

L-1/13

(CH-4)

CHEMICAL-BONDING & MOLECULAR STRUCTURE

CHEMICAL-BOND:

It is the force that binds the atoms to give the together within a chemical species.

Types:

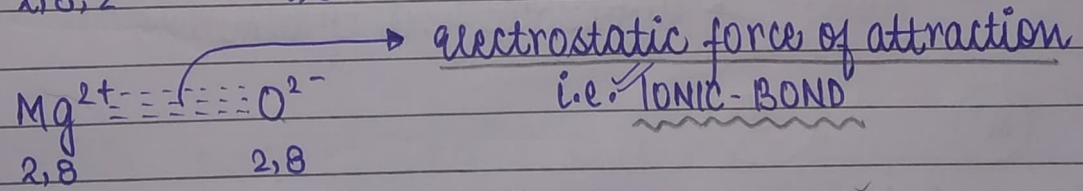
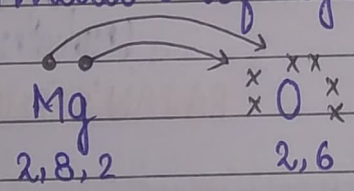
- 1) Ionic / electrovalent
- 2) covalent
- 3) Dative / co-ordinate
- 4) Metallic
- 5) van-Der waals forces

IONIC-BOND

electrostatic force of attraction

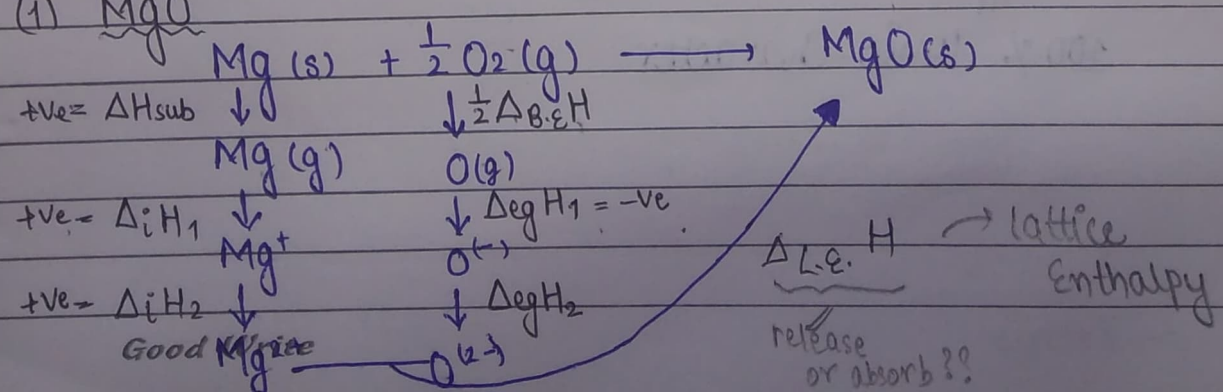
Metal and Non-metal react with each other to form Ionic-Bond

Eg. Formation of MgO



BORN-HABER CYCLE

(1) MgO



* {Energy = magnitude}

* Enthalpy
{ or { +ve
 -ve

DATE: ___/___/___
PAGE: _____

$\Delta_f H_{MgO}$ → enthalpy of formation of MgO

$$\Delta_f H_{(MgO)} = \Delta H_{sub} + \Delta_i H_1 + \Delta_i H_2 + \frac{1}{2} \Delta_{B-E} H + \Delta_{eg} H_1 + \Delta_{eg} H_2 + \Delta_{L.E.}$$

More Negative the value of enthalpy of formation, more stable will be the product

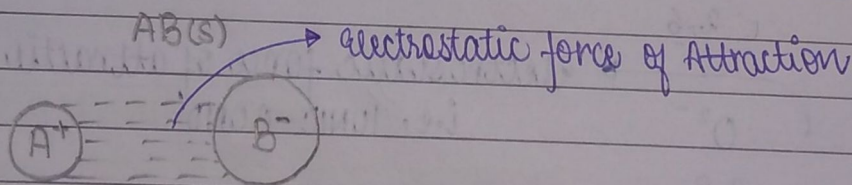
↙ Bond Dissocⁿ energy

Factors favouring the formation of ionic-bond :

- ① Enthalpy of ionization of the metal and the Non-metal should be Low (less +ve).
- ② Ionization enthalpy of metal should be low.
- ③ Electron gain enthalpy of the Non-metal should be more Negative.
- ④ Lattice Energy of the Ionic solid should be High.

(More Negative)

Covalent characters in ionic-solid : [FAJAN'S RULE]



100% ispherical

100% spherical

|||

100% Ionic-Character

polarising power (+)

Ability of an atom/cation to distort the e^- cloud of Anion towards itself.

polarisability (-)

Tendency of anion to be distorted by the cation.

* Polarisability $\propto$ size

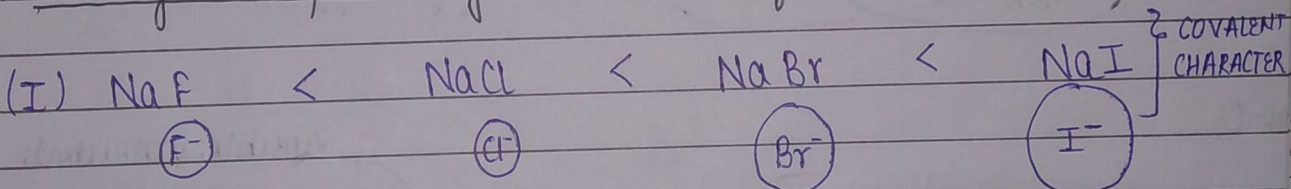
* Polarising power $\propto$ charge Density

$$\text{charge Density} = \frac{\text{charge}}{(\text{size})^2}$$

Fajan's Rule:

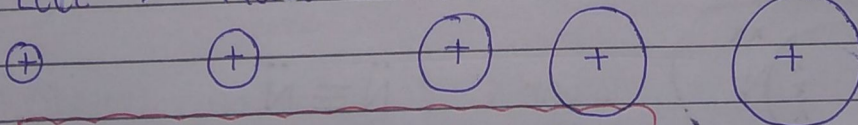
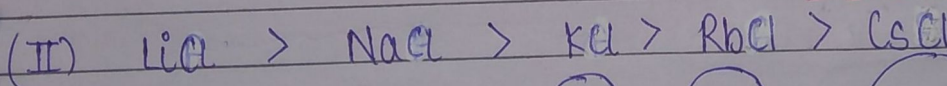
Higher the polarising power of cation as well as polarisability of Anion more will be the covalent character in ionic SOLID.

Arrange the following in the order of covalent character:

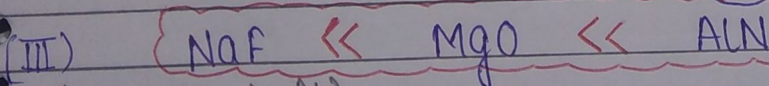


Anion size $\propto$ polarisability

NaI is soluble in Acetone due to its covalent Nature.



$\frac{1}{(\text{cation size})^2}$ Polarising power



$(\text{Na} > \text{Mg} > \text{Al})$ } Polarising Power MORE = MORE COVALENT
 $(\text{F} < \text{O} < \text{N})$ } Polarisability

cation having more than $8 e^-$ in its valence shell has more polarising power than a cation having $8 e^-$ in it.

eg. K^+
2, 8, 8

Cu^+
2, 8, 18

↳ more polarising power

i.e. $KCl < CuCl$ = Covalent Character

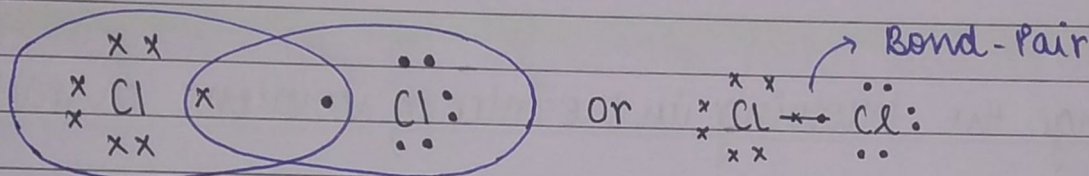
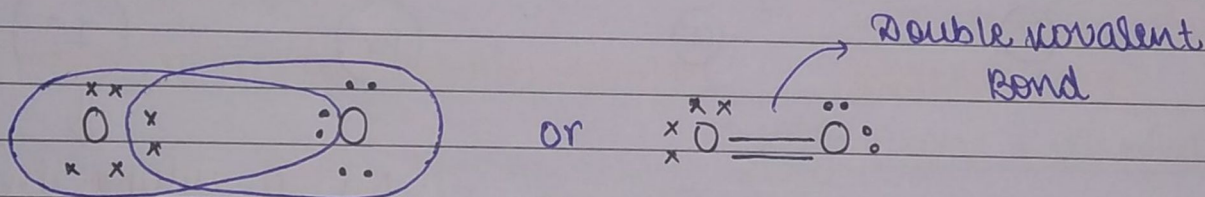
COVALENT- BONDING

- ## * LEWIS - CONCEPT OF

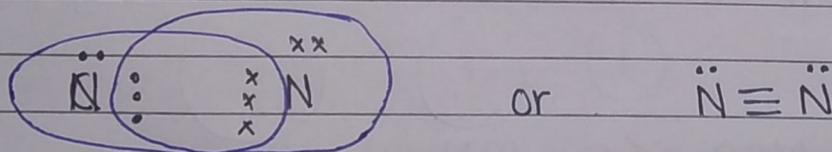
- 1) Lewis concept
- 2) VSEPR Theory
- 3) Valence Bond theory
- 4) Hybridization
- 5) MOT
- 6) Resonance
- 7) H-bonding

COVALENT - BONDING :

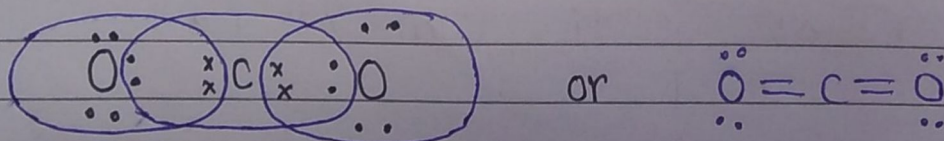
Cl₂

 $\# O_2$ 

N₂



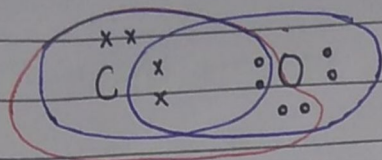
CO_2



* First complete octet of more EN element

DATE: ___/___/___
PAGE: ___

CO →



i.e. $\text{x} \text{C} \equiv \text{O} \text{:}$ (unequal sharing)

coordinate or dative Bond

CN_2^{2-}

Lewis-Str
 N_2O

NO_2^+

$\text{N}_3^{(-)}$

① Total Valence e^-

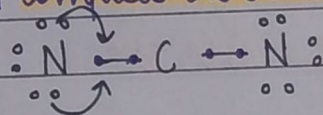
2

$$= \frac{4 + 2 \times 5 + 2}{2}$$

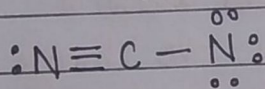
= 8 pairs of valence e^-

② put valence the least EN at Centre

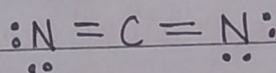
+ complete the octet of most EN atom(s)



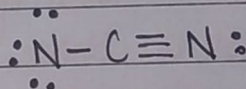
↓



①

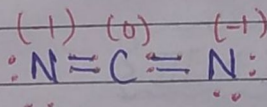
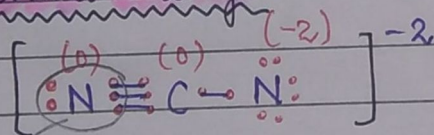


②



③

* formal-charge

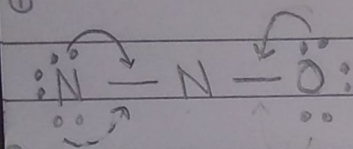


Net charge = $0 + 0 + (-2) = -2$ formal
Net charge = $-1 - 1 = -2$ formal

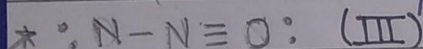
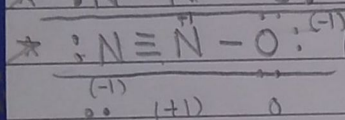
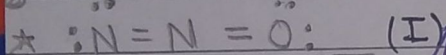
→ Since have 5 close e^- , i.e. equal valence e^- ∴ formal Charge = 0
if have extra = -ve
if have less = +ve

* N_2O

$$\begin{aligned} \text{TVE} &= \frac{5 \times 2 + 6}{2} \\ &= \frac{16}{2} = 8 \text{ pairs} \end{aligned}$$



(Resonating str. N_2O)



$(-2) \quad (+1) \quad (+1)$

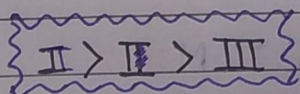
(3 Resonating str.)

Total formal charge = $-1 + 1 + 0 = 0$

* Resonating str. Having max. No. of atoms with formal charge zero or close to zero is the most stable str.

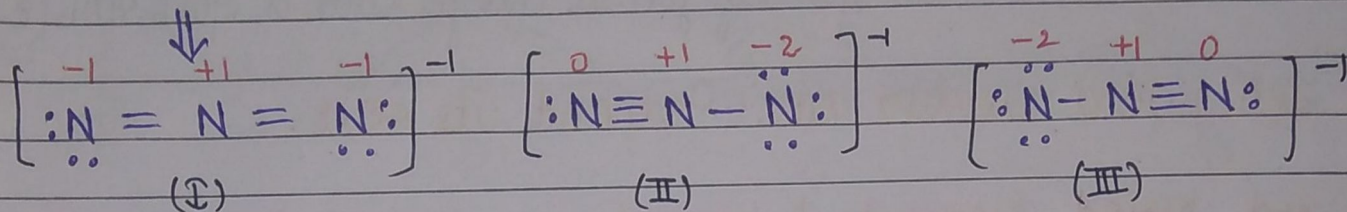
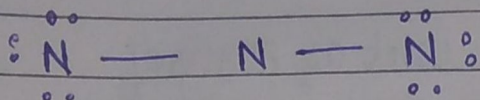
* Resonating str. Having Neg. charge on more EN atom is more stable than the resonating str. Having -ve charge on less EN atom

* Stability among I & II, III $\rightarrow$



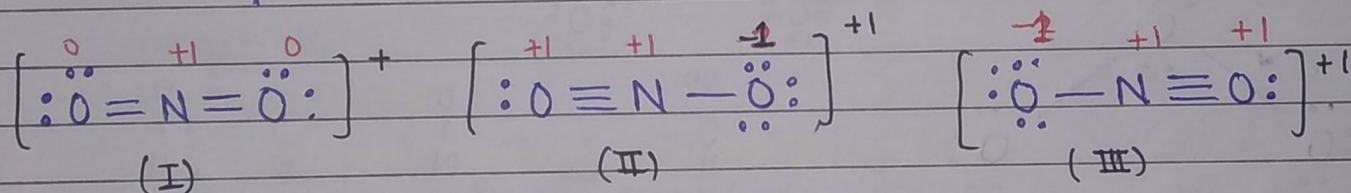
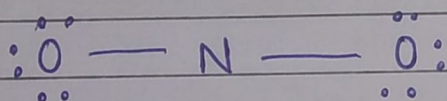
$$\frac{5 \times 3 + 1}{2} = 8$$

N_3^-

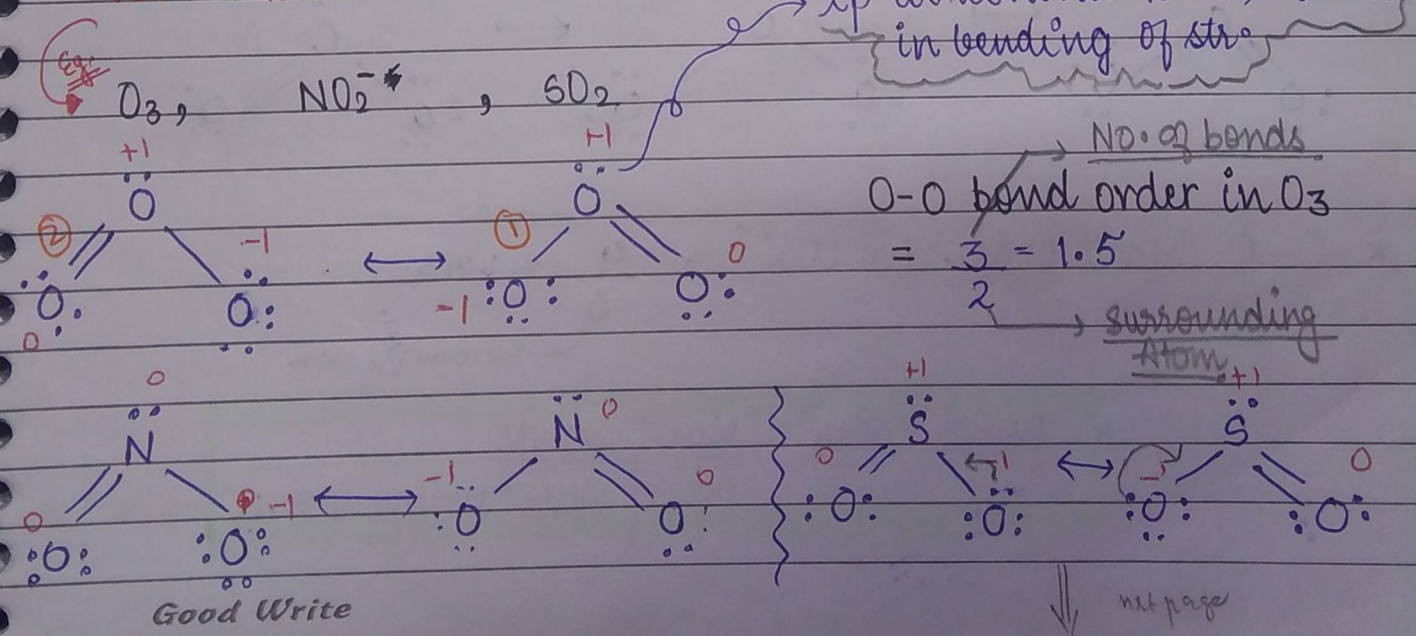


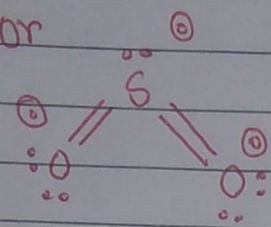
NO_2^+

$$\frac{5 + 2 \times 6 - 1}{2} = 8$$



* "Isoelectric species having same No. of Atoms are ISO-STRUCTURAL."



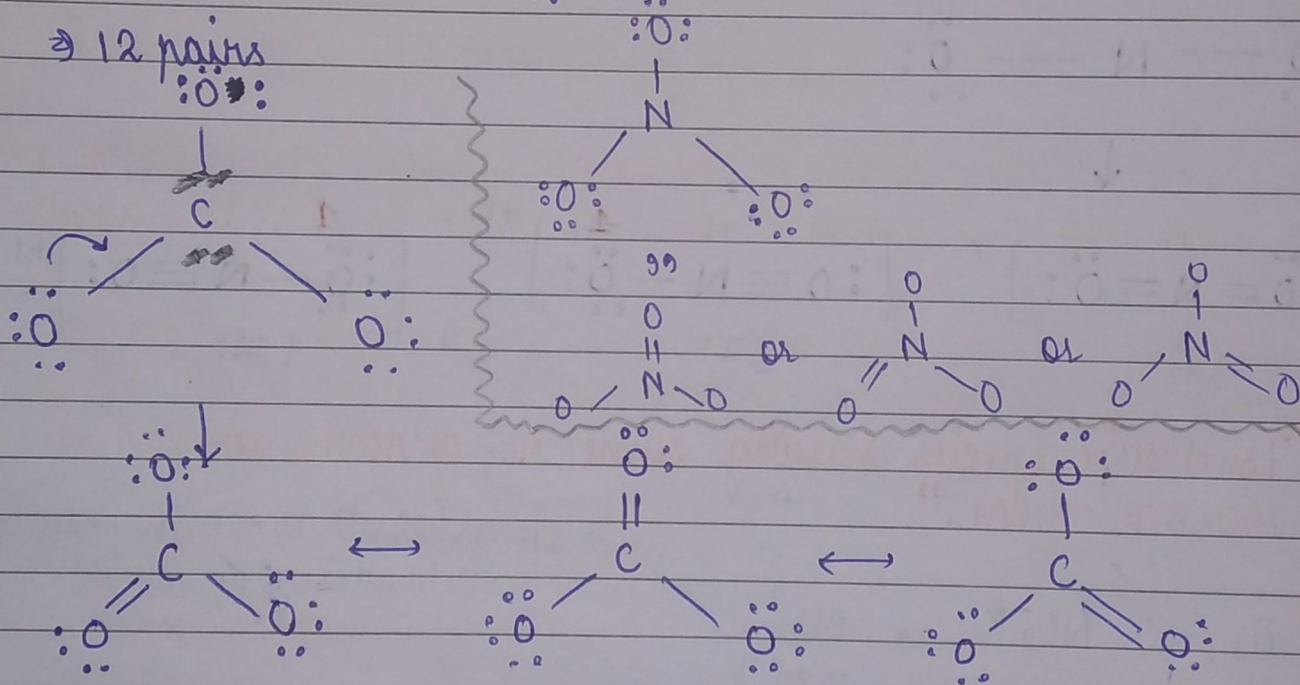
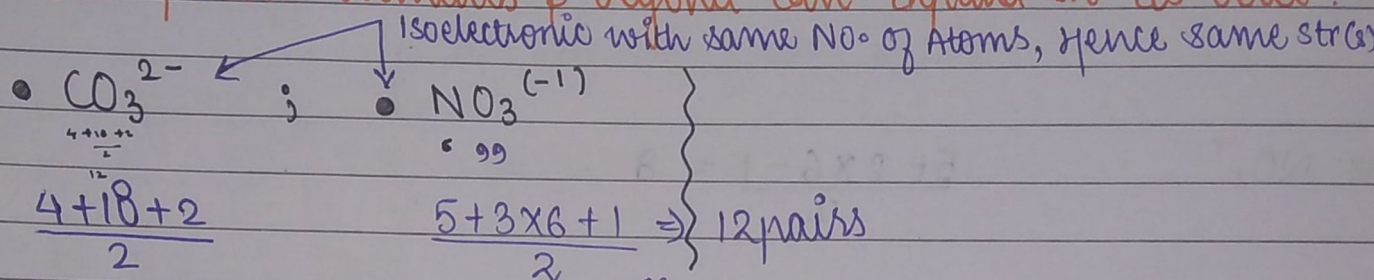


(more stable)

↳ sulphur expand its octet as Atoms of molecule having formal charge zero is MOST-STABLE.

* 2nd period element can't expand its octet.

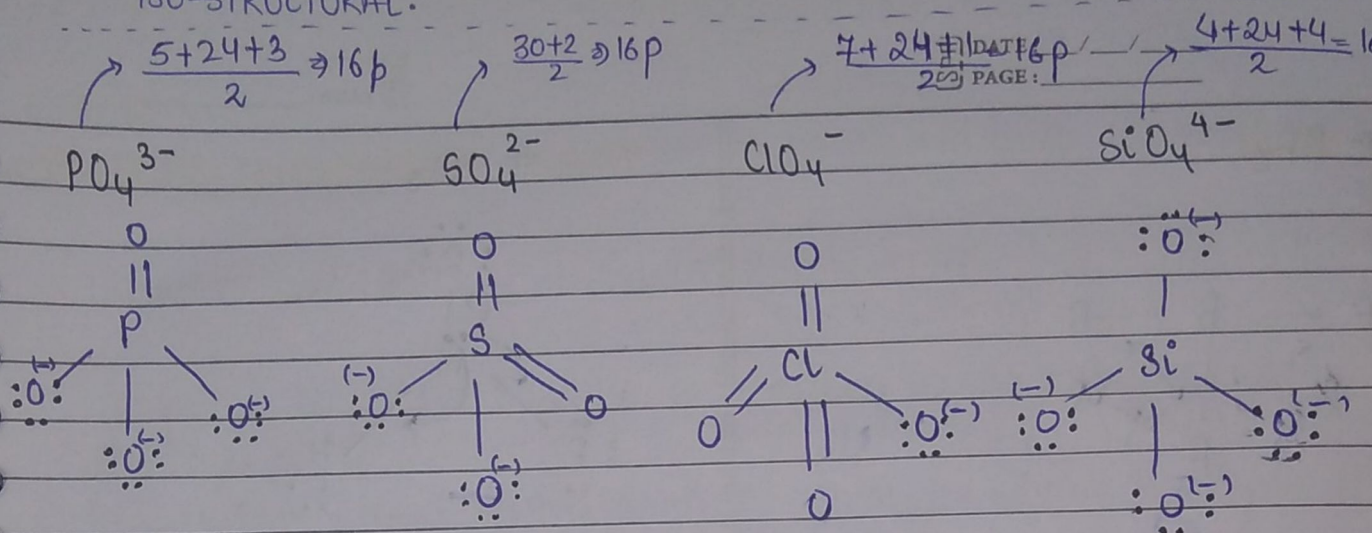
* 3rd period elements & beyond can expand its octet.



* C-O bond order in $\text{CO}_3^{2-} = \frac{\text{bonds}}{\text{surrounding atom}} = \frac{4}{3} = 1.33$

* Bond-order = $\frac{\text{No. of bonds}}{\text{No. of surrounding Atoms}}$

* Given 4 species are isoelectronic with same No. of atoms, Hence are ISO-STRUCTURAL.



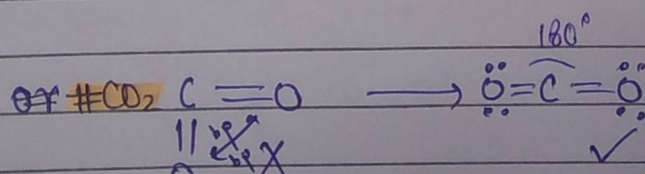
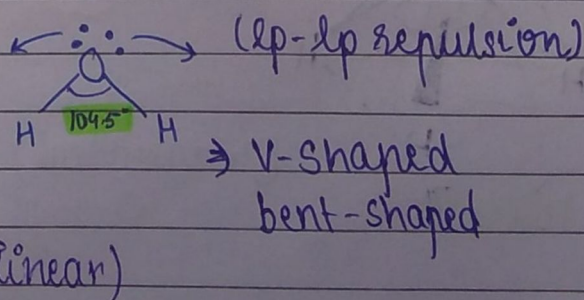
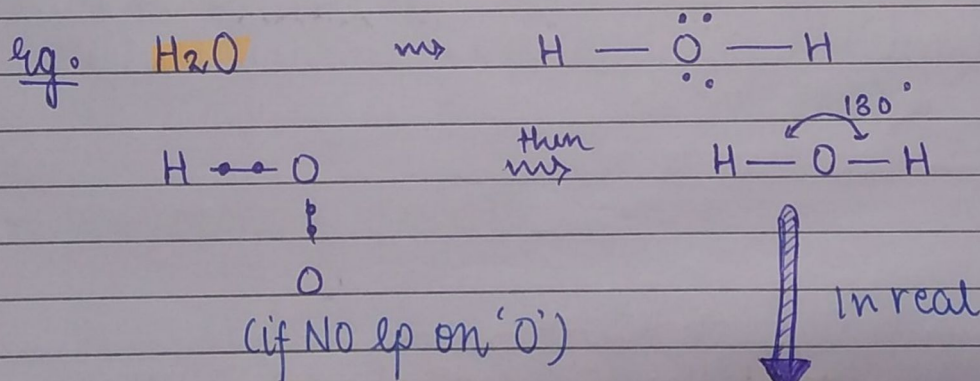
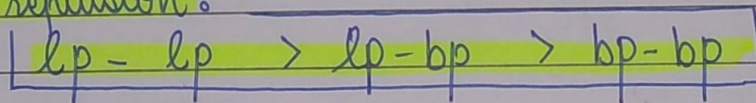
* 'O' with '-ve' charge make single bond.

* VSEPR Theory:

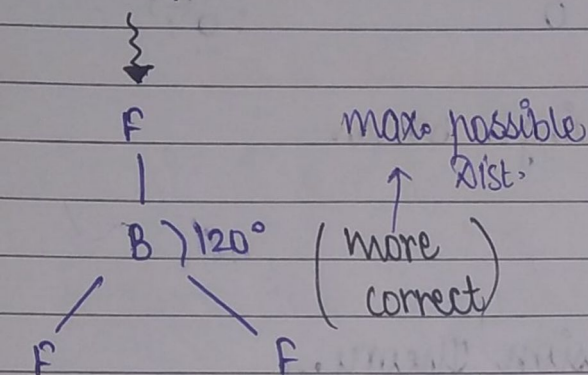
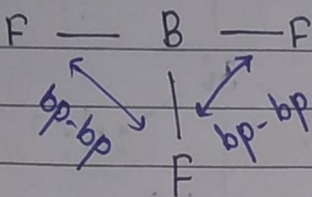
Valence shell electron-pair Repulsion Theory.

* In a chemical species lp e⁻ & bp e⁻ rearrange in such a manner so that there is minimum repulsion amongst them.

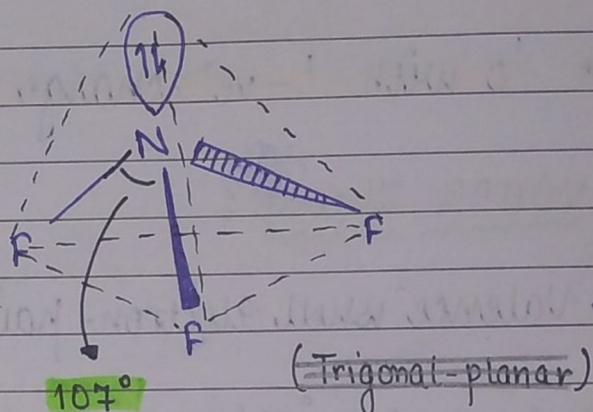
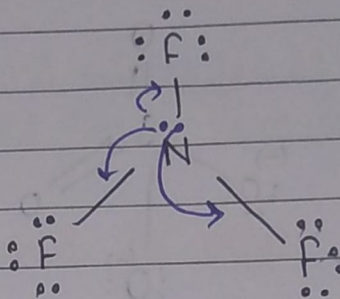
* order of repulsion:



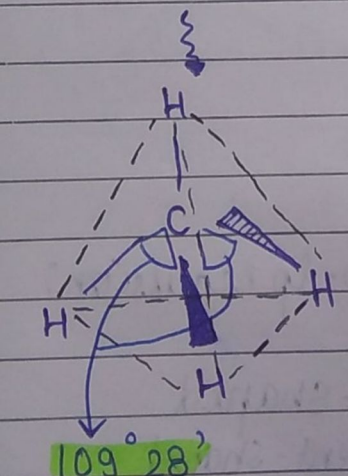
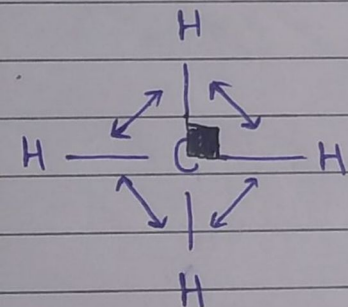
BF_3



NF_3



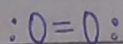
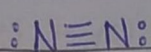
CH_4



* It has '6' $109^\circ 28'$ angles

L-3/15

VALENCE-BOND THEORY (VBT)



- ✓ chemical bond b/w 2 atoms is formed by overlapping of Atomic Orbitals.
- ✓ Higher the extent of overlapping, stronger will be the chemical bond.
- ✓ In each overlapping, max. of 2 e^- are involved with Anti-Parallel spins.

eg. (1) Formation of H_2



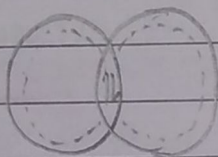
H

$1s^1$



H

$1s^1$



(2) Formation of HCl

$1s^1$

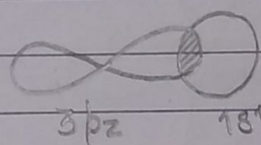
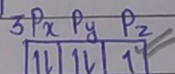
H $\rightarrow$



Cl $\rightarrow$



$3s^2$



(3) Formation of He_2

He :



$1s^2$

He :



$1s^2$

} overlapping of Atomic orbitals is not possible

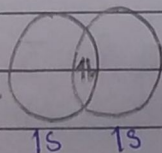
(4) Formation of $[HeH]^+$

$1s^2$

He :



H :



* Head-on overlapping of At. orbitals forms σ -Bond whereas

side-wise or Lateral overlapping of A.Os forms π -bond.

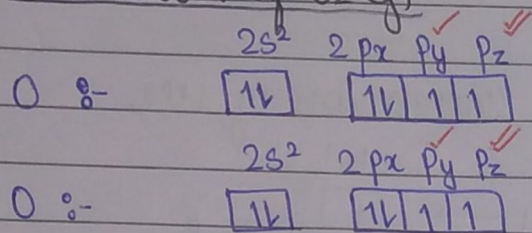
* σ -Bond is stronger than π -bond.

* Formation of π -bond b/w 2 Atoms is possible only when there is σ -Bond b/w them.

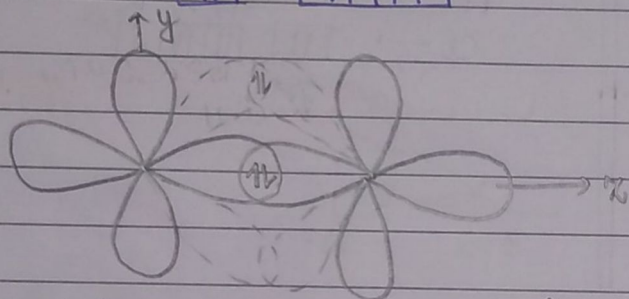
NOTE :- "In $O_2(g)$ Bond order is 2 & Both Bonds are π -bonds"

"In $B_2(g)$ Bond order is 1 & Bond is π -bond."

Formation of $O_2(g)$ $\rightarrow$ overlapping b/w same orbitals



* Acc. to VBT, O_2 should be Diamagnetic, but it is Paramagnetic in Nature.

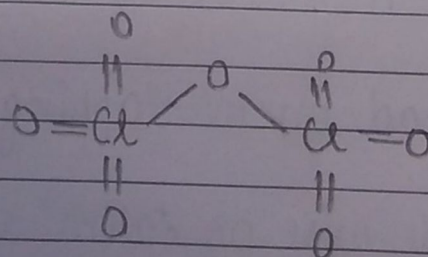


Covalency of an Atom in a chemical species is the Number of covalent Bonds formed by it in the chemical species.

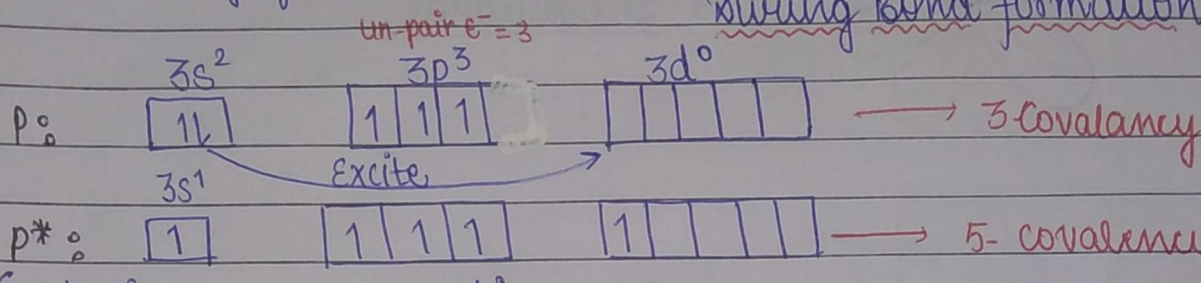
Eg. * $PCl_5 \rightarrow$ covalency of P = 5
 " " Cl = 1

* $PCl_3 \rightarrow$ covalency of P = 3
 " " Cl = 1

* $Cl_2O_7 \rightarrow$ covalency of Cl = 7
 " " O = 2

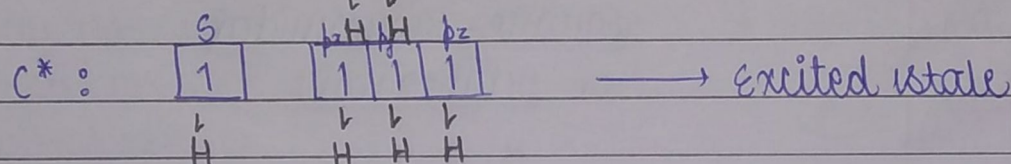
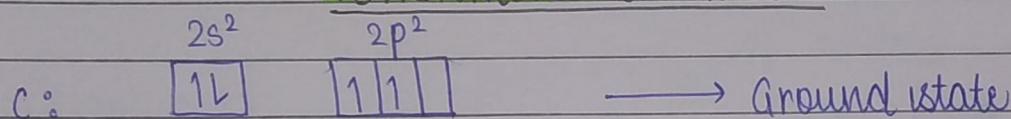


* Covalency of an Neutral Atom = No. of unpaired e⁻ in it during Bond formation

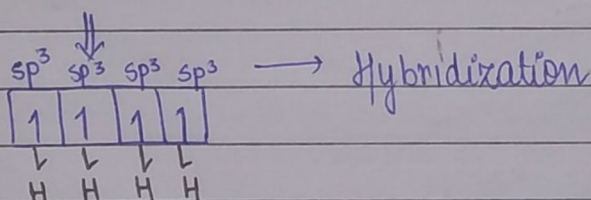


↳ during Bond formation

TETRAVALENCY OF CARBON

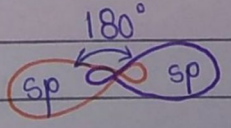
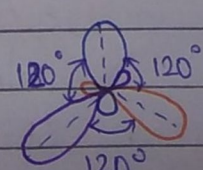


acc. to VBT $\downarrow$ 1st Type Bond $\hookrightarrow$ 2nd Type Bond (But in real, All 4 Bonds are similar)

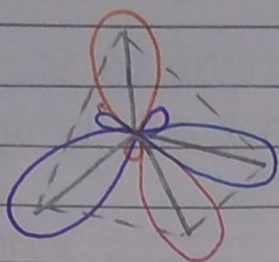


CONCEPT OF HYBRIDIZATION

"The phenomenon of Intermixing of A.O.s of an Atom to form Hybrid orbitals of equal energy and Equal No. of A.O.s intermixed is called HYBRIDIZATION."

TYPE	ORIENTATION OF HYBRID ORBITALS
* sp	 180° — LINEAR
* sp^2	 120° — TRIGONAL PLANAR

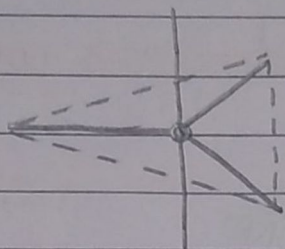
* sp^3



⇒ Tetrahedral

* sp^3d

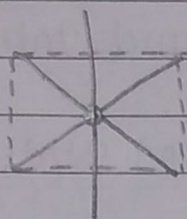
↓
 dz^2



Trigonal-bipyramidal

* sp^3d^2

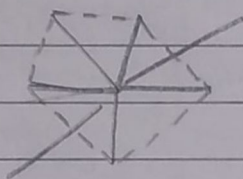
↙ ↘
 dx^2-y^2 dz^2



square-Bipyramidal
or Octahedral

* sp^3d^3

↙ ↘ ↙
 dx^2-y^2 dz^2 dx^2-y^2



Pentagonal-bipyramidal

* dsp^2

↓
 dx^2-y^2



square-Planar

* Finding Hybridization :-

• XeO_2F_2
 $\downarrow$
 $8 - 2 \times 2 - 1 \times 2 = 2 e^-$
 (Valence e^-)

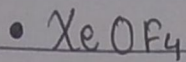
∴ l.p. = $\frac{2}{2} = 1$

Hybrid-orbitals = surrounding + lp atom

= 4 + 1

= 5

↓
 sp^3d

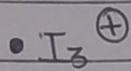
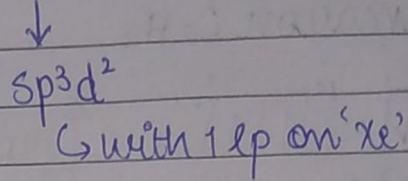


$$\downarrow$$

$$8 - 2 - 4 \times 1 = 2e^-$$

$$lp = 1$$

$$HD = 5 + 1 = 6$$

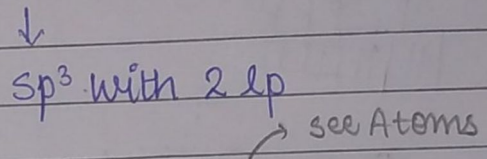


$$\downarrow$$

$$7 - 1 - 1 - 1 = 4e^-$$

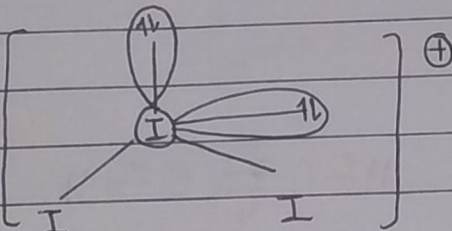
$$lp = 2$$

$$2 + 2 = 4$$



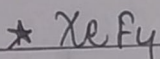
* Orientation / Arrangement of e^- pairs around central atom in

I_3^+ is Tetrahedral. V-shaped or Bent shaped



* shape or Geometry or str. of I_3^+ is Bent or V-shaped

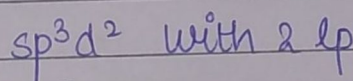
Ques-23/PYQ



$$8 - 4 \times 1 = 4$$

$$lp = 2$$

$$4 + 2 = 6$$

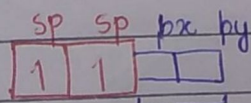
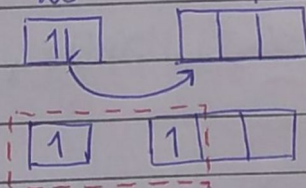
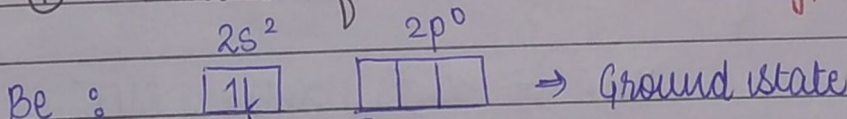


Geometry = square planar
Orientation = Octahedral

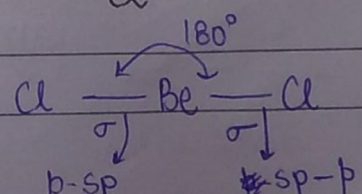
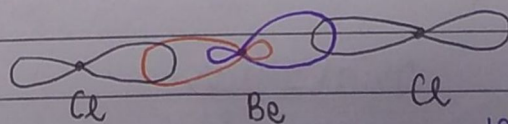
sp-hybridization

Eg ① Formation of BeCl_2

Geometry / shape = "Linear"

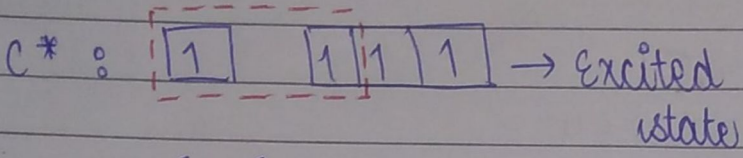
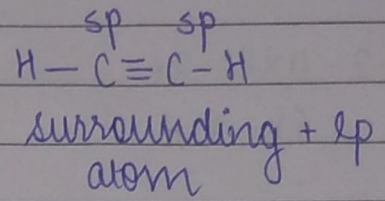
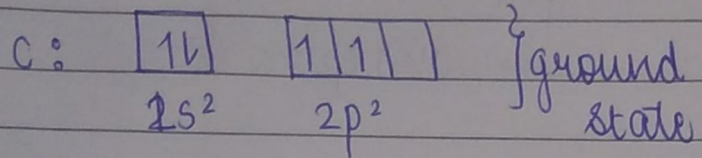


"vacant p-orbital"

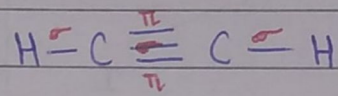
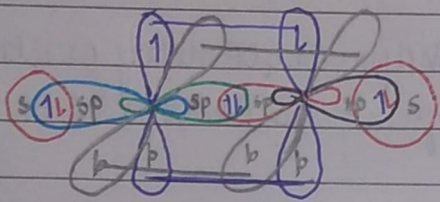
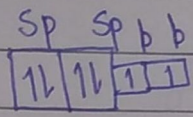


L-4/16

eg. ② Formation C_2H_2

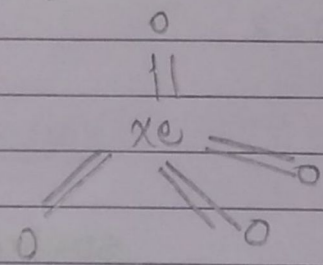
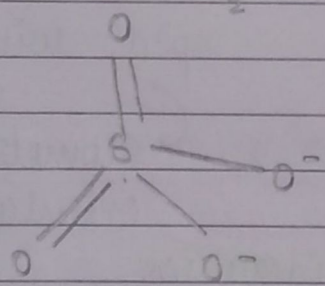
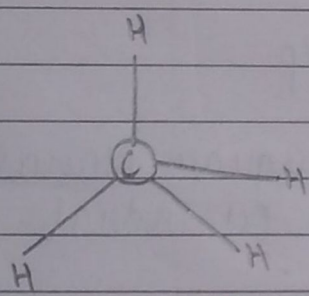
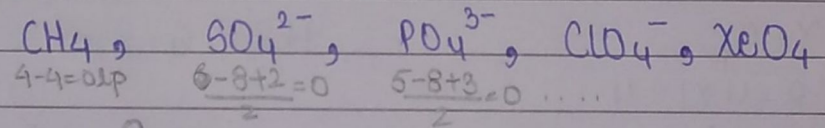


$2 + 0 \Rightarrow 2$
 ↓
 sp



sp^3 → Tetrahedral
 of central Atom

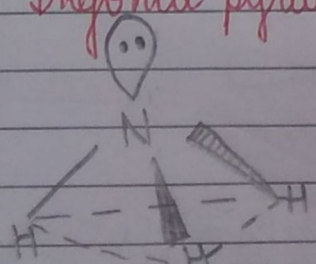
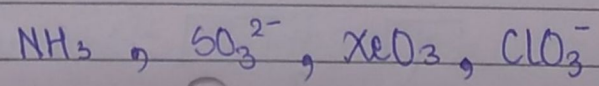
① $sp^3 + 0 \text{ lp}$



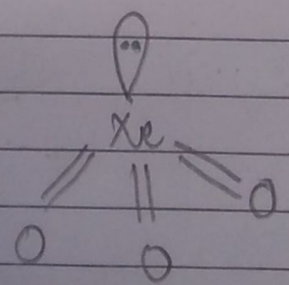
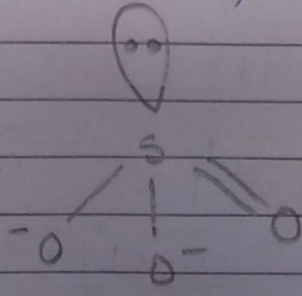
of Hybrid orbital

② $sp^3 + 1 \text{ lp}$

shape / geometry :
 trigonal pyramidal



triangular pyramidal



③ $sp^3 + 2lp$ (on central Atom)

↳ shape / Geometry

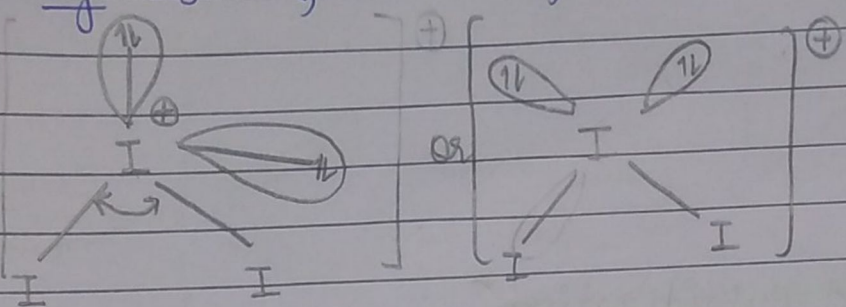
= Bent / V-shaped

(ask str. is not similar to others?)

Eg. I_3^+

ClO_2^-

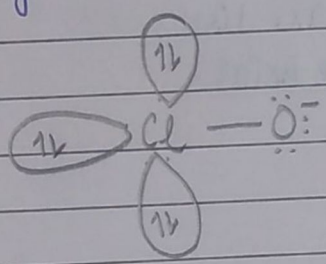
H_2O



④ $sp^3 + 3lp$

If No. of lp on central Atom is 3, then shape / geo. would be Linear

Eg. ClO^-



sp^2 - hybridization

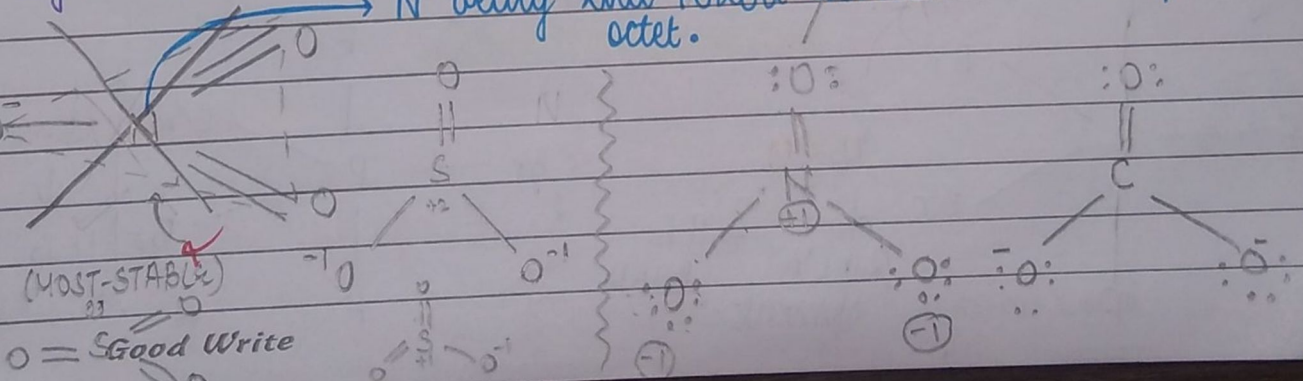
① $sp^2 + 0lp$ (on central Atom)

Geo / shape

↳ Trigonal planar

Eg. CO_3^{2-} , NO_3^- , SO_3

'N' being 2nd period element does not expand its octet.



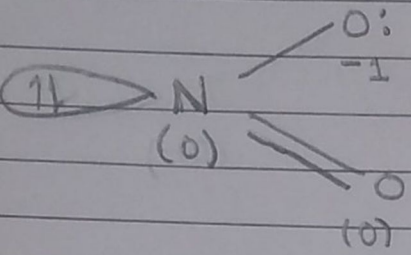
(MOST-STABLE)

o = Good Write

(on central Atom)

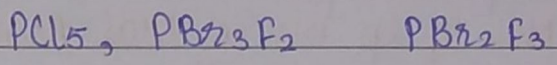
② $sp^2 + 1lp$

Eg: SO_2 , NO_2^-
 $6 - 2 \times 2 \Rightarrow 2e^- \Rightarrow 1lp$ $5 - 2 \times 2 + 1 \Rightarrow 1lp$

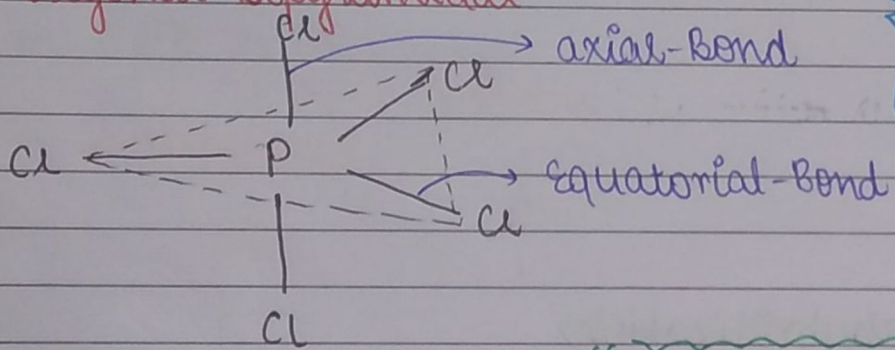


sp^3d Hybridization

① $sp^3d + 0lp$ (on central atom)



Trigonal Bipyramidal

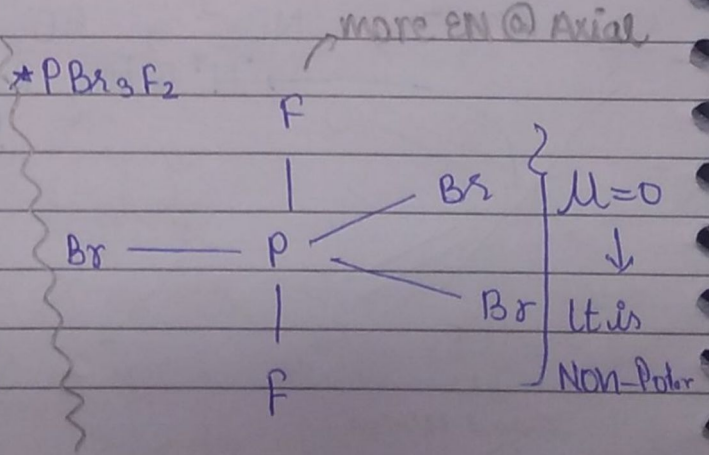
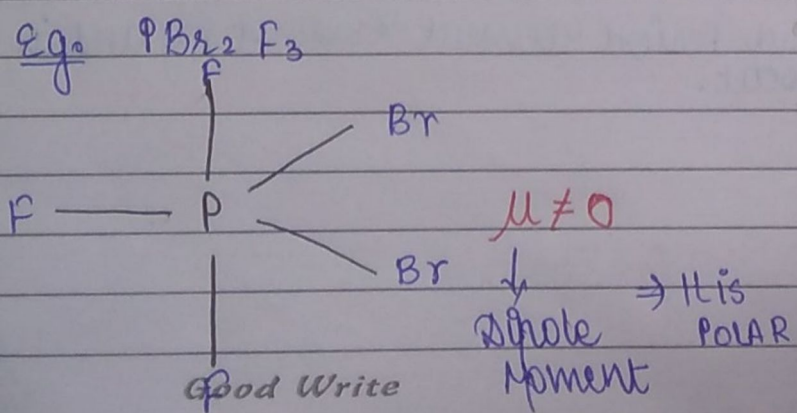


{ NOTE: put more EN atom at max. dist. Here Axial }

* $n(\angle 90^\circ) = 6$
 * $n(\angle 120^\circ) = 3$

* "In sp^3d (PCl_5), axial Bond is longer in length than Equatorial Bond"

* No. of Cl-P-Cl linkages in PCl_5 is : 10

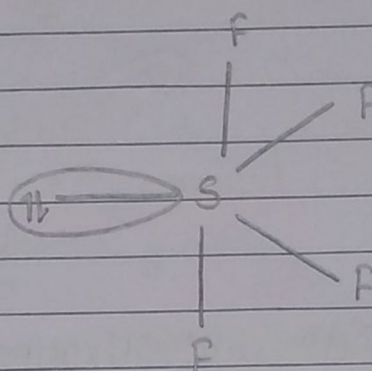
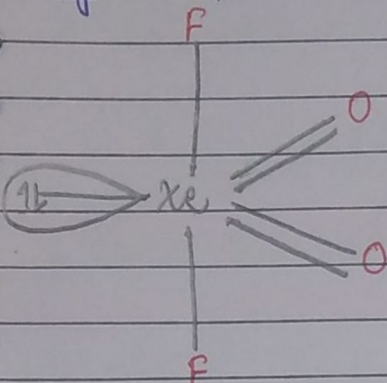


★ $sp^3d + 1lp$

↳ shape / Geometry
see-saw

eg. SF_4

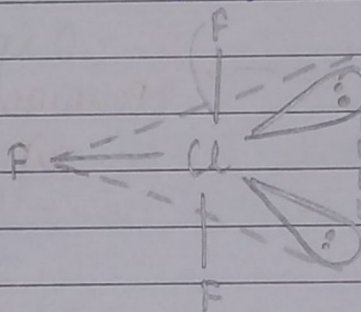
XeO_2F_2



★ $sp^3d + 2lp$

↳ shape / geo
T-shape
(distorted)

ClF_3

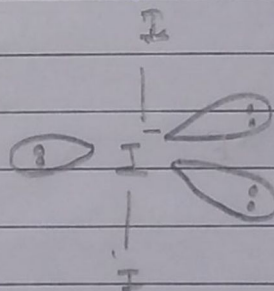
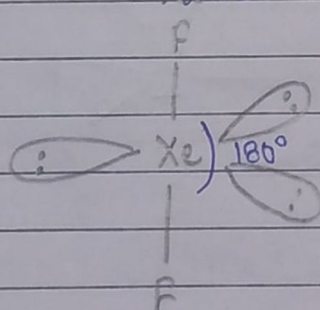


★ $sp^3d + 3lp$

↳ linear

XeF_2

I_3^-

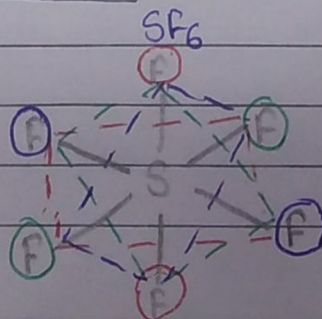


sp^3d^2 hybridization

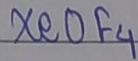
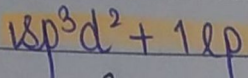
★ $sp^3d^2 + 0lp$

↳ shape / geo
Octahedral or square
bipyramidal

Good Write

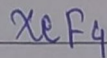
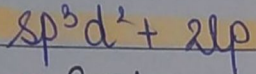
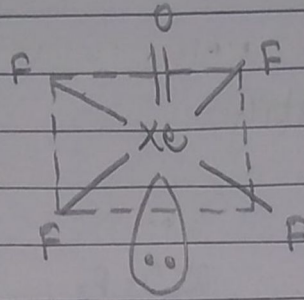


All S-F Bonds
are identical
in SF_6



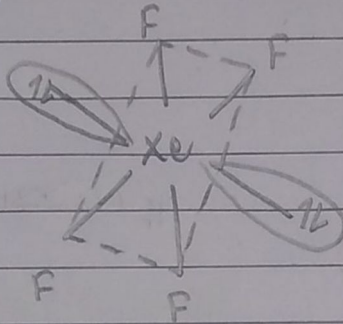
Geo / shape

square pyramidal



Geo / shape

square planar

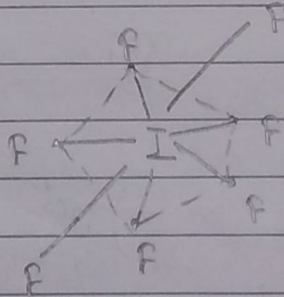
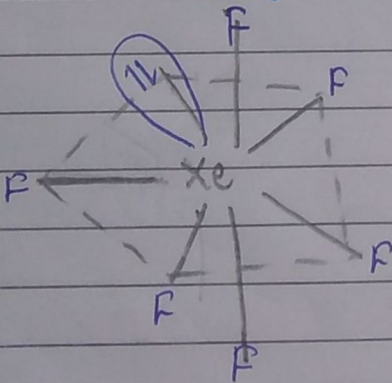
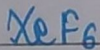

 sp^3d^3 hybridization

1 lp

(Distorted octahedral)

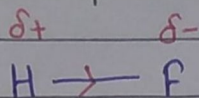
0 lp

(Pentagonal Bipyramidal)



L-5/17

Dipole Moment



Dipole Moment = $q \times d$

* S.I. unit = C-m

* 1 debye (D) = 10^{-18} esu-cm

% Ionic character = $\frac{\mu_{\text{observed}} \times 100}{\mu_{\text{calculated}}}$ → Experimental

$\frac{q \times d}{\text{unit charge}}$ → given
 $\parallel$
 $1.602 \times 10^{-19} \text{ C}$
 $\parallel$
 $4.8 \times 10^{-10} \text{ esu}$

Quesⁿ: μ_{obs} (HF) = 1.78 D & H-F bond length is 92 pm
Cal. % ionic character in H-F

$$\frac{\mu_{\text{observed}} \times 100}{\mu_{\text{calculated}}} = \frac{1.78}{1.60 \times 10^{-19} \times 92 \times 10^{-12}} \times 100$$

REMINDER 
solve the quesⁿ
by putting units

$$\Rightarrow \frac{178}{160 \times 92} \times 10^{19+12+2}$$

$$\Rightarrow \frac{178}{160 \times 92} \times 10^{33}$$

$$\Rightarrow \frac{89}{46 \times 16} \times 10^{32}$$

$$\Rightarrow 1$$

solution

$$\frac{1.78 \times 100 \times 10^{-18}}{4.8 \times 10^{-10} \times 92 \times 10^{-10}}$$

$$\Rightarrow \frac{178 \times 10^{22} \times 10^{-18}}{480 \times 92}$$

$$\Rightarrow \frac{178}{48 \times 92} \times 10^3$$

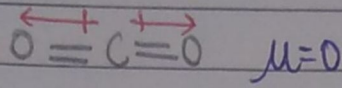
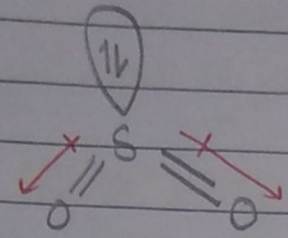
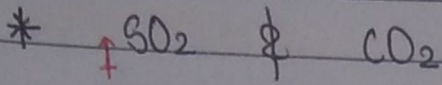
$$\Rightarrow \frac{8900 \times 10^3}{2208}$$

$$\Rightarrow 0.04 \times 10^3 \Rightarrow 40\%$$

Good Write

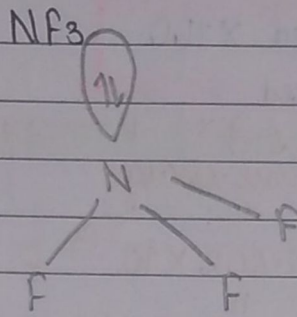
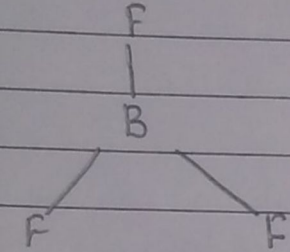
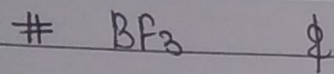
$$\begin{array}{r} 92 \\ 24 \\ \hline 368 \\ 184 \\ \hline 2208 \end{array}$$

$$\begin{array}{r} 46 \\ 3 \ 16 \\ \hline 576 \\ 46 \\ \hline 736 \end{array}$$



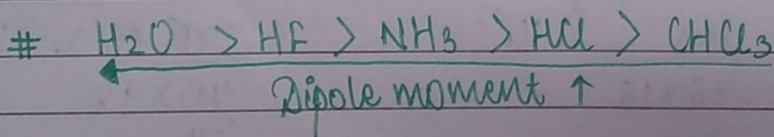
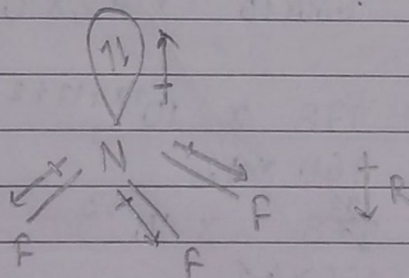
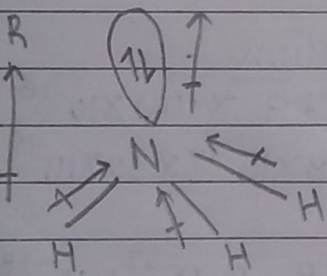
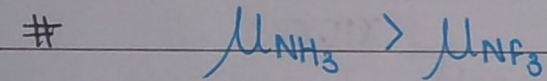
In CO_2 , bonds are polar but CO_2 molecule is Non-Polar.

Polar
i.e. $\mu \neq 0$



$\mu = 0$
Non-Polar

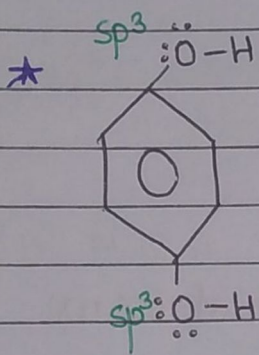
$\mu \neq 0$, Polar



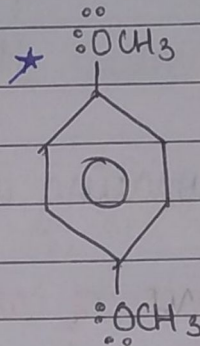
* $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$ $\rightarrow$ Dipole moment

* $\text{CH}_3\text{Cl} > \text{CH}_3\text{F} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$ $\rightarrow$ Dipole moment

* $\text{CH}_3\text{Cl} > \text{CH}_2\text{Cl}_2 > \text{CHCl}_3 > \text{CCl}_4$ $\rightarrow$ Dipole moment

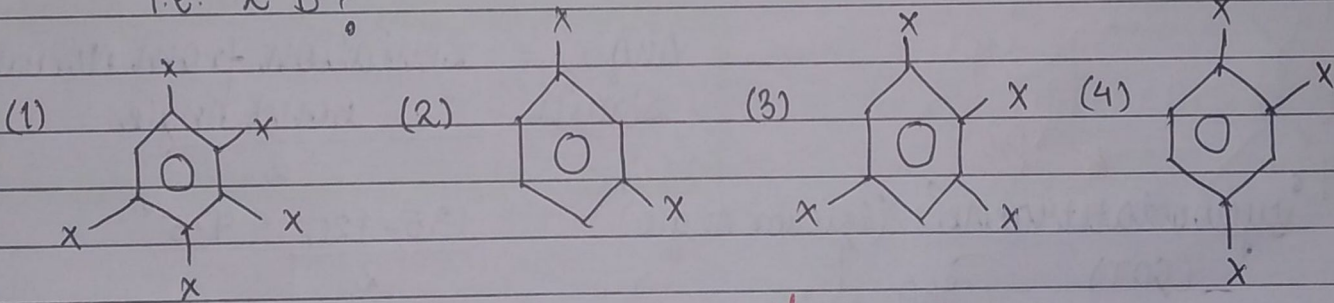


$\mu \neq 0$
"POLAR"



$\mu \neq 0$
Polar

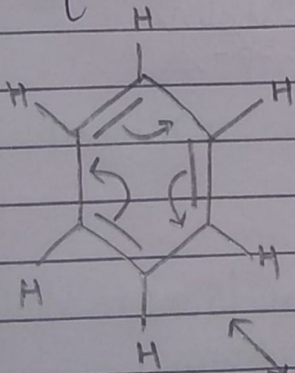
Quesⁿ If a Dipole moment of X is a small Atom. is αD , $[\text{EN}(X) > \text{EN}(C)]$ & Then which of the following has same Dipole moment i.e. αD ?



Ans. All of these.

Hint: R is A @ 120°

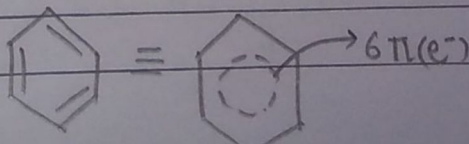
Resonance



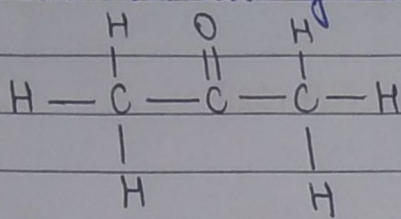
$\text{C}-\text{C} \Rightarrow 154 \text{ pm}$
 $\text{C}=\text{C} \Rightarrow 133 \text{ pm}$

* In Benzene All C-C Bond lengths are Equal i.e. 139 pm .

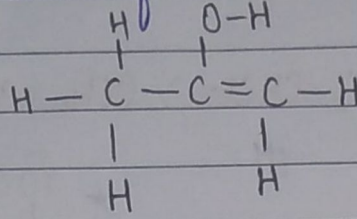
Good Write



- In order to explain, properties of a molecule we draw its various str. called **RESONATING STR. or CANONICAL FORM**
- In all resonating str. position of atoms should be fixed.



(I)

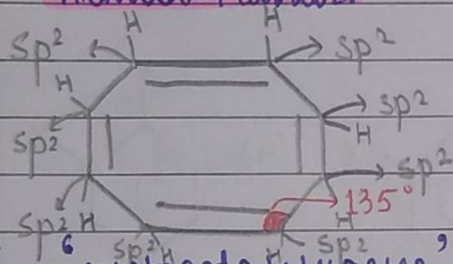


(II)

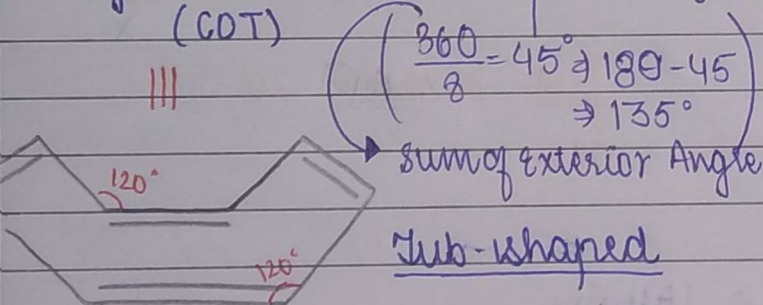
'I' & 'II' are not resonating str. to each other.

- There is no real existence of canonical forms, actual str. is **Resonance Hybrid str.**

- For resonance to be significant, molecule must be **PLANAR or Almost Planar.**



cyclooctatetraene (COT)



Tub-shaped

$$\text{Angle} = \frac{\text{Deviation from Normal Strain}}{\text{Bond Angle}}$$

$$= \frac{135 - 120}{2} = 7.5^\circ$$

get to know by hybridisation of carbon (here sp^2 - 120°)

- Resonating str. having max^m No. of atoms with formal charge zero or close to zero will be most stable str.

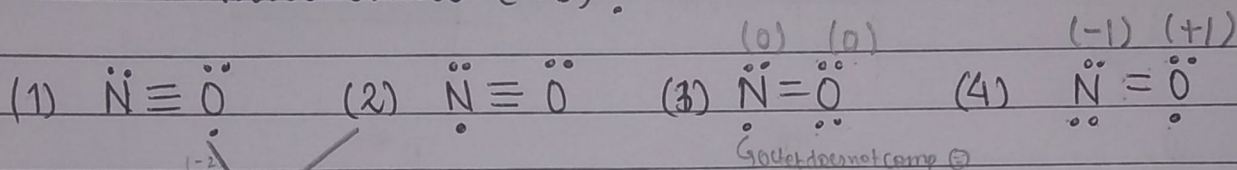
- Resonating str. having -ve charge on E.N. atom is more stable than the str. having -ve charge on less E.N. atom.

Resonance energy — always Neg.

★ $\left| \frac{\text{Resonance energy}}{\text{stability}} \right| \propto$

★ Higher the No. of resonating str., higher will be stability

Quesⁿ: Identify the most stable resonating structure of Nitric oxide (NO)?



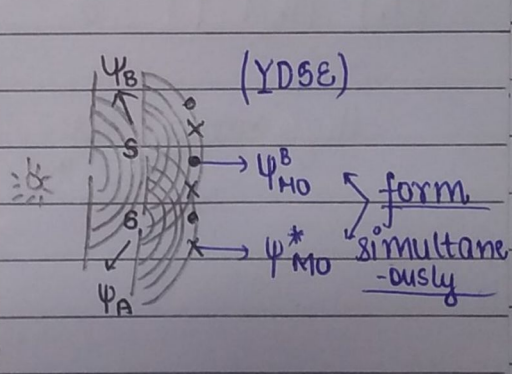
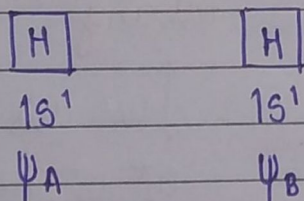
octet is expanded
(str. wrong)

Ans. opt (3)

(elements of 2nd group does not expand its octet)

Molecular Orbital Theory — MOT is based on LCAO approximation

Acc. to LCAO approximation atomic orbitals of different atoms combine to form molecular orbitals



$$\psi_A \pm \psi_B = \psi_{M.O.}$$

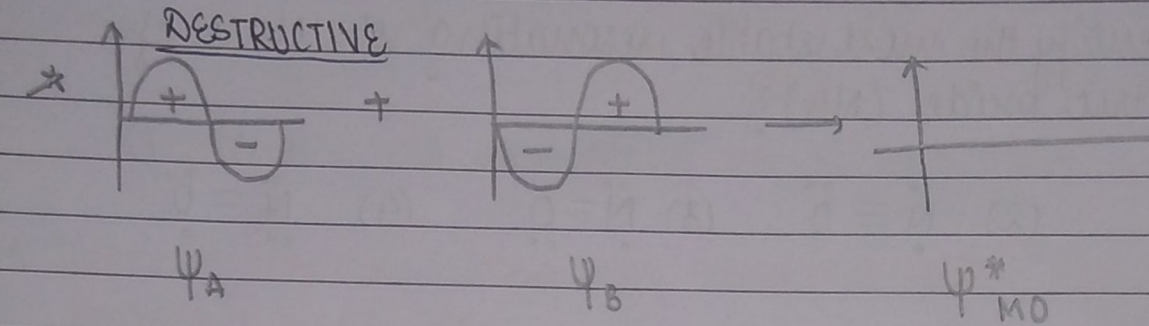
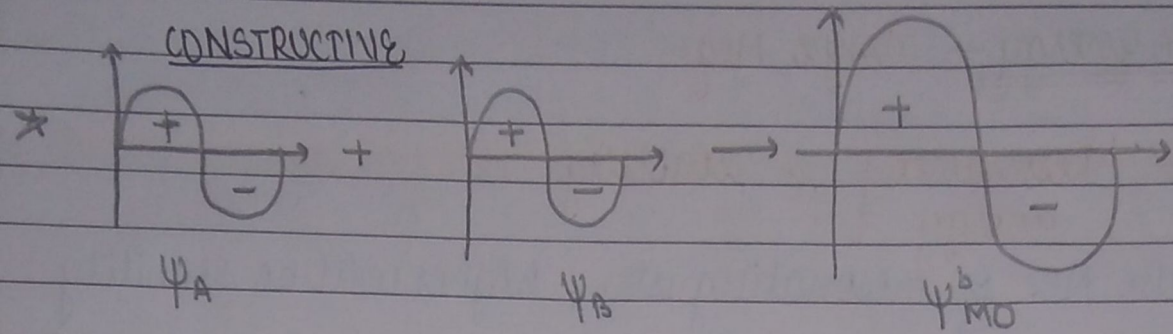
$$\rightarrow \psi_A + \psi_B = \psi_{M.O.}^b$$

$$\rightarrow \psi_A - \psi_B = \psi_{M.O.}^*$$

★ ψ_A & ψ_B are Atomic orbital wave function

★ ψ_{MO}^b = Bonding molecular orbital wave function

★ ψ_{MO}^* = Antibonding molecular orbital wave function



1s 2s $2p_x \ 2p_y \ 2p_z$

M.O. $\sigma_{1s}, \sigma_{1s}^*, \sigma_{2s}, \sigma_{2s}^*$

1↓ ↑↓ ↑↓ ↑ N

1↓ ↑↓ ↑↓ ↑↓ 0



High energy diff.

→ with 2s-2p mixing

$\pi 2p_x = \pi 2p_y, \sigma 2p_z, \pi^* 2p_x = \pi^* 2p_y$

↑ use this
if N_2^-, N_2^{2-}

B_2
 C_2
 N_2

$\pi 2p_x = \pi 2p_y, \sigma$

$\sigma 2p_z, \pi 2p_x = \pi 2p_y, \pi^* 2p_x = \pi^* 2p_y$

→ without 2s-2p mixing

$\sigma^* 2p_z$

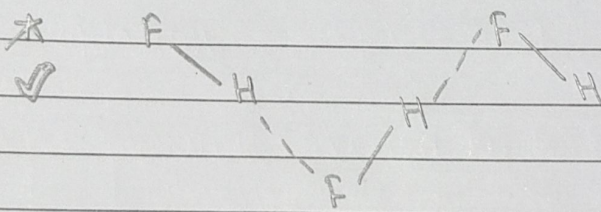
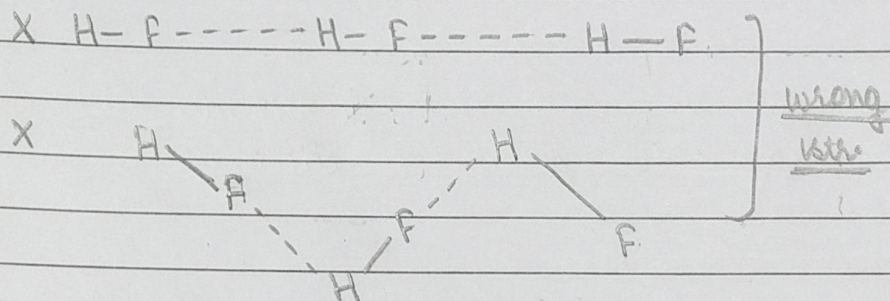
↑ use this

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

O_2
 F_2
 Ne_2

HYDROGEN-BONDING

* Hydrogen Bonding energy of $\text{H-F} > \text{H}_2\text{O}$



→ VSEPR
→ Bonding @ 'F' (due to lp-lp repulsion)
→ more No. of H-bonds

* Boiling Point of $\text{HF (l)} < \text{H}_2\text{O (l)}$
(20°C) (100°C)
19.8°C

* ~~Boiling Point order~~

- $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$ → H-Bonding order
- $\text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te} < \text{H}_2\text{O}$ → BP / MP

• $\text{HCl} < \text{HBr} < \text{HI} < \text{HF}$ → BP * All are gases @ Room Temp.

• $\text{HCl} < \text{HBr} < \text{HF} < \text{HI}$ → M.P.

molecular mass H-Bonding molecular mass

- $\text{PH}_3 < \text{AsH}_3 < \text{NH}_3 < \text{SbH}_3 < \text{BiH}_3$ → BP
- $\text{PH}_3 < \text{AsH}_3 < \text{SbH}_3 < \text{NH}_3 < \text{BiH}_3$ → MP

→ molecular-mass
→ Intramolecular force of Attraction