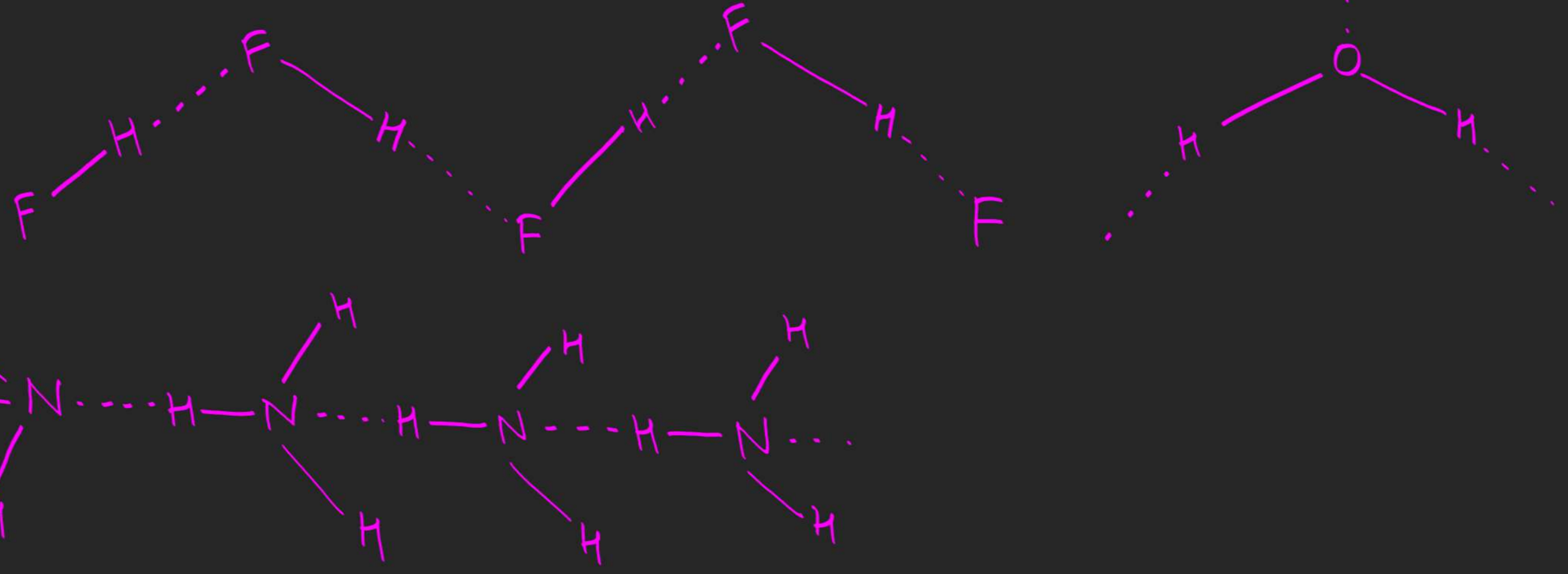
extent of H-bonding $\propto$ no. of H-bond

	H_2O (ice)	>	H_2O (l)	>	impure water	>	NH_3	$\approx$	HF
No. of H-bond	(4)	>	(3)		(3)		(2)		(2)

H_2O_2

(4)

Shape



Strength of H-bonding

a) $H-F\cdots H-F$ b) $H_2O\cdots HOH$ c) $H_3N\cdots HNH_2$

$a > b > c$

a) $H-F\cdots H-F$ b) $H_2O\cdots H-F$ c) $H_3N\cdots H-F$

$c > b > a$

a) $H-F\cdots H-F$ b) $H-F\cdots H-OH$ c) $H_3N\cdots H-OH$

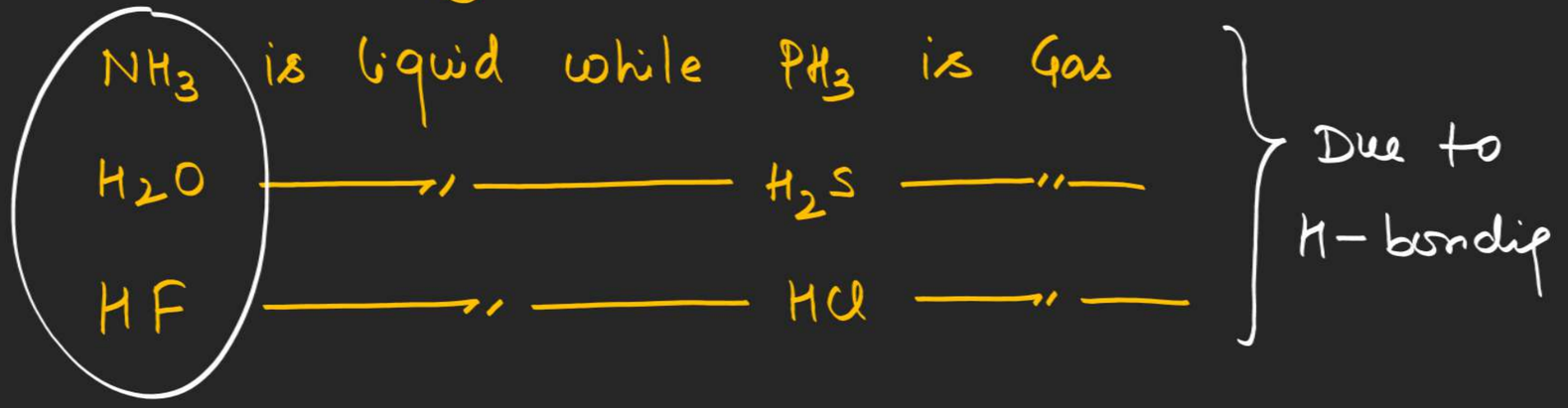
$a > c > b$

ex overall H-bonding $\Rightarrow$ $H_2O > HF > NH_3$

Application

i) Due to H-bonding ⟹ Phase Gas → Liquid → Solid

ex



is liquid while PH_3 is Gas

High B.P. in their Group

ii) B.P. increases due to H-bonding

$H_2O_2 > H_2O > H_2O > HF > NH_3$

(Pure) impure

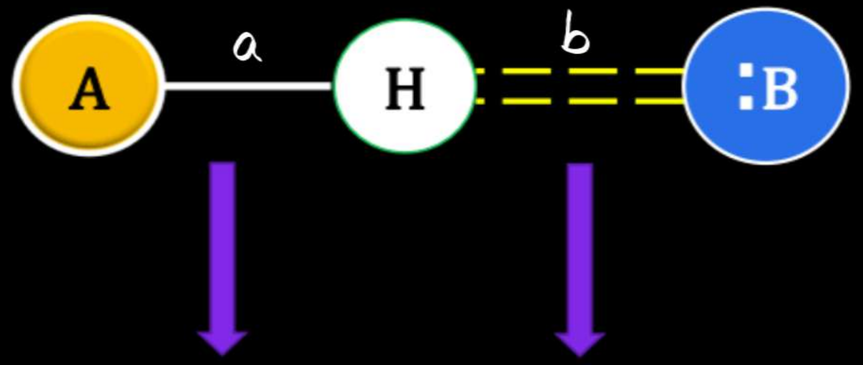
(iii) solubility ↑ in water

iv) Volatality ↓

v) Visocity ↑

Surface tension

Hydrogen Bonding



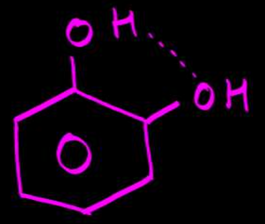
Bond Length	less	more
Bond strength	More	less
Bond Energy	More	less

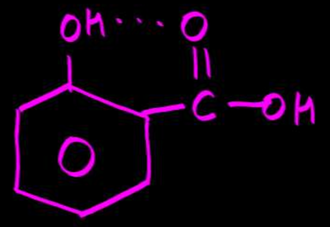
Type of H-bonding

Intra-molecular H-bonding

⇒ In the molecule itself

ex





Having H-bonding species at (1,2) / ortho position

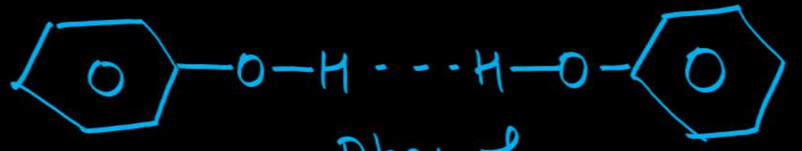
ex Weaker than intermolecular

Intermolecular H-bonding

⇒ B/ω molecules of same / diff type

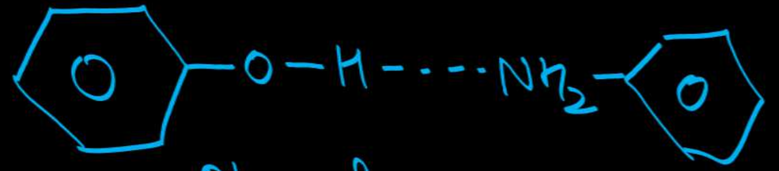
ex H—F ··· H—F

ex



Phenol

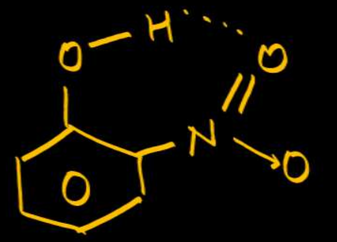
ex



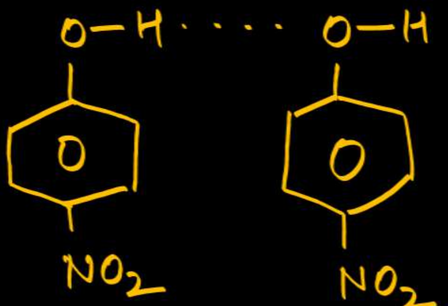
Phenol Aniline

Consequences of intermolecular Hydrogen Bond :

1. Associatiation of molecules $\propto$ inter-molecular H – Bonding
2. Volatility : $\frac{1}{\text{in inter-molecular H – Bonding}}$
3. Effect in physical state $NH_3(\ell)$ $PH_3(g)$
4. Boiling Point $\propto$ inter-molecular H – Bonding
5. Surface Tension & Viscocity $\propto$ inter-molecular H – Bonding



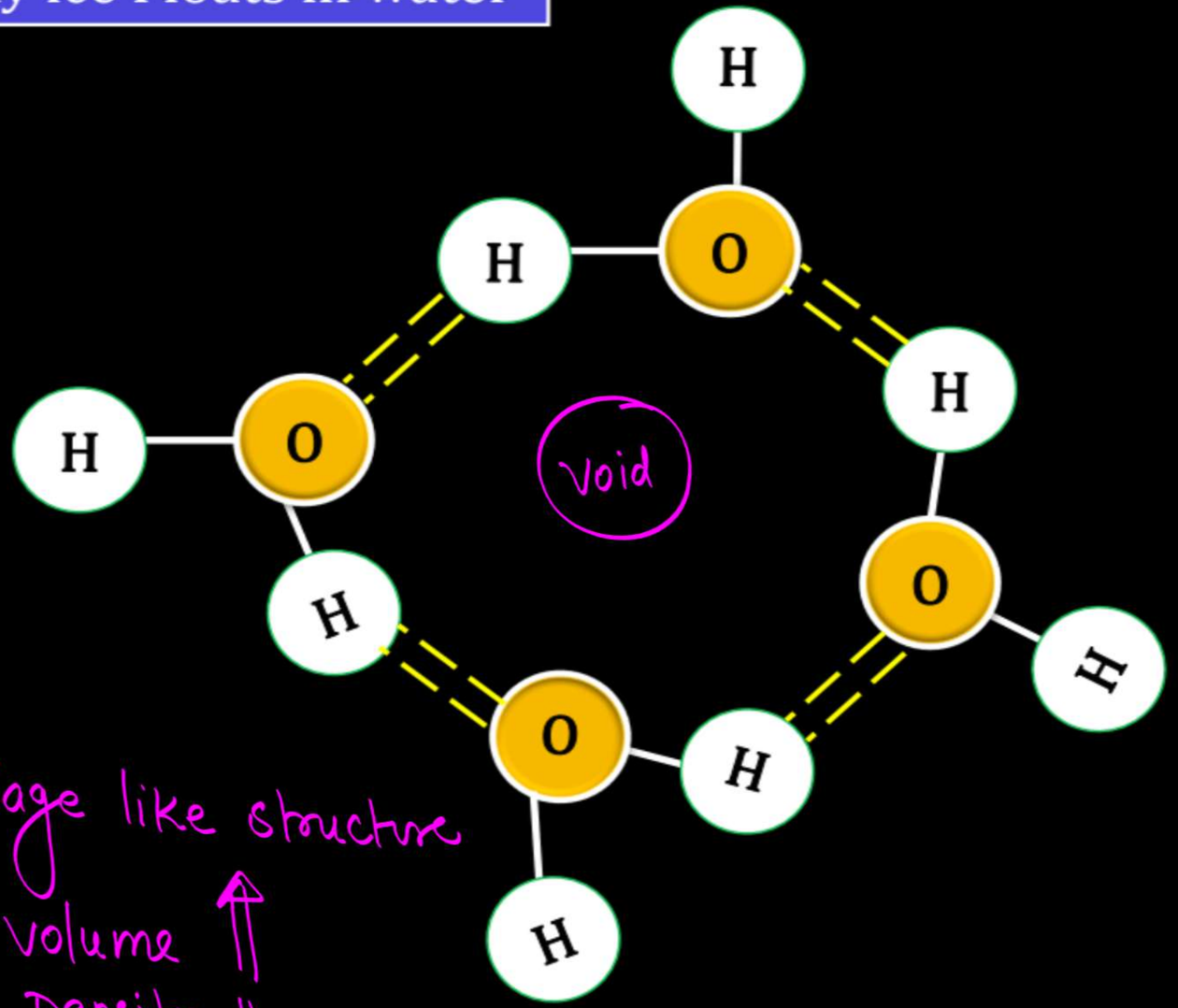
O - nitrophenol
(intramolecular H-bonding)



P - nitrophenol
(intermolecular H-bonding)

H-bonding strength	less	more
B.P.	less	more
Volatile	more	less
Viscosity	less	more
S.T.		
ΔH_{vap}	less	more

Why ice Floats in water

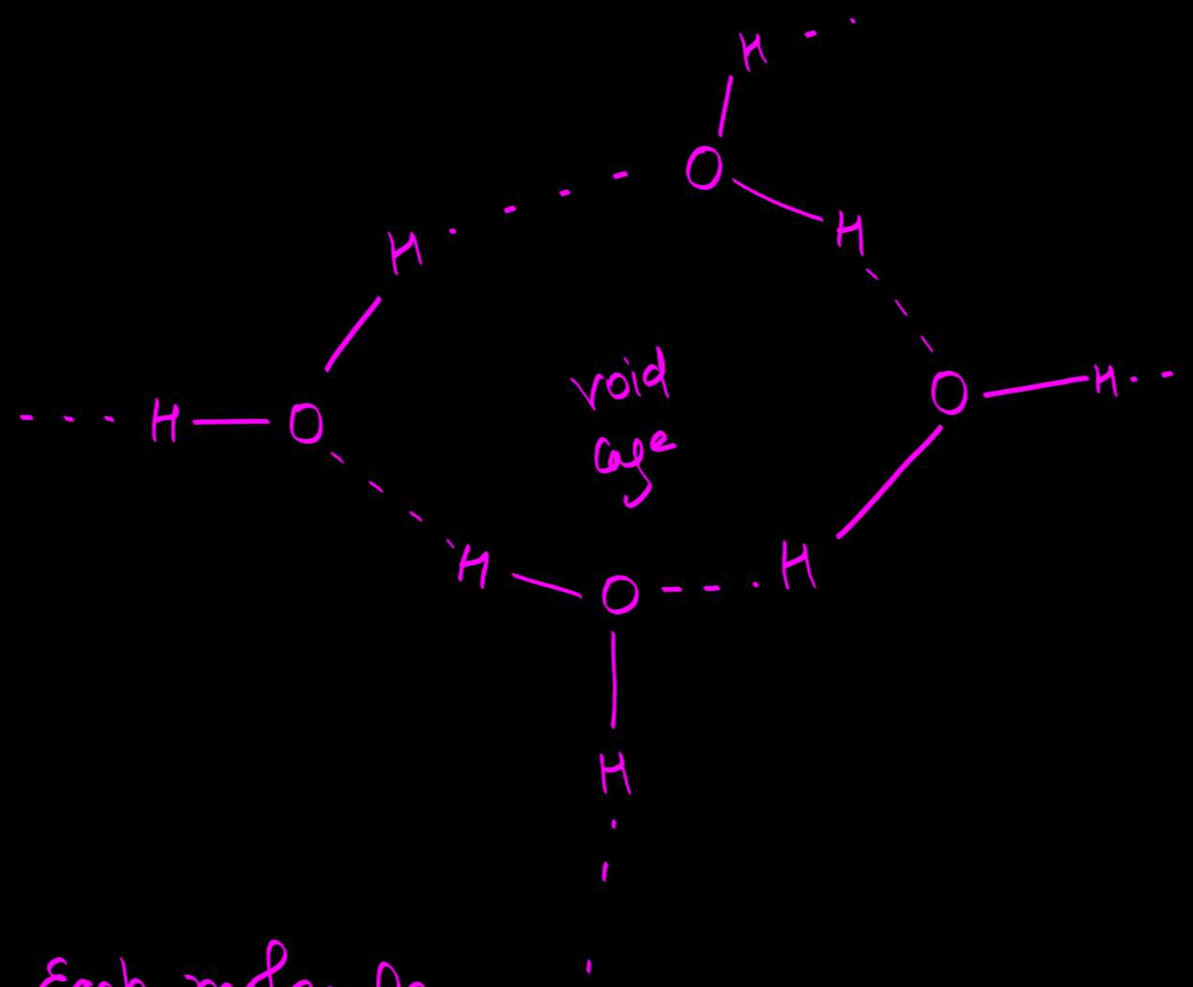


Cage like structure

volume ⇑

Density ⇓

ice floats on water



Each molecule has 4 (H-bonds)

Weak Forces

Vanderwaals force

Ion – Ion > Ion – Dipole > Dipole – Dipole > Ion – Induced dipole > Dipole – Induced Dipole > London

(H-bonding)

a) NaCl ..... KCl (ion-ion)

b) NaCl .... HCl (ion-dipole)

c) HCl .... HI (dipole-dipole)

d) NaCl .... CO_2 (ion-induce dipole)

e) HCl .... SO_3 (dipole-induced dipole)

f) CO_2 .... He (LDF)

↳ molar mass
↳ surface area

g) HF ... H_2O (dipole-dipole)

Weak Forces

Ion – Ion > Ion – Dipole > Dipole – Dipole > Ion – Induced dipole > Dipole – Induced Dipole > London

$\left(\propto \frac{1}{r}\right)$ $\left(\propto \frac{1}{r^2}\right)$ $\left(\propto \frac{1}{r^3}\right)$ $\left(\propto \frac{1}{r^4}\right)$ $\left(\propto \frac{1}{r^6}\right)$