

* non planar -
190 → 12

MOT →

Draw back of VBT →

It does not explain -

(i) Paramagnetic behaviour of O_2

liq O_2 → pale blue colour

(ii) existence of odd electron species.

(iii) Fractional bond order.

(iv) ionisation energy of $O_2 < O$, $N_2 > N$

(v) B_2 & C_2 having only π bonds.

(vi) CO BO = 3, $CO^+ \cdot BO > 3$

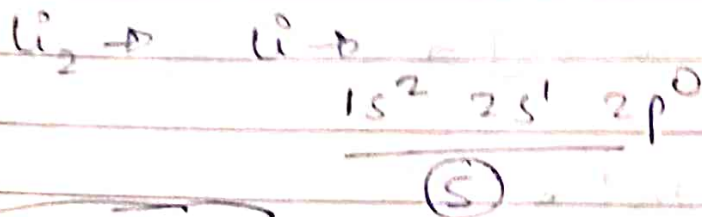
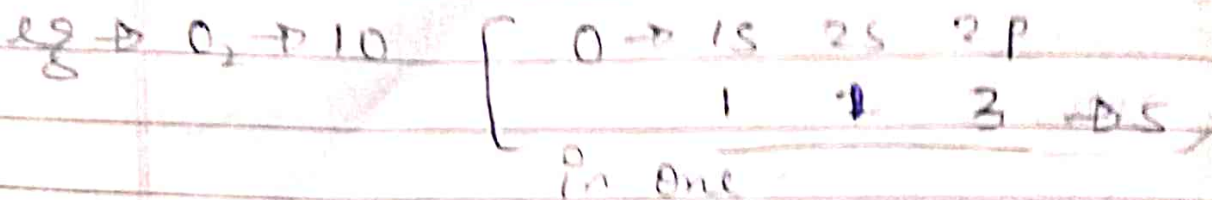
(vii) Colour of halogen

* Molecular Orbital theory →

(i) As electron in an atom present in electronic atomic orbital & in molecule present in molecular orbital.

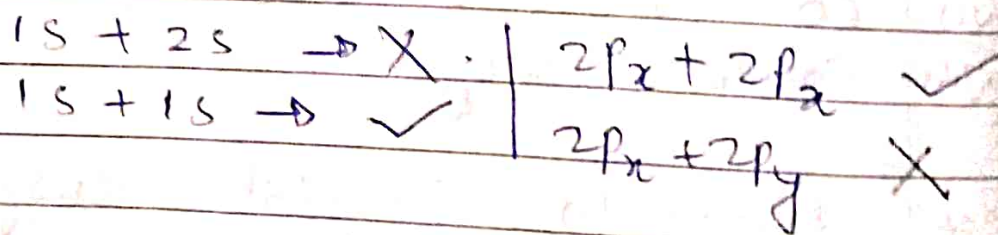
(ii) All atomic orbitals losses their

identify and form new molecular orbital in same number



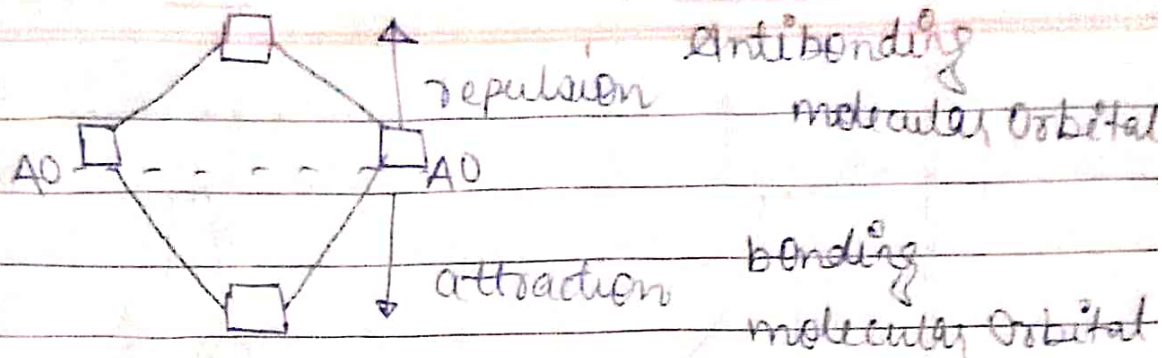
\Rightarrow almost same energetic atomic orbitals participate in mixing.

\Rightarrow molecular orbitals can be differ in shape, size, orientation, energy depends on atomic orbitals which participate in bonding.



$\Rightarrow e^-$ are filled in these molecular orbitals by $(n+1)$ Hund's rule & Pauli

\Rightarrow Sum of energy of two AO = two MO

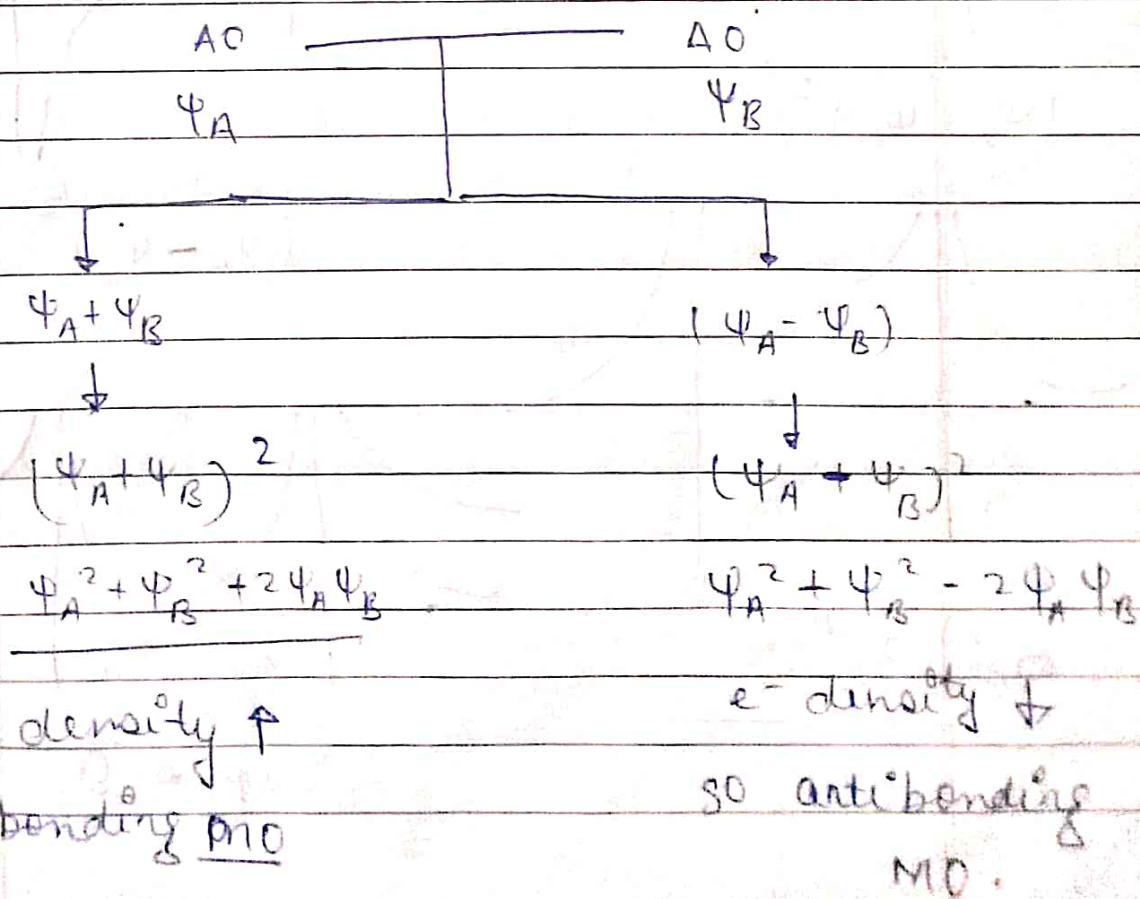


* Atomic orbitals are molecules orbital are polycentric (two nucleus or more than two)
linear combination of atomic orbitals →

LACO model.

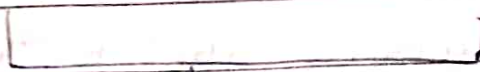
e^- → Dual nature

two atomic orbital →



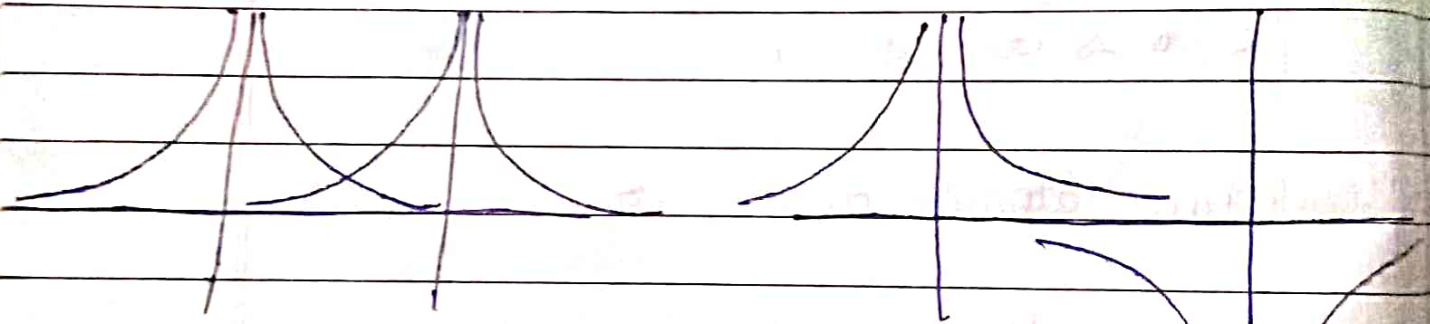
$\psi_A (1s)$

$\psi_B (1s)$



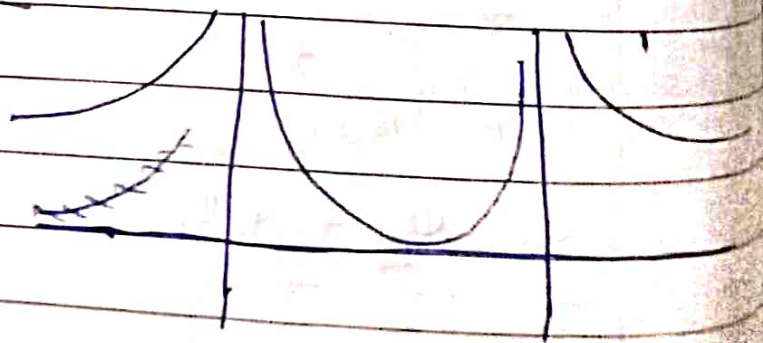
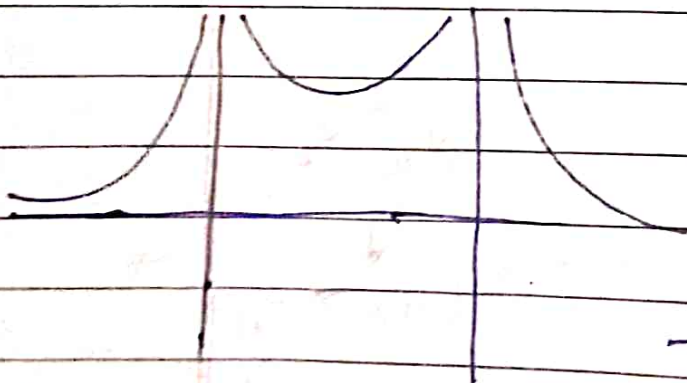
$\psi_A + \psi_B$
(constructive)

$(\psi_A - \psi_B)$
(destructive)



$(\psi_A + \psi_B)^2$

$(\psi_A - \psi_B)^2$

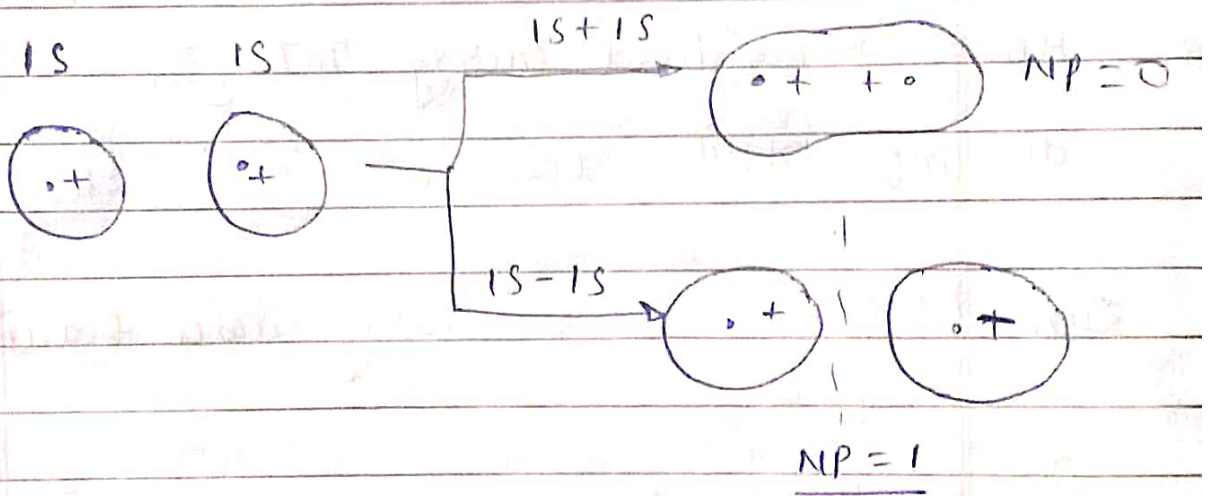


attraction

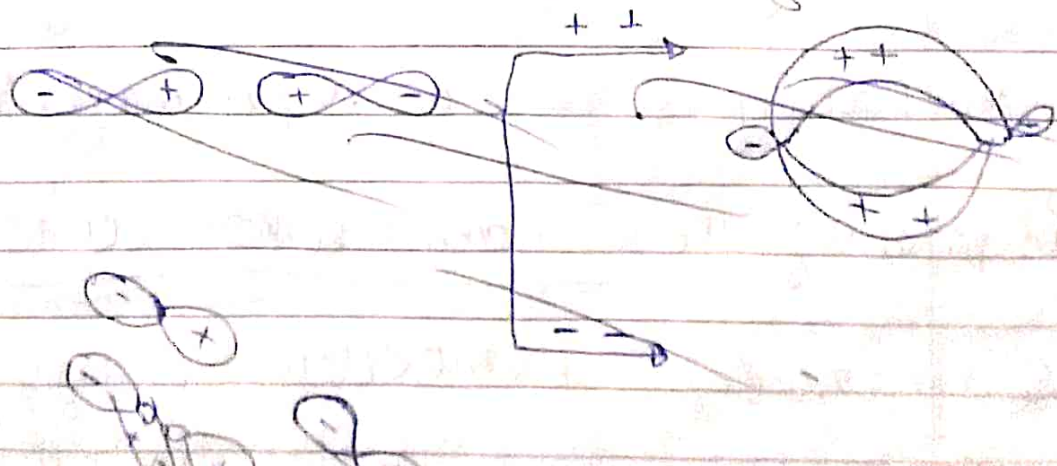
repulsion

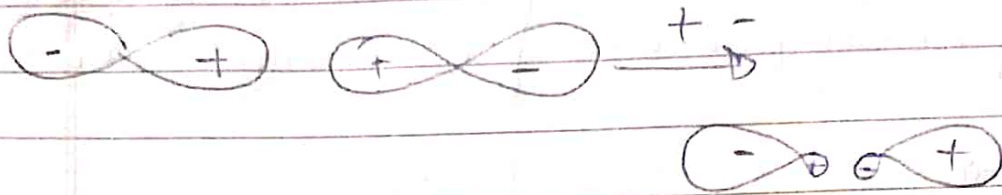
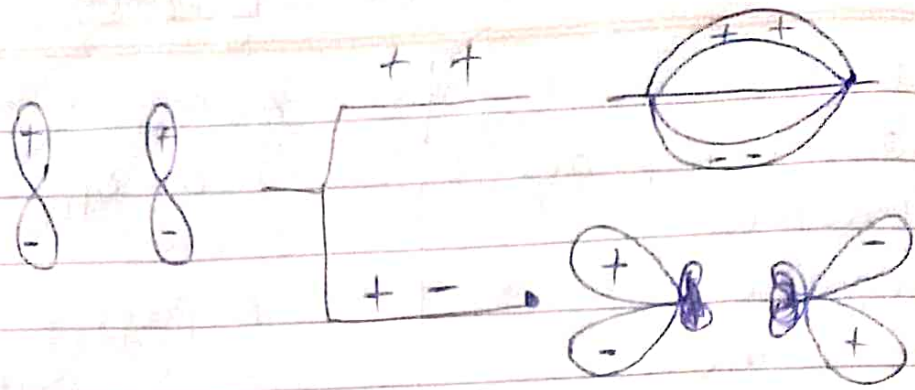
$\sigma_2, f_2 \rightarrow \text{in phase}$
 remaining $\rightarrow \text{one}$

BMO	ABMO
\rightarrow AO in same phase	AO in opposite phase
\rightarrow constructive	destructive
\rightarrow attraction	repulsion
\rightarrow energy $<$ AO	energy $>$ AO
\rightarrow stability $>$ AO	stability $<$ AO
\rightarrow if nodal plane = x	if the nodal plane $x+1$
name \rightarrow σ, π, δ	name $\rightarrow \sigma^*, \pi^*, \delta^*$



centre of symmetry about phase \rightarrow grade sign





HOMO \rightarrow Highest energy भरत हुआ
 की MO जिसमें last e^- जाता है

LUMO \rightarrow Lowest energy wala having space.

की MO जिसमें New electron enter करे.

SOMO \rightarrow singly occupied MO

MO having single $e^- \rightarrow$ paramagnetic

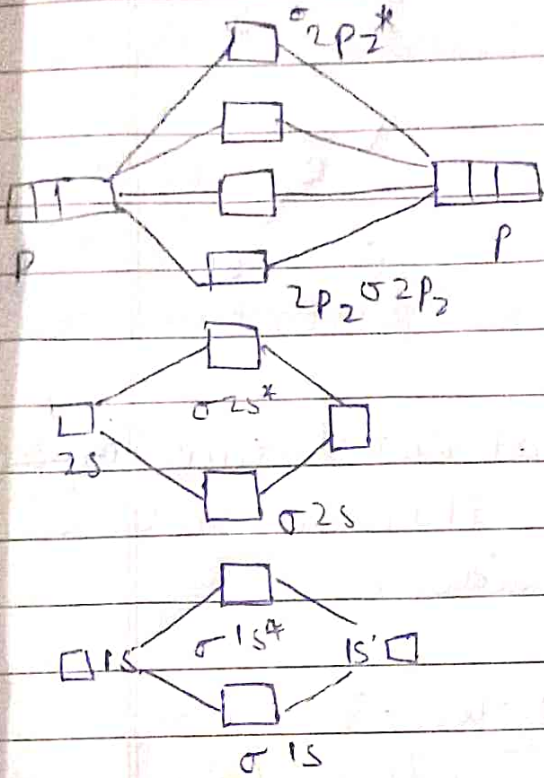
in paramagnetic = HOMO = SOMO = LUMO

Diamagnetic - HOMO < LUMO energy

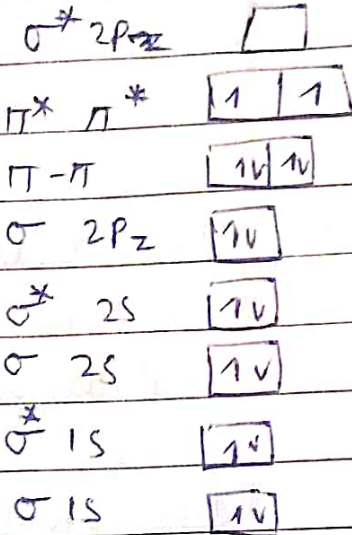
σ stronger than π

species.

Energy diagram for O_2 , F_2 , N_2 & their charge \uparrow



$O_2 \rightarrow$



$O_2 \rightarrow$ paramagnetic.

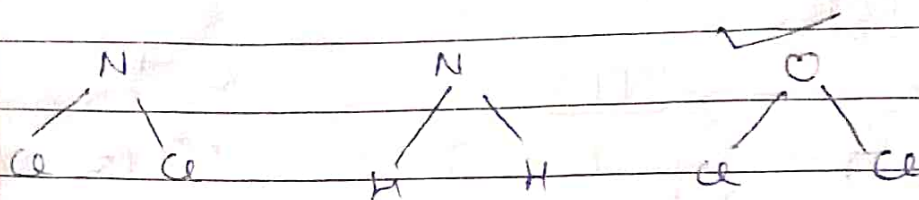
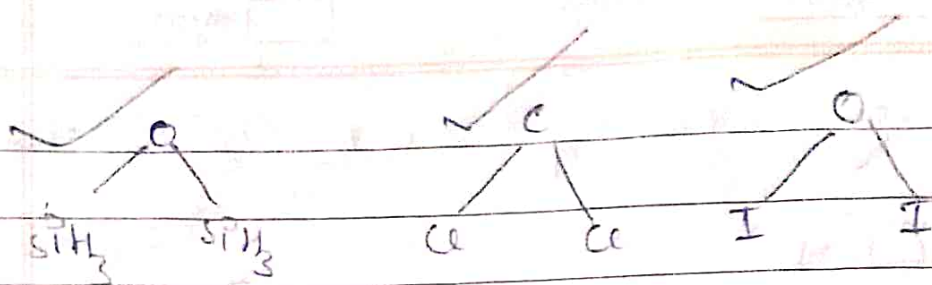
HOMO = LUMO = SOMO = π^*

Case two \rightarrow when type is same \rightarrow SN \rightarrow same

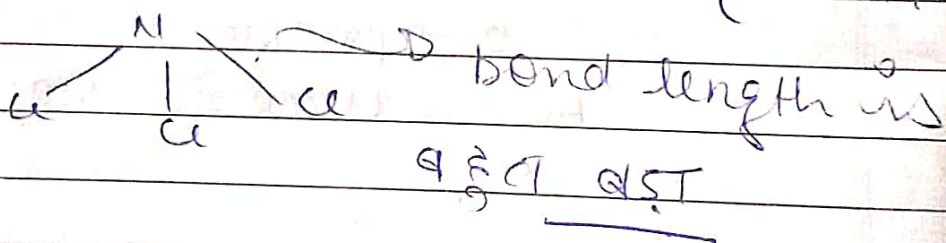
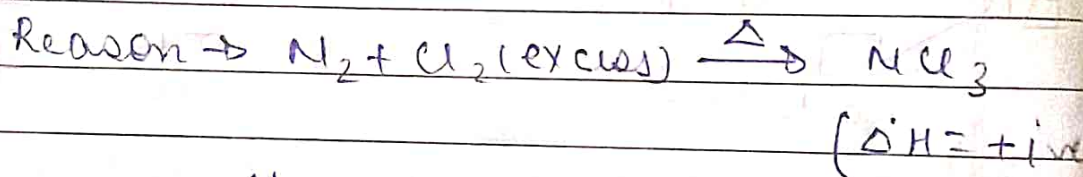
\rightarrow molecule \rightarrow sec molecule have/has drago's rule
 \rightarrow steric hinderance (steric hinderance repulsi

loan pair - loan pair
 repulsion

\rightarrow when C & O having
 at least two large group/atom
 like $\rightarrow C / Br / I / R /$ silane group.



→ In case of 'N' → at least two $\text{Cl}/\text{Br}/\text{I}$ is present then no steric hindrance is considered.

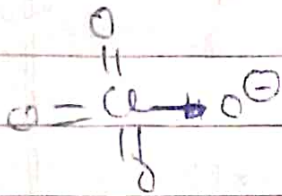
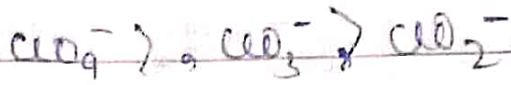


among all trihalide of N only NCl_3 is stable.

* When 'N' is central atom at least two R/silane creates steric hindrance.

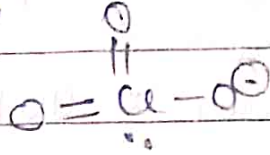
Note → NH_3

(iii) Bond order & bond angle



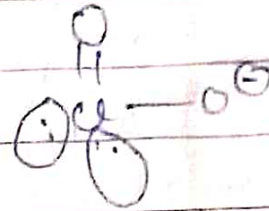
(i)

$B = \underline{1.75}$



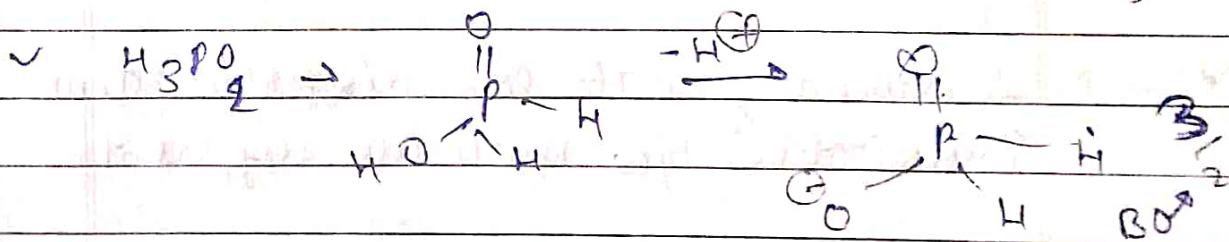
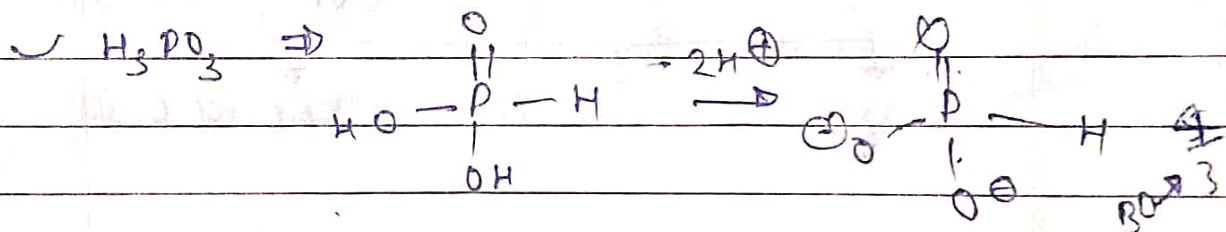
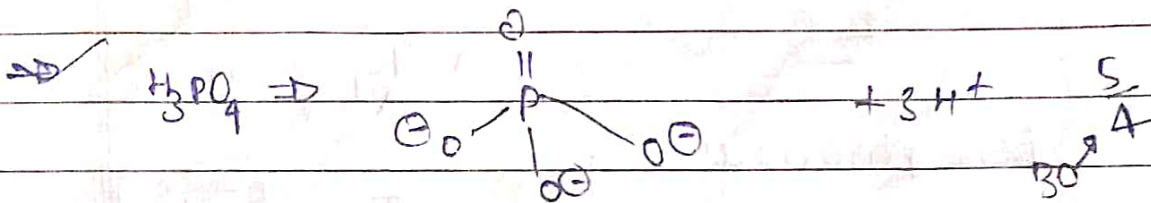
(ii)

1.66

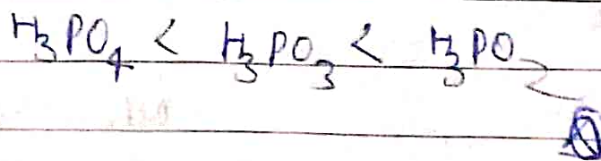


(iii)

1.5



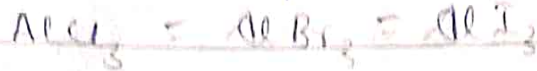
Hence \rightarrow angle \rightarrow



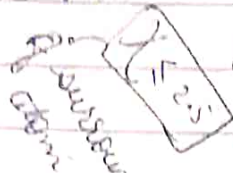
in other the angle is 90

(III)

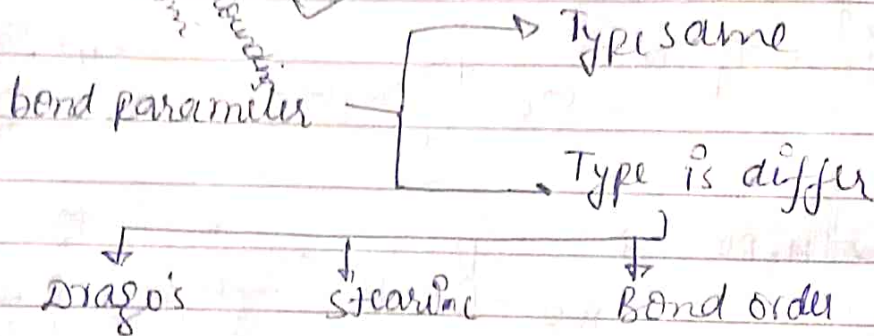
(IV) Surrounding with central is same



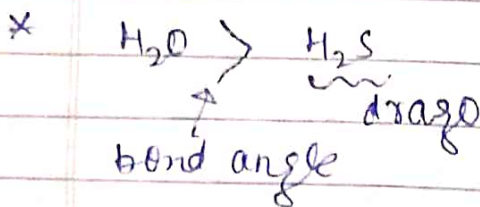
Drago's rule → CA → 3d block



SN = 4



(V) → Surrounding with CA = different and investigation b/w molecule different.



α $S > O$

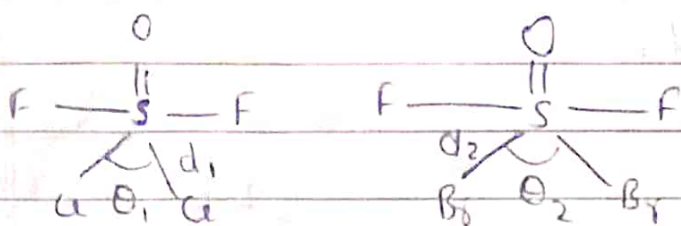
$PF_3 > PH_3$ drago's rule

$OCF_2 > H_2O > OF_2$

steric hindrance.

$SF_2 > H_2S$ drago's rule.

in trigonal bipyramidal more electronegative atom is at axial position.



$\beta_2 > \beta_1$ α

$(d_1 \& d_2) \neq \alpha$ { Ist mind on shell and the electronegativity }

Bent's rule \rightarrow

Type same

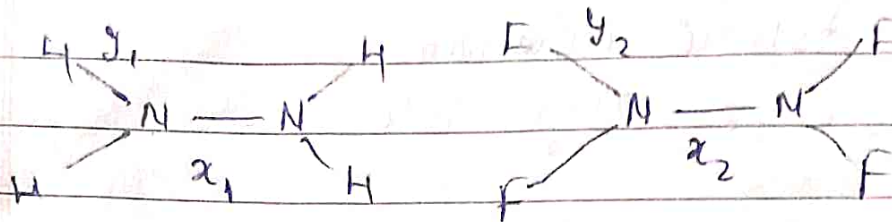
\rightarrow BO = same

sp² surround w/ot CA = differ. but in investigation is same.

Bent's rule suggest more electronegative atoms or group occupies more % p / less s⁺ charact.

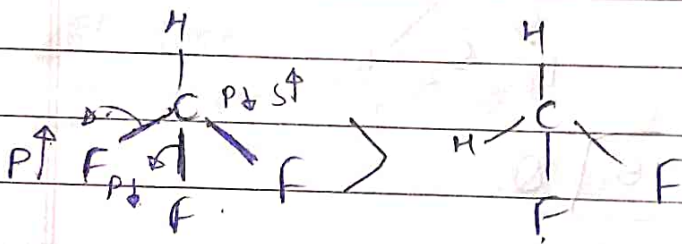
for finding bond length if shell no is same then only use E.N factor.

** \uparrow bond length more



$$\alpha_1 > \alpha_2$$

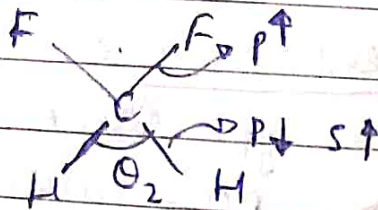
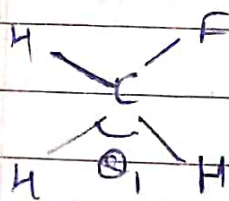
$$\gamma_2 > \gamma_1$$



Bent's rule

3B: $\angle CFC$

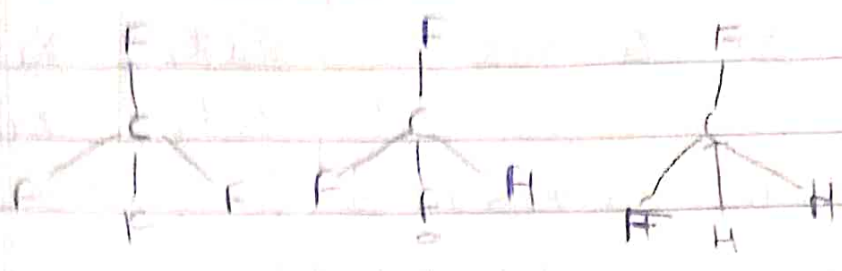
50%



$$\theta_2 > \theta_1$$



$$H = 2:1$$



F → 4p = 25% 3p = 33-33% 2p = 50%

Q₁ > Q₂ > Q₃

- Q. Species like PCl_5 , PF_5 exist but not PH_5 -
 " " SF_6 exist but not SH_6
 " " XeF_4 exist but not XeH_6
 " " SF_4 exist but not SH_4

repulsion dominant → steric hindrance

d orbital contraction because due to F bonded with S which creat δ+ charge on S atom due to which d orbital contraction happen so.

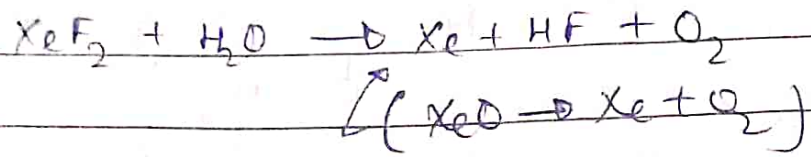
$\text{SX}_6 = (\text{x} = \text{Cl} | \text{Br} | \text{I})$
 $\text{SiX}_6^2- = (\text{x} = \dots)$
 $\text{PX}_6^- = (\text{Br} | \text{I})$
 $\text{BX}_4^- = (\text{Cl}^-, \text{Br}^-, \text{I}^-)$

→ lone pair-repulsion
 $\Delta(\text{XeF}_3^-)$ does not exist
 → +ive charge generate which lower the energy and creat attraction

density \rightarrow X



XeF_2	XeO
XeF_4	XeO_2



dipole moment \rightarrow

quantitative

Dipole moment is a measurement to know the extent of polarity

\rightarrow It is defined as product of charge and distance b/w them. It is a vector quantity and direction is from +ive to -ive.

$\mu = \text{charge} \times d$

Unit = coulomb-meter
 esu-cm
 (c.g.s)

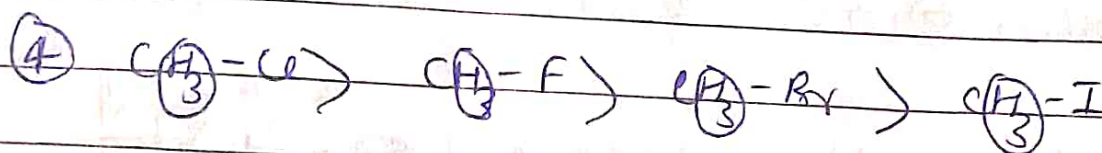
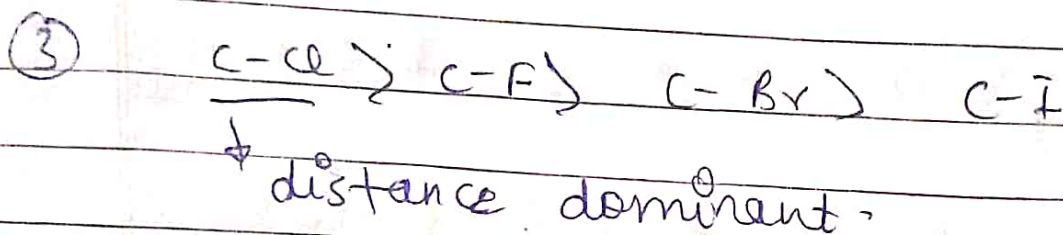
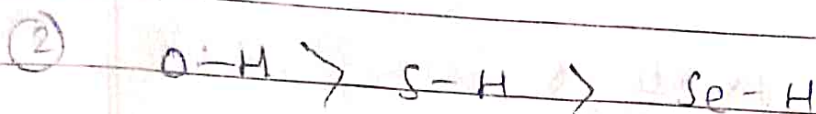
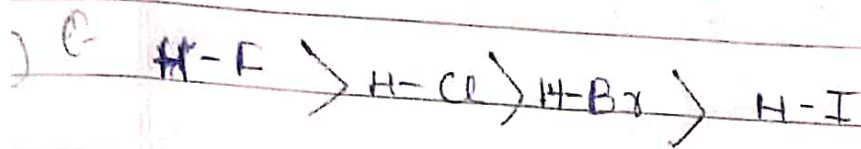
Debye (unit).

$1D \rightarrow 10^{-18} \text{ esu-cm}$
 $= 3.3 \times 10^{-30} \text{ coulomb-meter}$

Note \rightarrow in dipole moment charge dominant over distance. except (c-c) (distance dominant).

dipole moment order →

relate dipole moment
with
polarity



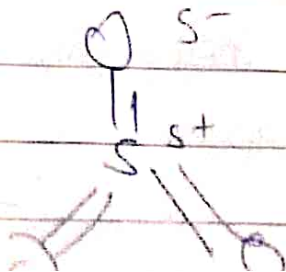
→ if more than one dipole moment is present in molecule.

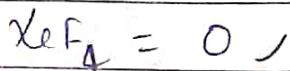
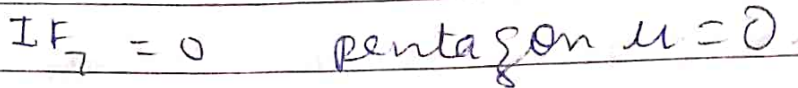
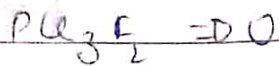
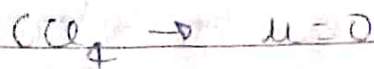
$$\mu_r = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta}$$

✓ Case No 1 → when surrounding are same w.r.t. central atom or symmetric



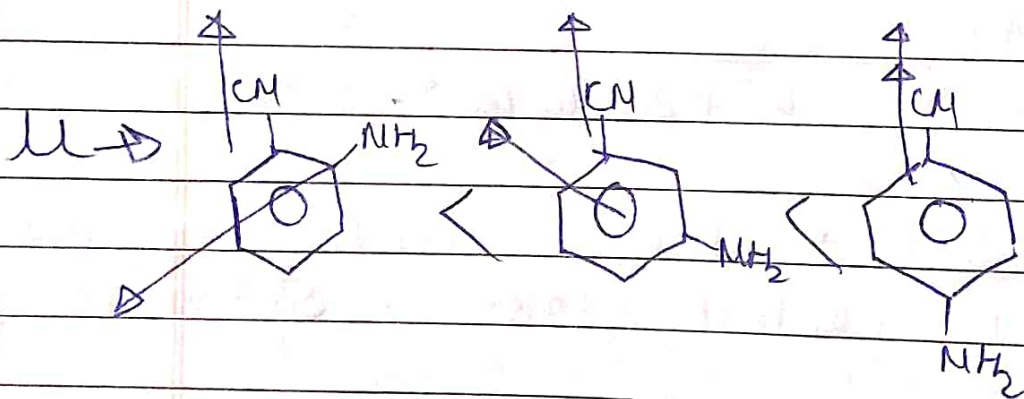
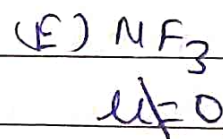
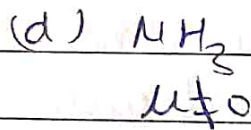
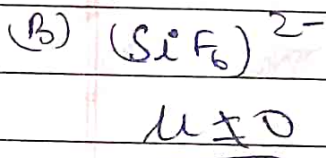
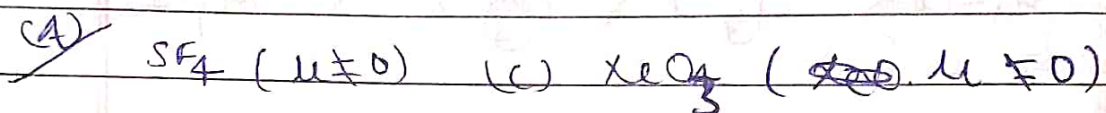
→ bonds are polar and molecule is non-polar.





molecule

Q. Select ~~correct~~ ^{correct} option in terms of μ -



Application of dipole moment

% of ionic character = $\frac{\mu_{exp}}{\mu_{theoretical}} \times 100$

a % of Ionic character in HCl molecule having bond length of 1.02 \AA and observed dipole moment is 1.27 D .

$$\mu_{\text{theoretical}} = 1.67 \times 10^{-19} \times 1.02 \times 10^{-10}$$

$$\Rightarrow 1.632 \times 10^{-29} \text{ D}$$

$$\frac{1.27 \times 3.3 \times 10^{-30} \times 10^0}{1.632 \times 10^{-29}}$$

$$1.632 \times 10^{-29}$$

$$\Rightarrow \frac{1.27 \times 33}{1.632} \Rightarrow 25.68\%$$

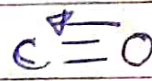
*



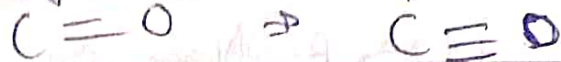
$\mu_{\text{theor}} > \mu_{\text{obs}}$



theoretical



observed

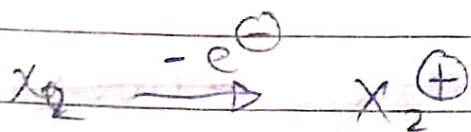


→ gerade are defined for homonuclear symmetrical

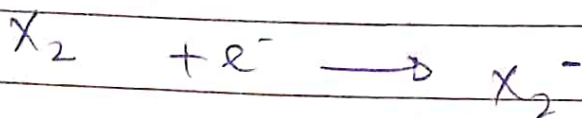
trick → nodal plane → even

ungerade → nodal plane → odd

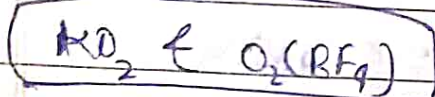
$$\frac{\text{no of proton}}{\text{no of } e^-} \propto \text{IE} \uparrow$$



BO n $n+0.5 \rightarrow$ oxidation



BO n $n+0.5$ reduction



Molecular energy level for Hetero-nuclear species \rightarrow

like - CO | NO | NO⁺ | CO⁺ | HF | NH₃⁺ etc.

\rightarrow every heteronuclear species undergo s-p mixing, irrespective of no of protons. (H-F) NO

s-p mixing s-p mixing

\rightarrow have unique molecular energy level

Some parameters of Heteronuclear species like NO can be predicted using generation of Homonuclear.

NO \rightarrow will follow sp mixing.

IE \rightarrow N > O > NO

NO₂⁺ > NO⁺ > N > O > NO > NO⁻ > NO₂⁻

NO undergo oxidation

Colour in Halogen due to Homo-Lumo electronic transition \rightarrow

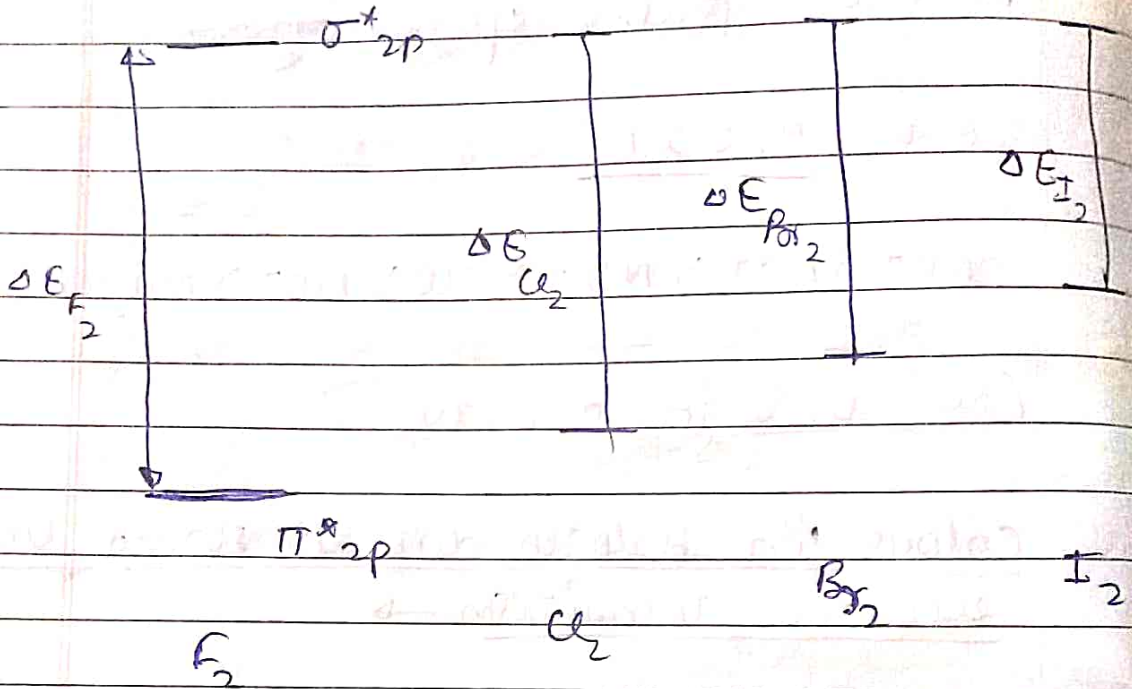
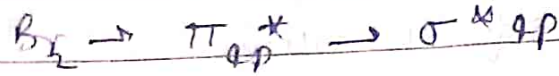
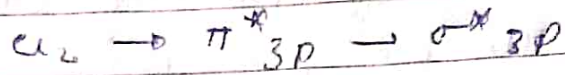
F₂ \rightarrow
 \rightarrow

Colour in any compound arises due to \rightarrow

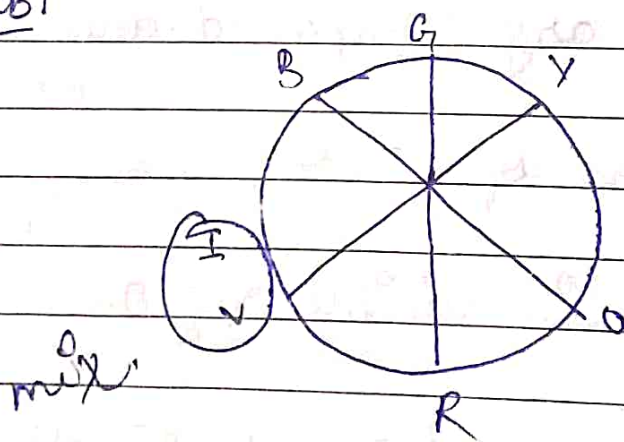
- ① Excitation of e⁻
- ② Emission in visible region

In F₂ \rightarrow excitation of e⁻ is from Homo (π^*_{2p}) to Lumo (σ^*_{2p})

excitation of e^- from HOMO (π^*_{2p}) to LUMO (σ^*_{2p})



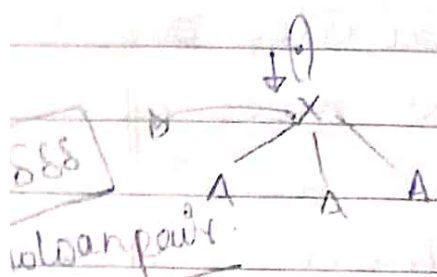
$$\Delta E = F_2 > Cl_2 > Br_2 > I_2 \quad \lambda_{ab} = I_2 > Br_2 > Cl_2 > F_2$$



emitted is complementary of absorption

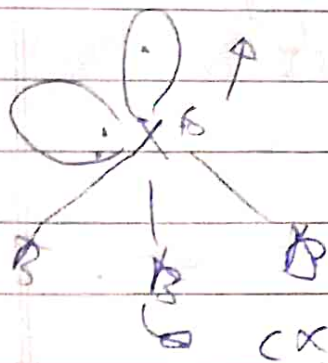
repulsion b/w $2e^-$ $2e^-$
 single bond - single bond > single bond -
 $2e^-$ odd electron
 $1e^-$

Hybridisation of odd e^- species \rightarrow



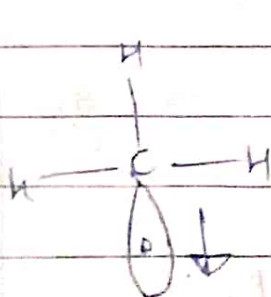
if X more EN then odd e^- will become more direction and will hybridise.

if central atom with ~~odd~~ +ve δ & with lone pair will not hybridise.



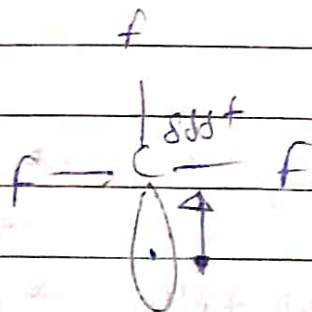
\rightarrow (repulsion) will not participate in hybridisation

(X is more EN too) but lone pair.



sp^2

~ 120



sp^3

$> 109^\circ 28'$

odd e^- species are paramagnetic

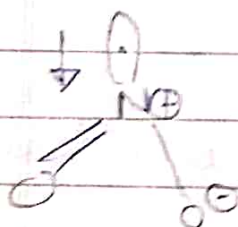
hybridisation mean have
directional property



$$K_2 > K_1$$

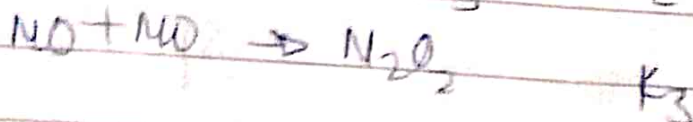
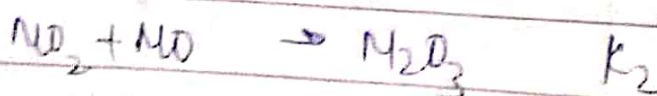
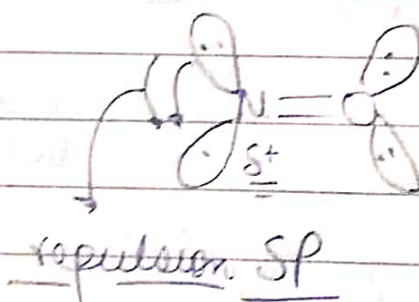
because in \textcircled{II} have directional
property so will have more to

do temp \rightarrow \textcircled{I} need more temp
as compare to \textcircled{II} for dimerisation

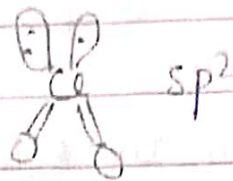
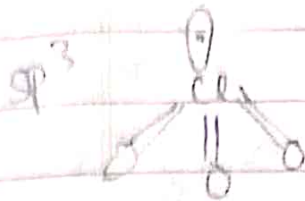
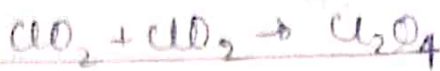


sp^2

$$BA > 120^\circ$$



$$K_1 > K_2 > K_3$$



$\boxed{BA > 109^\circ 28'}$

$BA < 120$

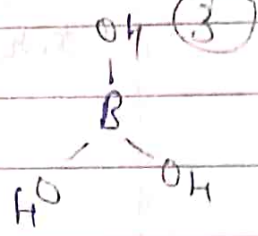
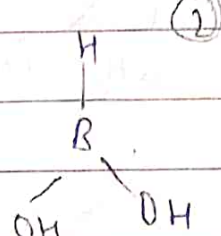
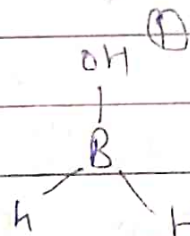
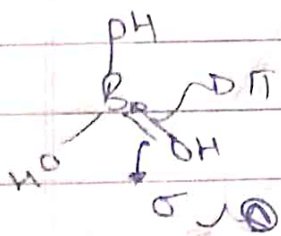
117° (lone pair)

↑
+ive charge lone pair

↓
no hybridisation

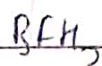
Application of Back bonding →

① Bond length due to B-B always decreases and B-E due to B-B (back bonding) ↑



(B-O) bond energy ↓

I) 2) > III



①

②

③

$\frac{4}{3}$

$\frac{3}{2}$

2

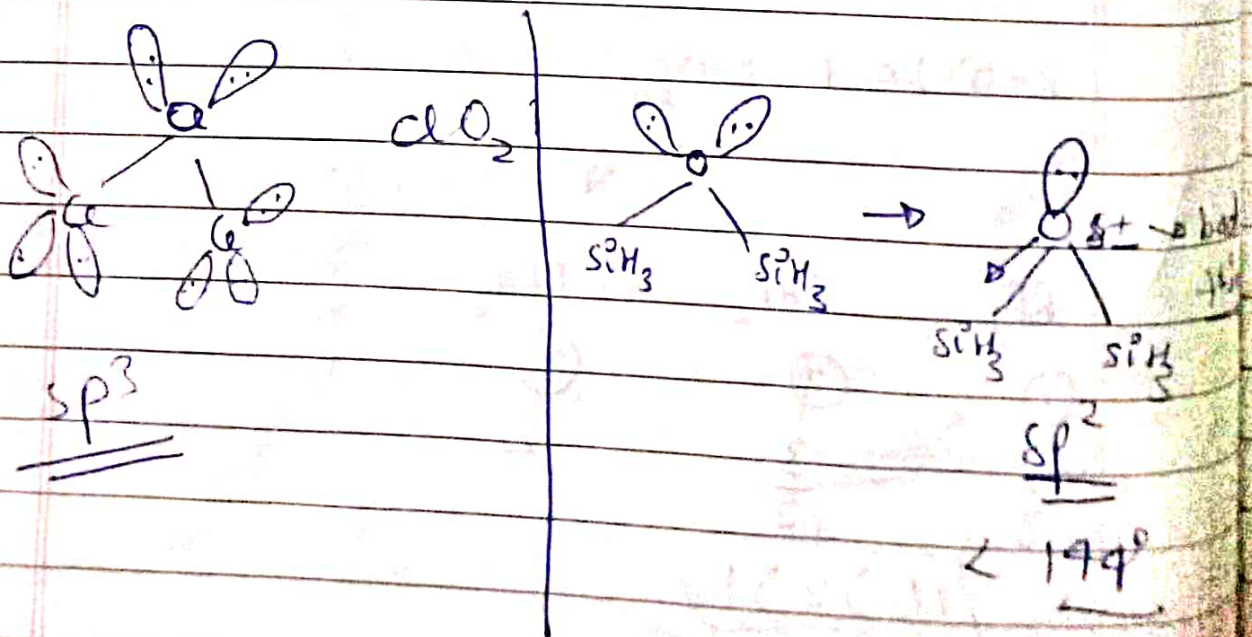
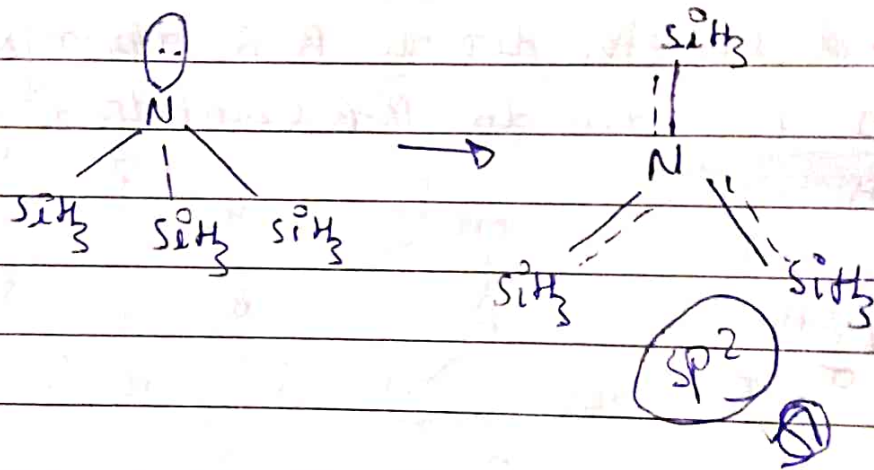
$\boxed{III > II > I}$

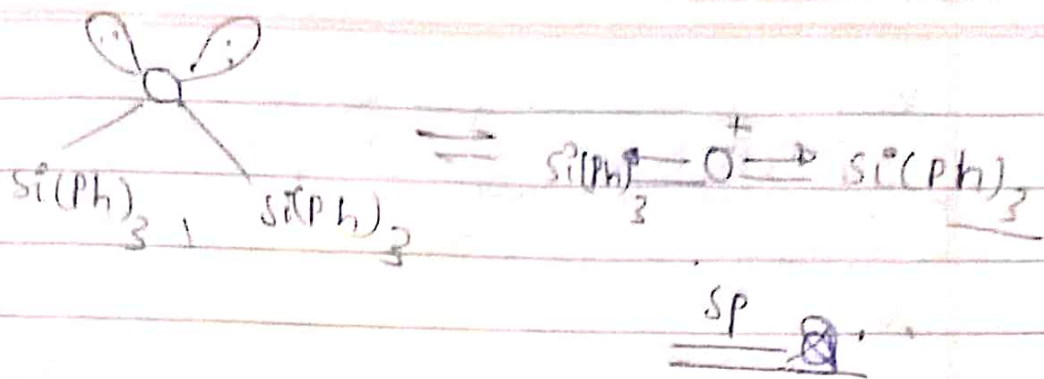
$BF_3 < BF_4^-$
 bond length \rightarrow $BF_3 < BF_4^-$

$BO \rightarrow 1.33 \quad | \quad 1$

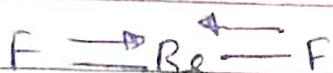
\rightarrow Hybridisation due to B-B may change or remain same \rightarrow

if acceptor site ~~is~~ ^{has no lone pair} involved in π & vacant orbital is present then donor atom hybridisation will change



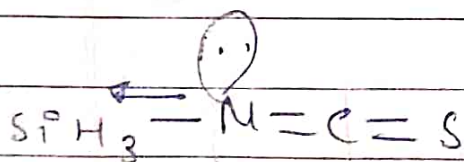


BeF₂ → back bonding

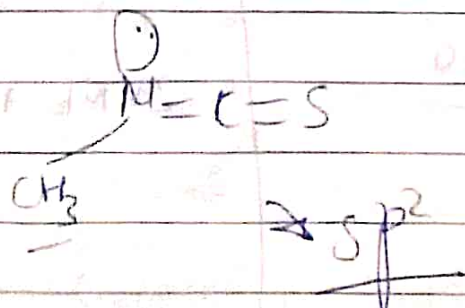


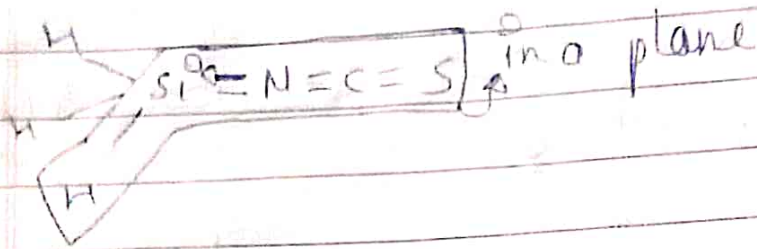
Q → which of the give statement is incorrect for SiH₃NCS →

- (a) ~~It is sp~~ is sp² hybridised.
- (b) Max^m no of atom in one plane is equal to 5.
- (c) considering SiH₃ as a point. It is a planar species.
- (d) Both B & C are correct.



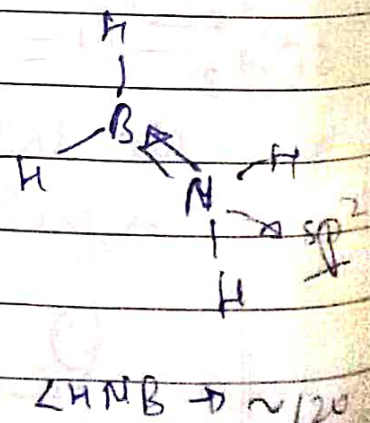
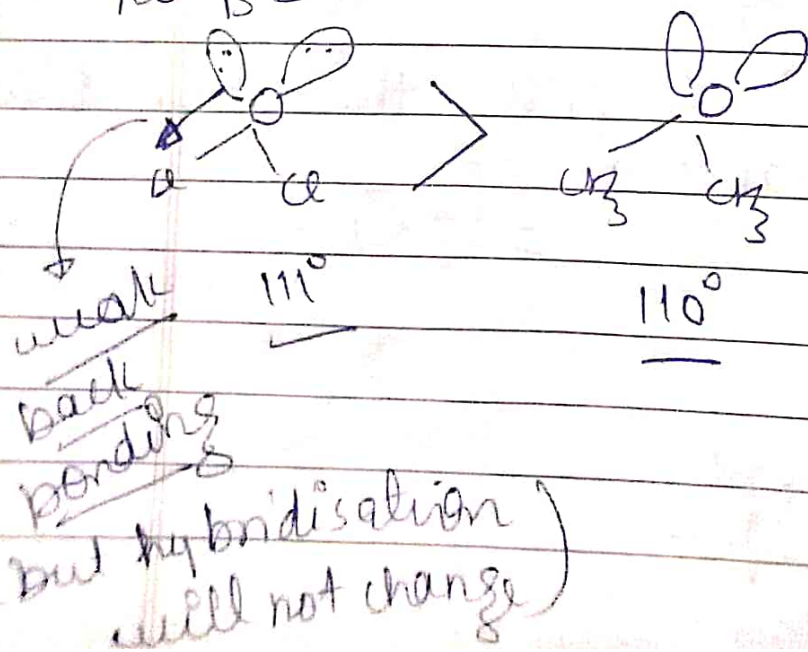
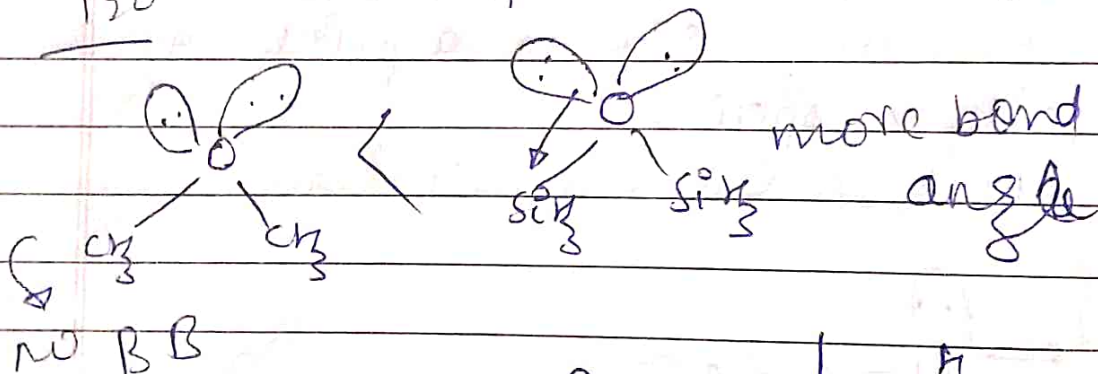
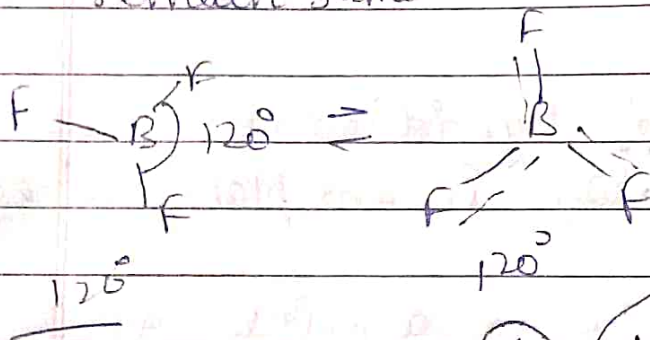
No lone pair is present thus hybridisation will change to sp.



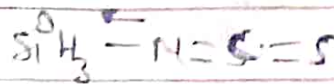
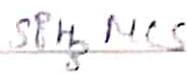
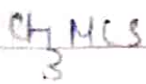
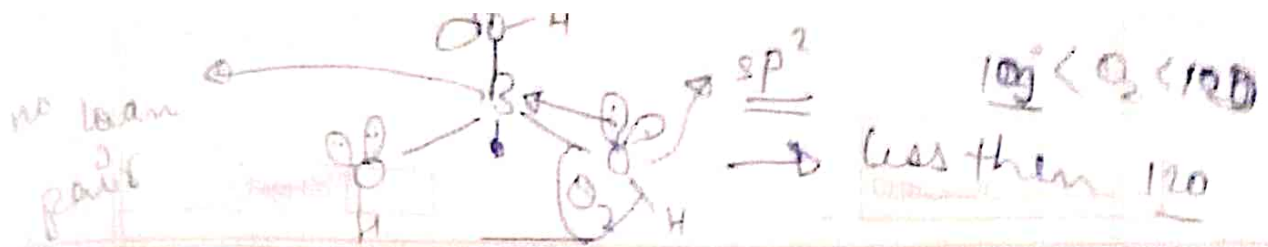


$\text{N}(\text{SiH}_3)_2$ is planar if we consider SiH_3 as a point group.

→ Due to BB, bond angle may increase or remain same.



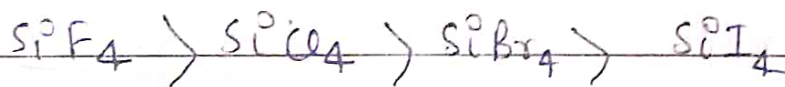
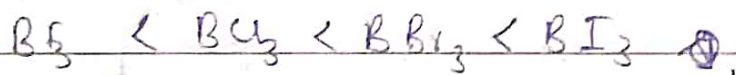
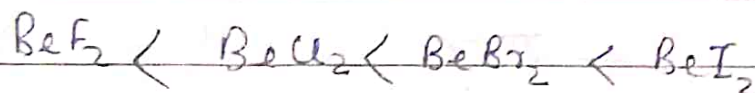
but hybridisation will not change



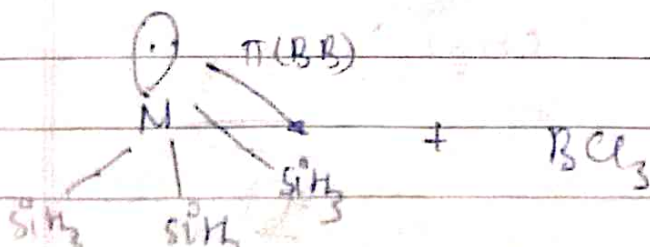
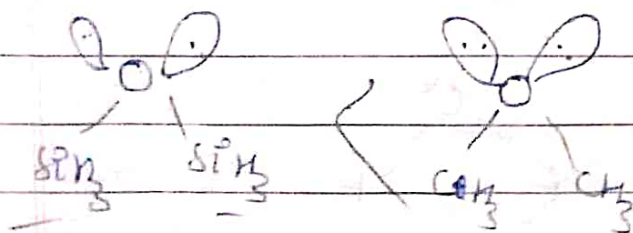
BB

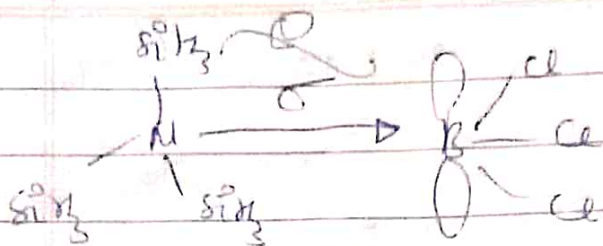
No BB

→ Due to back bond Lewis acid character & basic character decreases

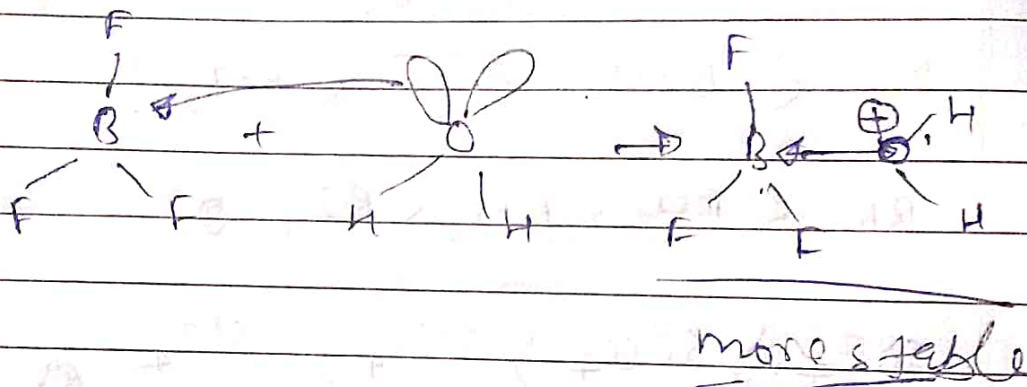


Lewis basic character →

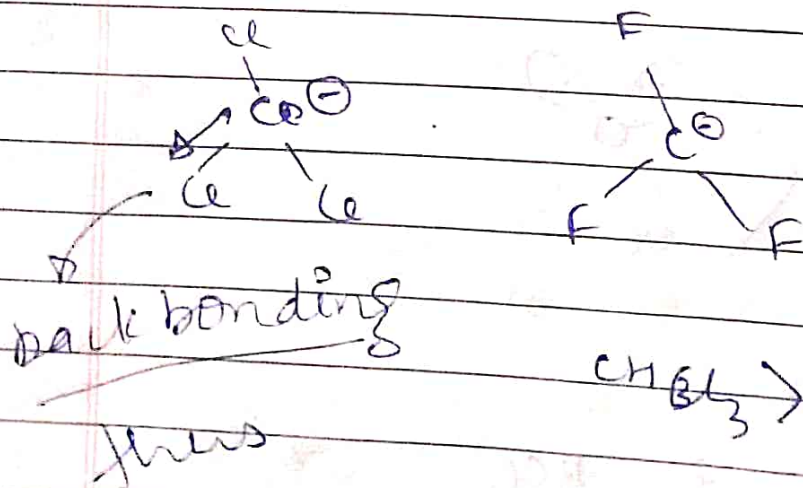




most favourable because
 lone pair is making σ bond instead
 of π dative bond due to BB.



Due to back bonding acidity of
 aqueous acid \uparrow

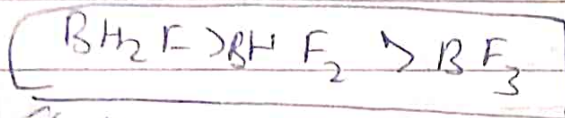




more stable

BB

extent of BB.

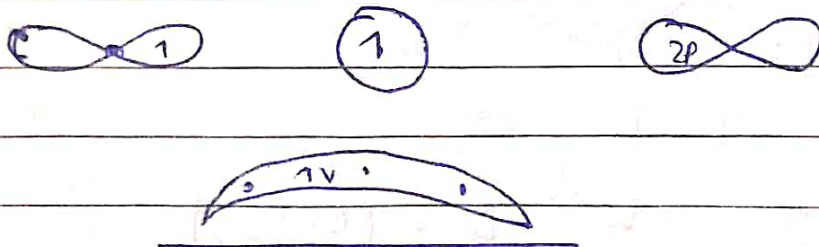


→ Bond order

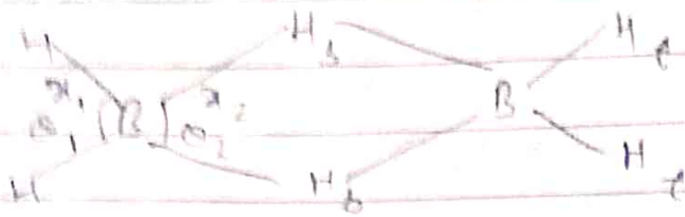
se stability.

Bridge bonding →

electron deficient compound involved in bridge bonding or compound which is unstable in its monomer form.



bond length sum of shell/period

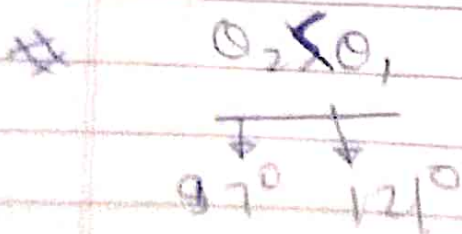
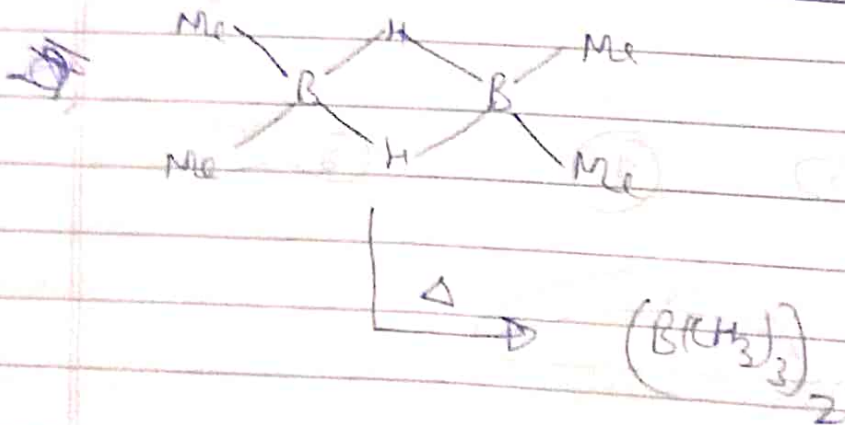
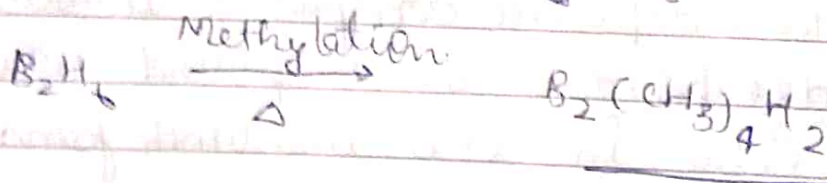


Max^m no. of atom in one plane = 6

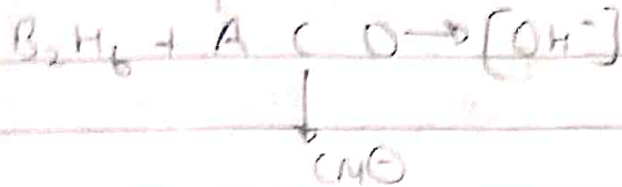
Bond length $\alpha_2 > \alpha_1$

Bond energy $\rightarrow B-H_b > B-H_e$

Bond energy $\propto \frac{1}{\text{bond length (only 2 C)}}$



Amine (NH_3 / RNH_2 / R_2NH)

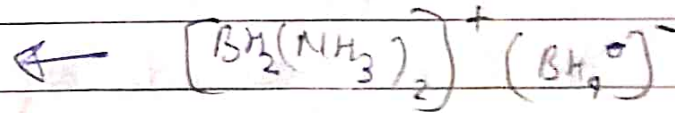
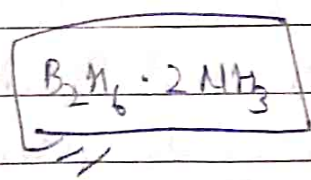
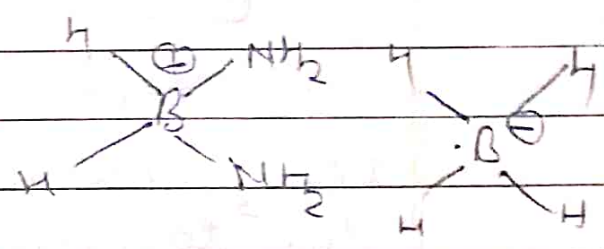
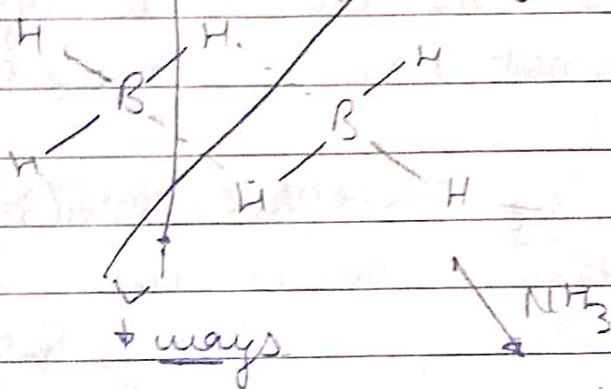


→ unsymmetrical cleavage

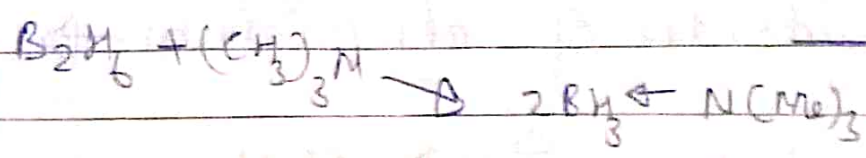


\downarrow
 $\text{R}_3\text{N} / \text{H}_2\text{O} / \text{CO} / \text{PH}_3 / \text{PF}_3 / \text{Pyridine} / \text{ether} / \text{thioether}$

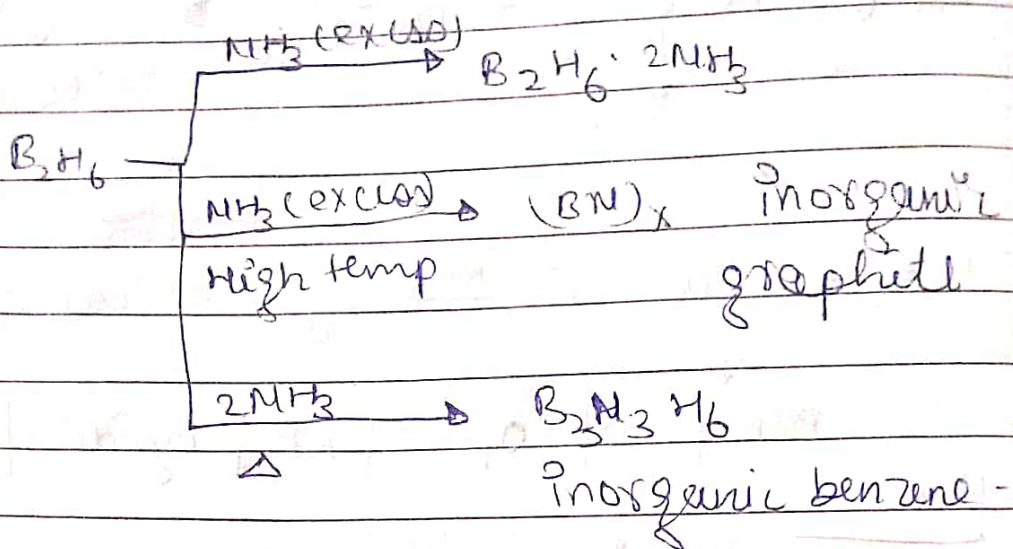
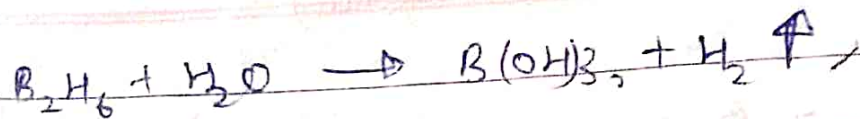
→ unsymmetrical
 → symmetrical



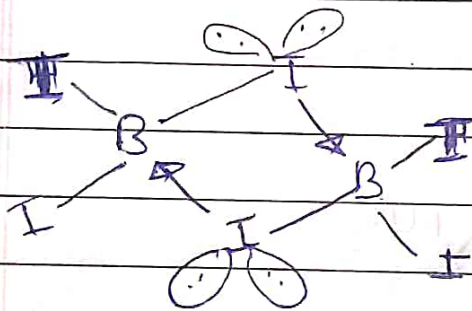
ionic bond



IT
 can
 will
 IIT
 any



Chloride, Bromide and iodide of Boron does not form bridge bond

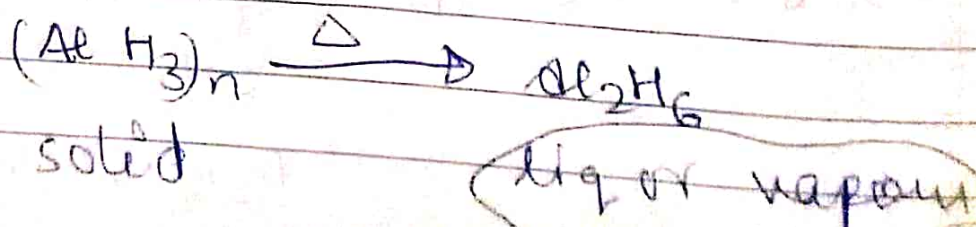


steric repulsion
so it does not
form bridge bond

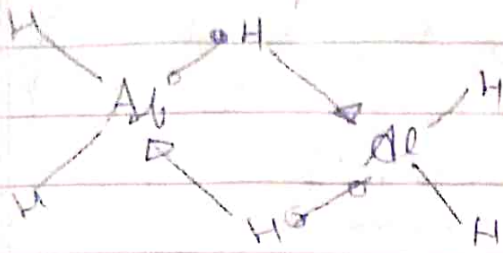
$B(Me)_3$ does not form bridge bond
due to steric reason

* Compounds of Aluminium
Beryllium will also do same.

(i) hydrides of aluminium \rightarrow



banana of bridge bond.



→ Al → sp^3 , CN=4, (2c, 2e) → 4

→ (3c, 2e) → 2.

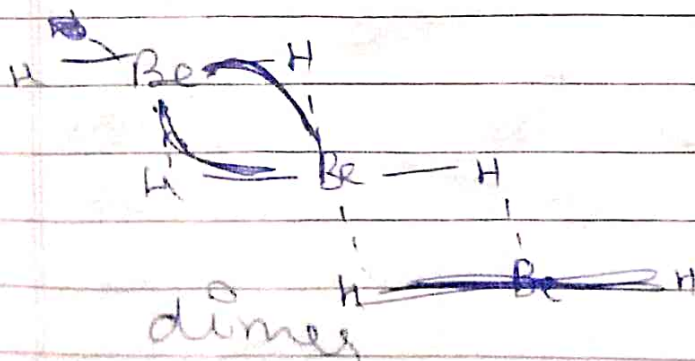
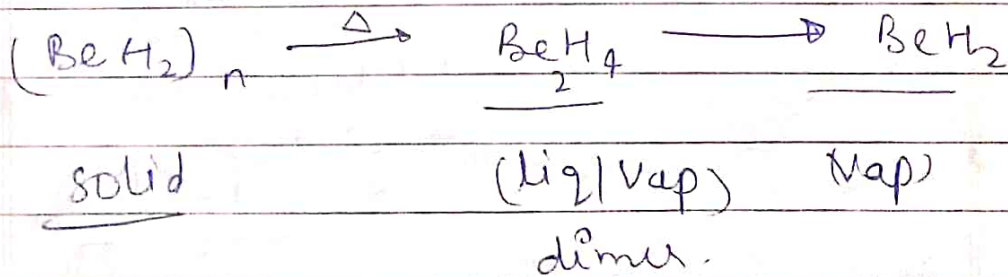
→ Non planar.

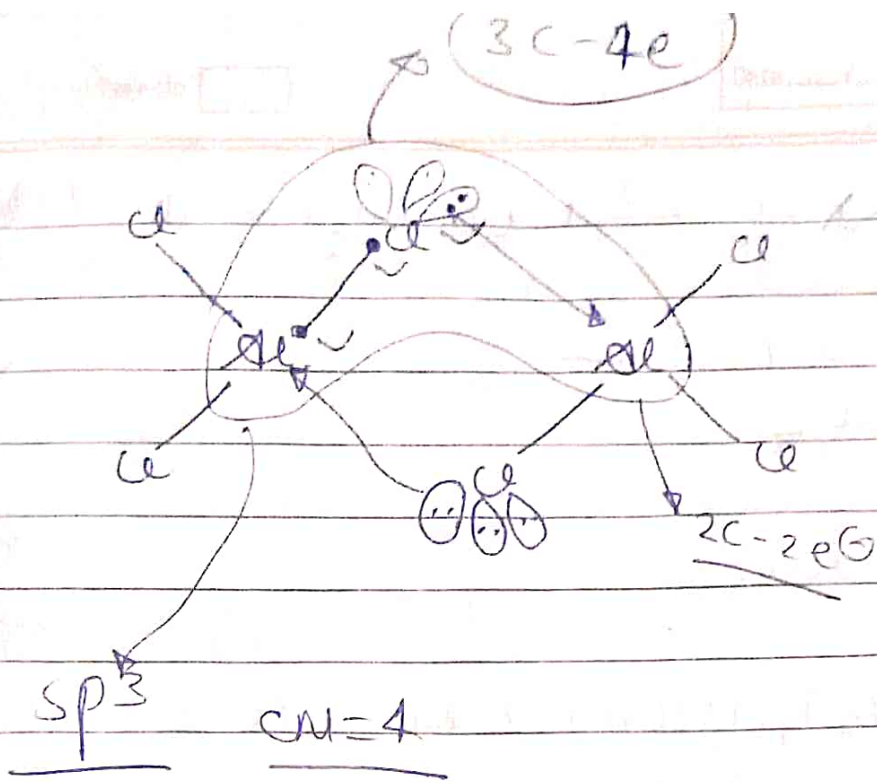
→ max^m no of atom in a plane → 6

→ $\mu=0$ non polar.

(AlH₃)_n In ^{polymetric} dimeric form CN=6 sp^3d^2

Hydride of 'Be' →





MO of $2c-2e \rightarrow 4$

" " $3c-4e \rightarrow 0$

" " $3c-4e \rightarrow 2$

non planar. $n=0$

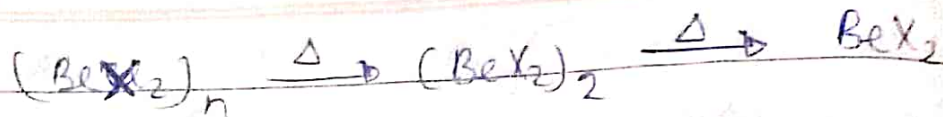
$(AlCl_3)$ polymeric form

CN of $Al \rightarrow 6$ sp^3d^2

$3c-2e \rightarrow 0$

all are $3c-4e$

$AlBr_3$ & AlI_3 exist as dimers in solid also.

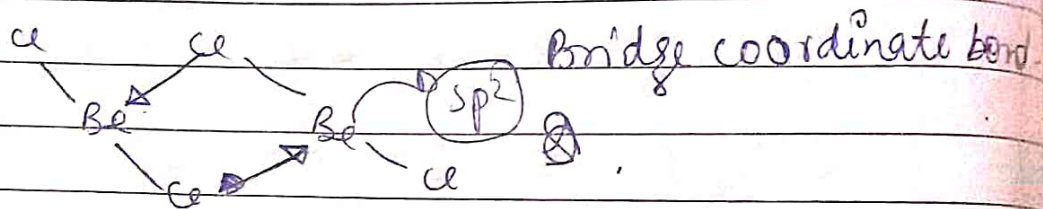


$X \rightarrow \text{Cl, Br, I} \rightarrow$

CN $\rightarrow 4$

no steric
hindrance.

$\rightarrow (\text{BeF}_2)_n$ (solid) look like silicate str.



\rightarrow No of $3c-2e^- \rightarrow 0$

$2c-2e^- \rightarrow 2$

$3c \rightarrow 4e^- \rightarrow 2$

planar

\rightarrow polymeric form \rightarrow

No of $2c-2e^- \rightarrow 0$

all are $3c-4e^- \checkmark$

non plane- sp3

BeF_2 form bridge bond.
 \downarrow
covalent.

BeF_2
 \downarrow
in polymeric
form all are
3 centre 2 el.

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

\downarrow
has

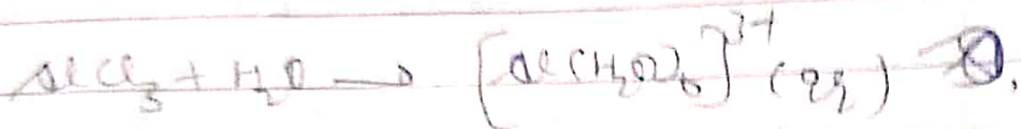
3 centre

2 electron

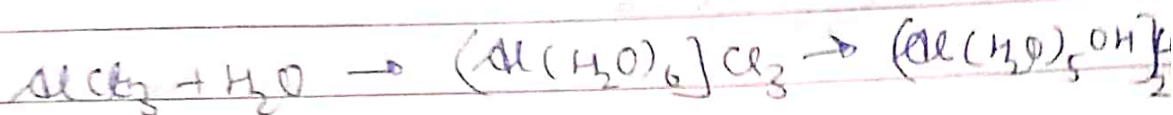
band

NOTE

$AlCl_3$ (s) is covalent, (solid) but in aq. solⁿ, it is ionic in nature.



In $[Al(H_2O)_6]^{3+}$ has water coordinated water.



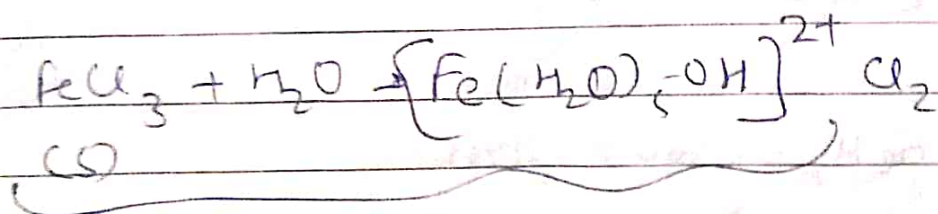
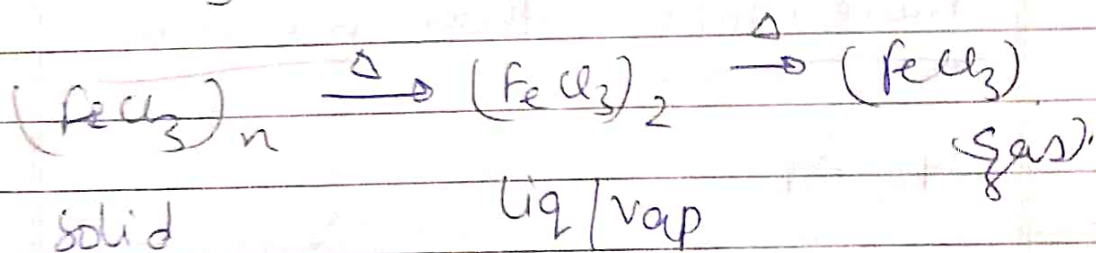
aqueous solⁿ of $AlCl_3$ is acidic in nature.

+HCl

↓

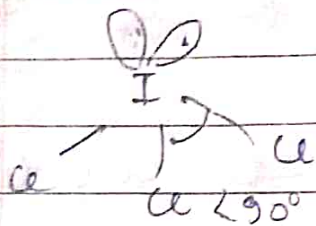
acidic

→ $FeCl_3$ bonding is similar to $AlCl_3$.

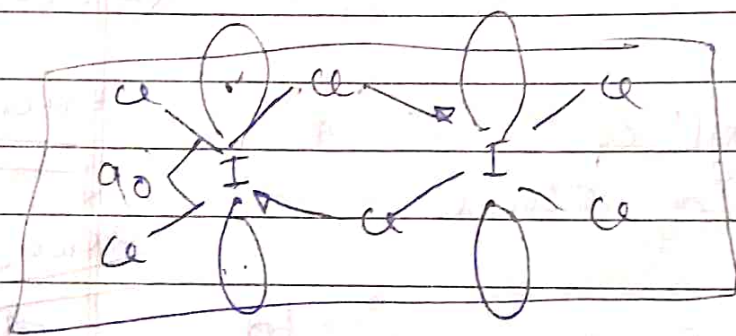


also acid in nature in aqueous solⁿ.

ICl_2 (monomer) and exist as dimer
in liq (I_2Cl_4)



dimer \rightarrow



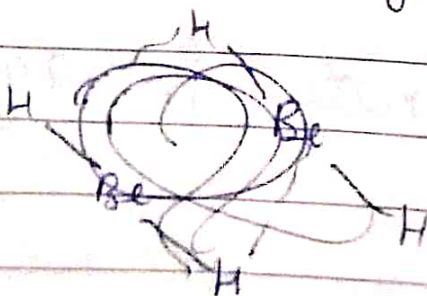
planes
 $\mu = 0$

more stable than monomers

lp-lp - 180°

$\angle \text{I-Cl-I} \rightarrow 90^\circ$

~~$\text{BeH}_2 \rightarrow$ solid form~~



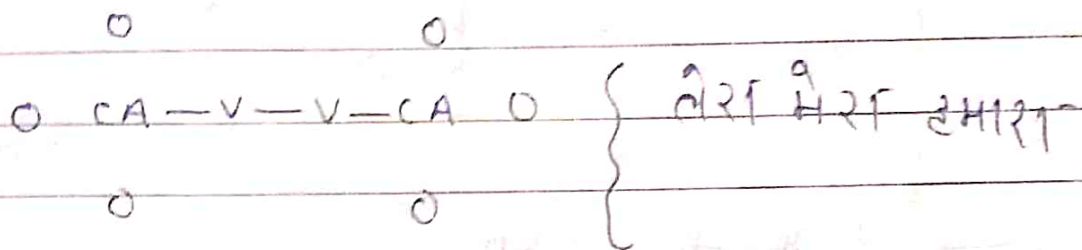
27/10/2020

Structure drawing

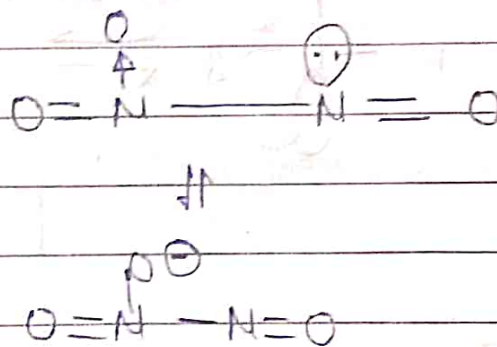
for one central atom →

symmetrically placed around C.A.

for two central atom →

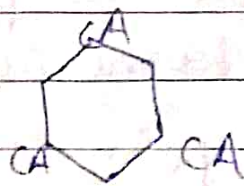


N_2O_3

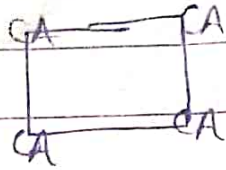


for central atom →

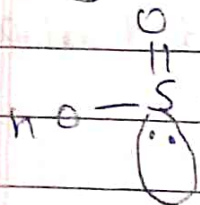
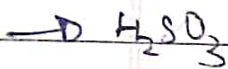
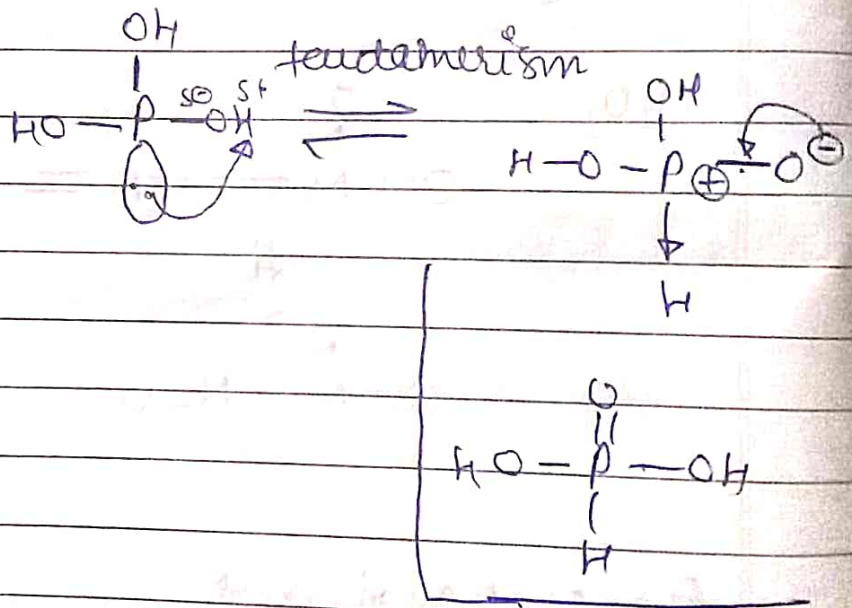
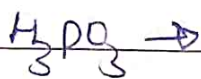
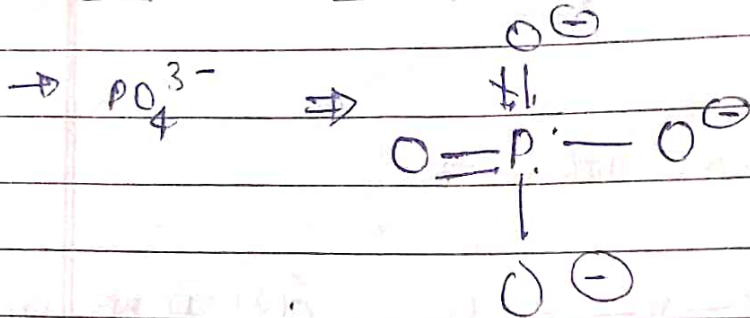
if (No of CA < No of bonded atom)



for 4 central atom \rightarrow



for one central atom \rightarrow

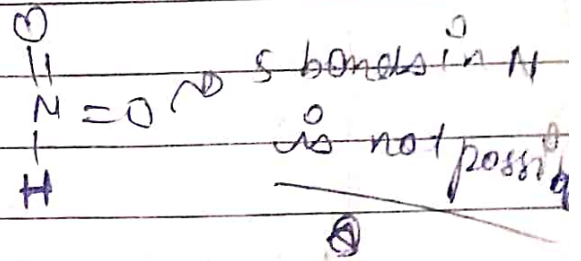
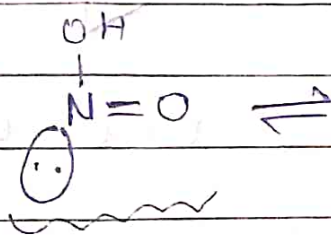


\rightarrow there is possibility of tautomerism but it is major product

$\text{HClO}_3 \rightarrow$ major

$\text{O}=\overset{\text{O}}{\underset{\cdot\cdot}{\text{Cl}}}-\text{O}-\text{H} \rightarrow$ can undergo the process of tautomerism but ~~due to~~ e^- donating capability of Cl^+ is minor so.

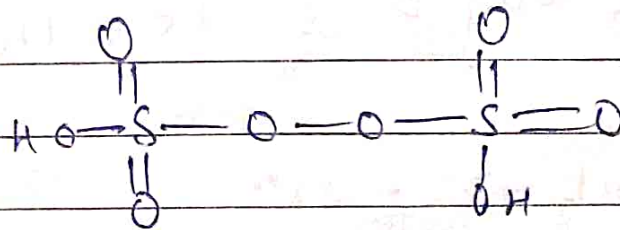
$\text{HNO}_2 \rightarrow$



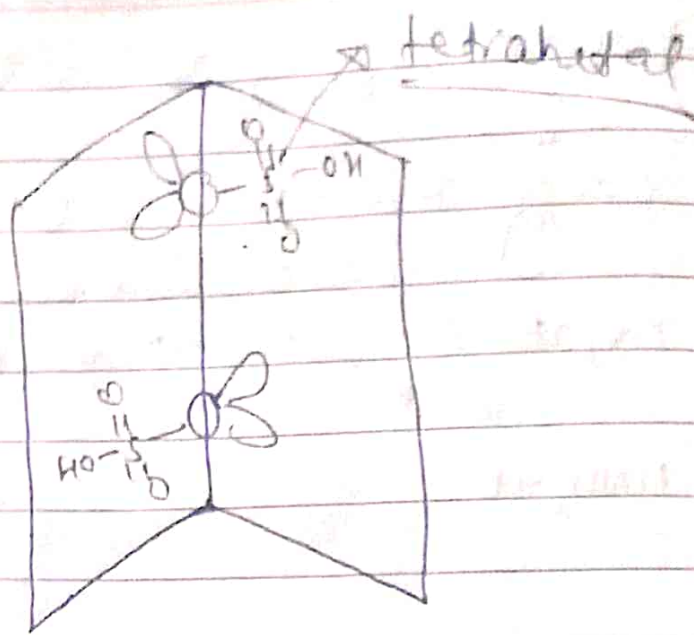
no tautomerism

structure for two central atoms \rightarrow

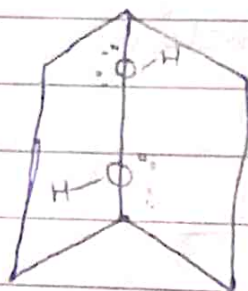
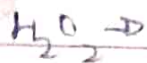
$\text{H}_2\text{S}_2\text{O}_8 \rightarrow$



Note \rightarrow when two c.n. like $-\text{O}-\text{O}-$ or $-\text{S}-\text{S}-$ are present then they are open book like structure.

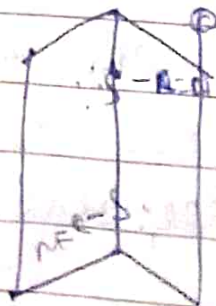
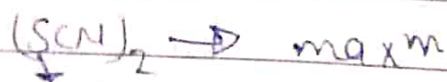


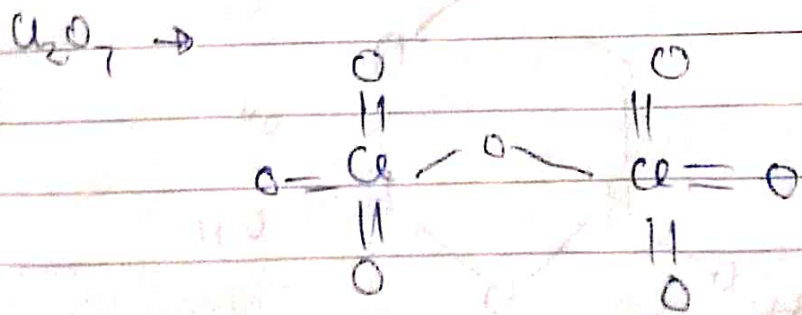
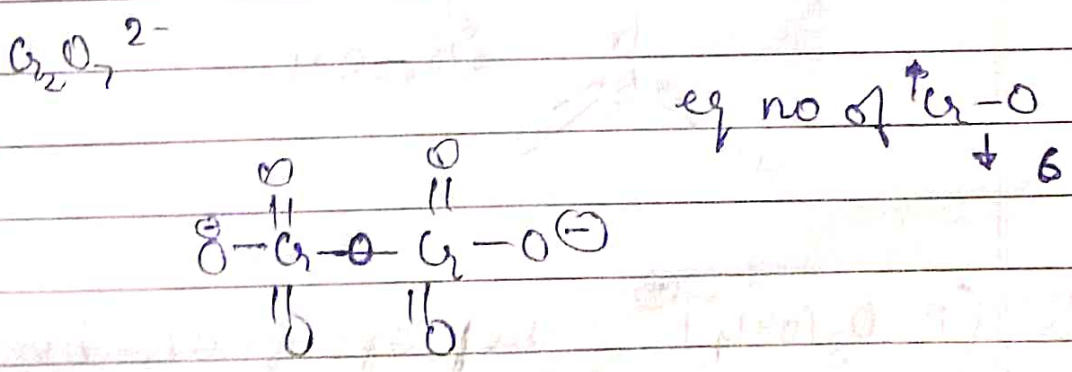
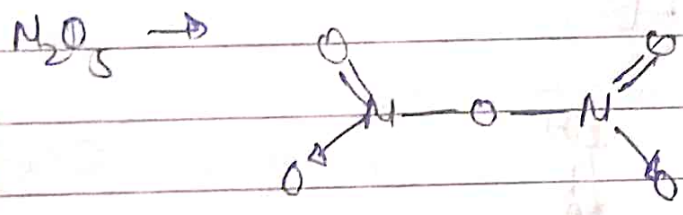
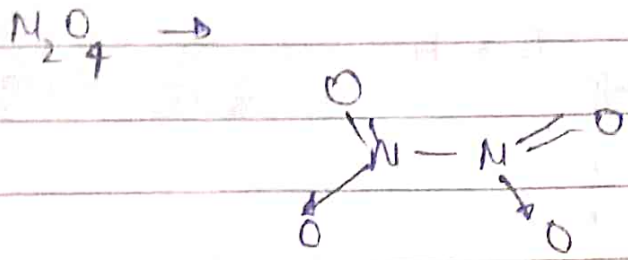
max^m 5 atoms are in a plane



3 atoms in a plane

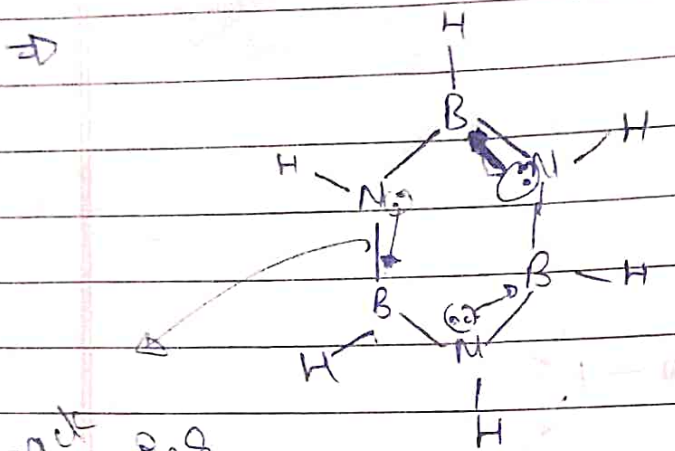
similarly $\rightarrow S_2F_2 \mid S_2Cl_2 \mid H_2S_2 \mid O_2F_2$ etc





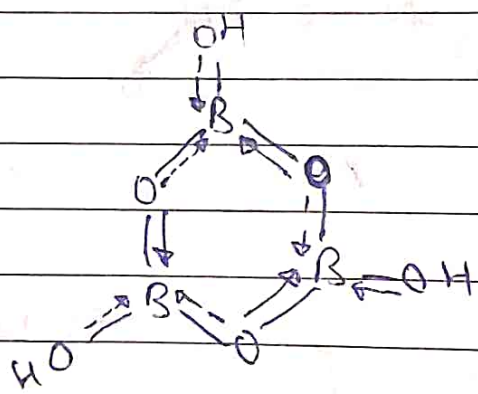
Structure of 3-centre →

less electronegative is central atom



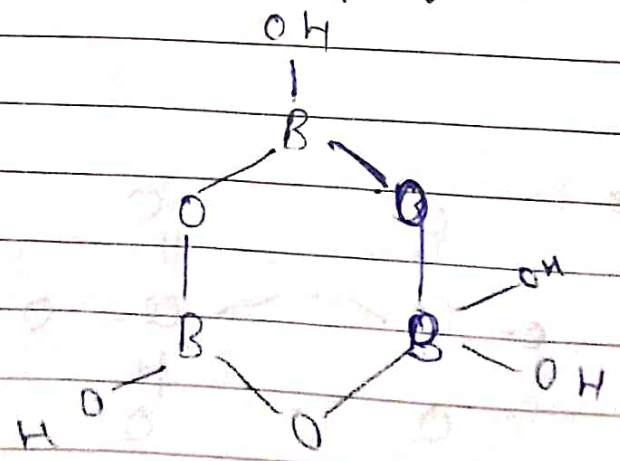
back bonding

② $B_2O_3(OH)_3$ →

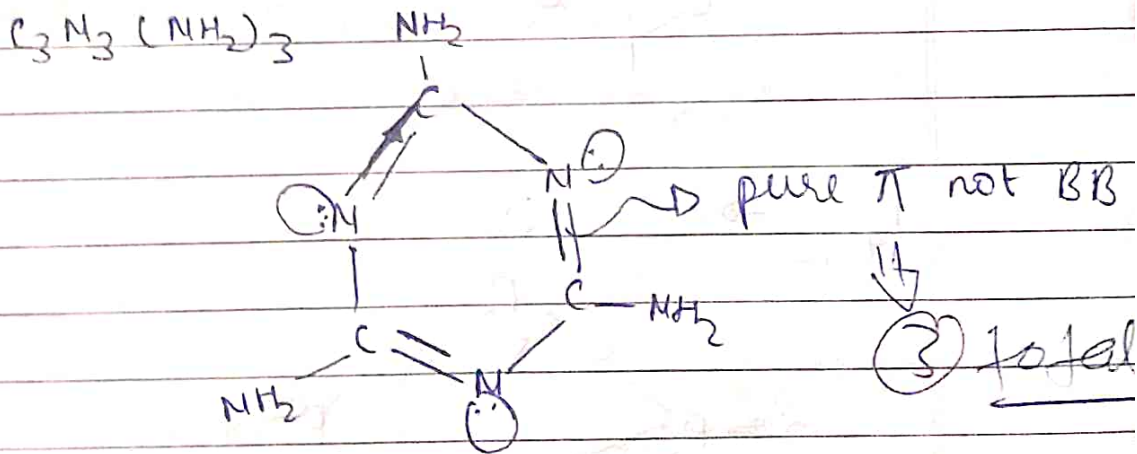
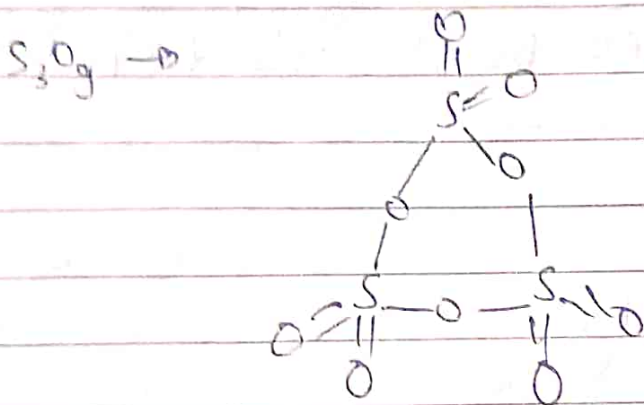
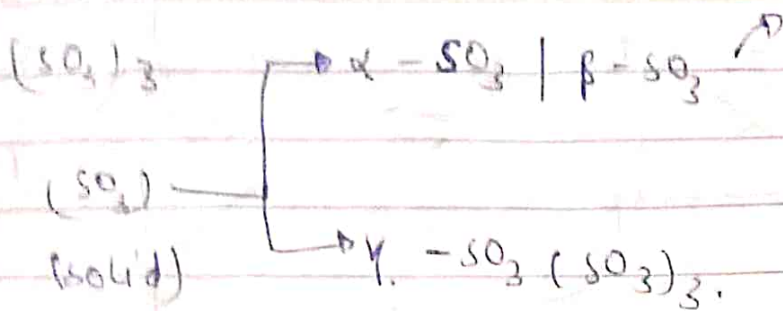
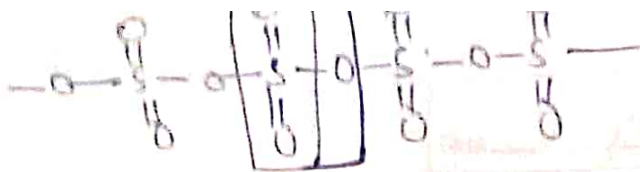


③ $[B_3O_3(OH)_4]^-$

~~no~~ of B-O-B bonds



2 boron atoms are involved in back bonding

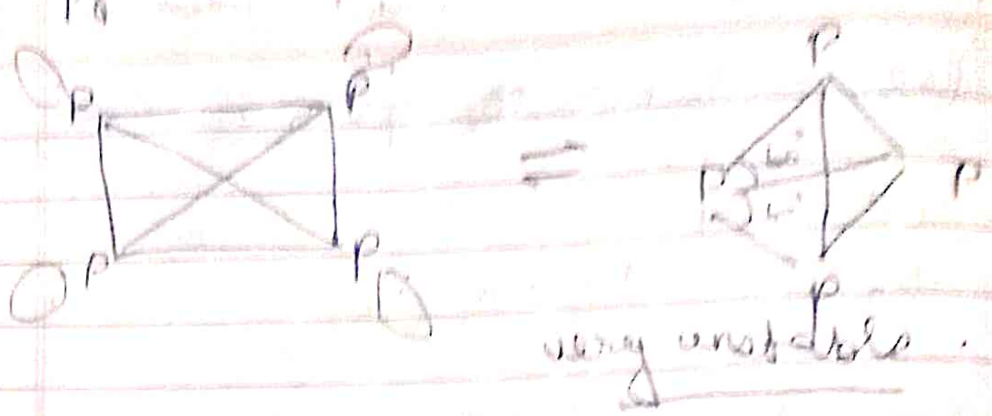


(melamine)

no of B-B = 0

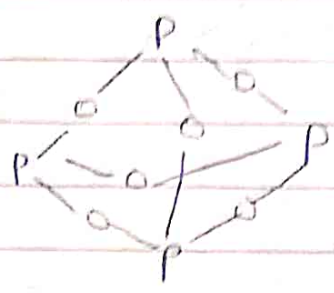
Structure for 4-central atoms

P_4 → white phosphorus

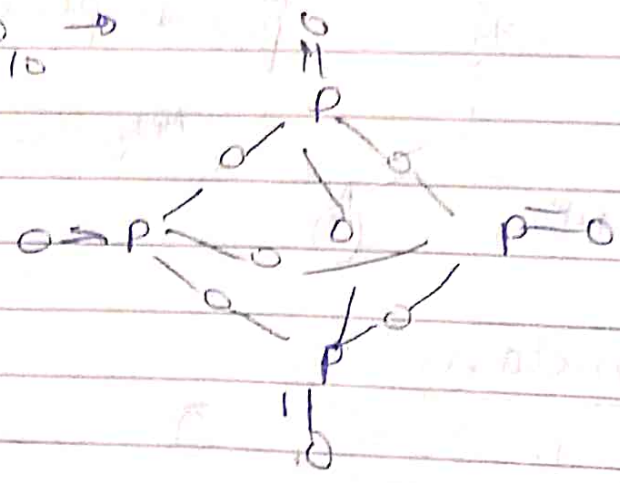


no of $\angle 60$ bond angle = 12

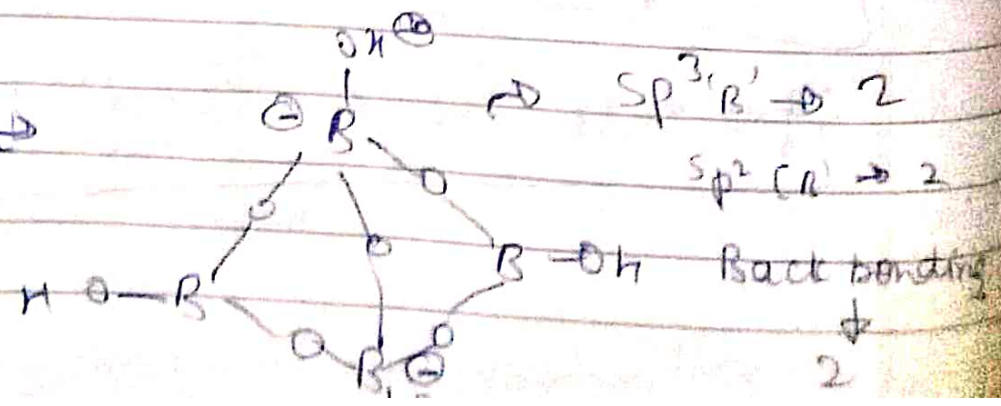
$P_4O_6 \rightarrow$



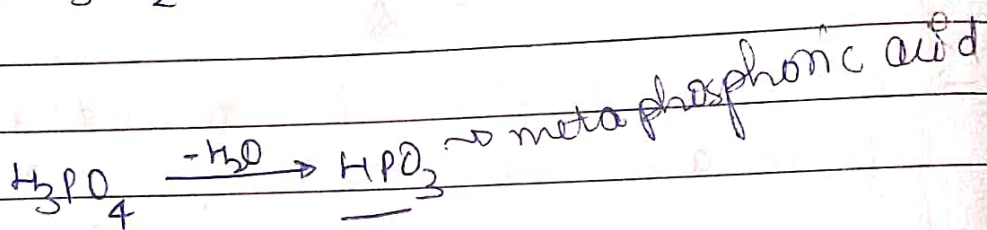
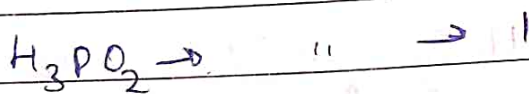
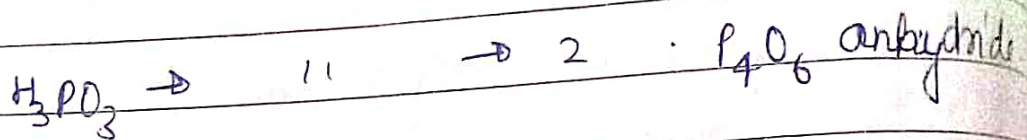
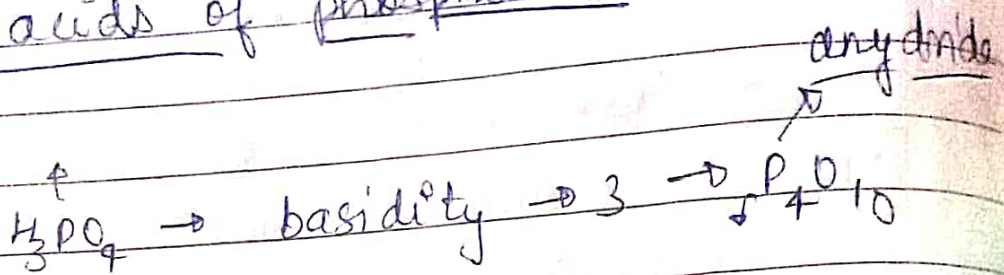
$P_4O_{10} \rightarrow$



Borane

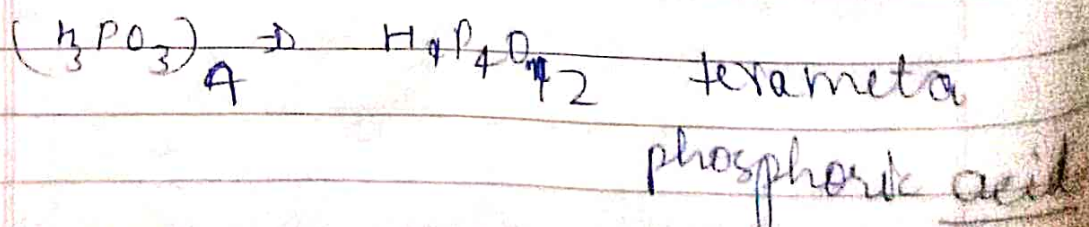
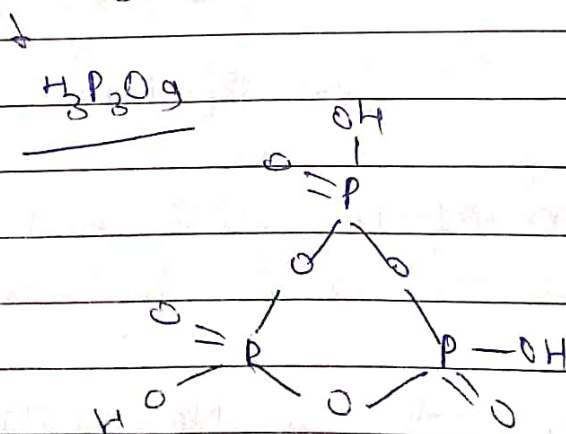


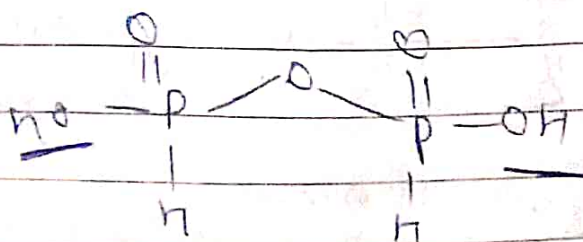
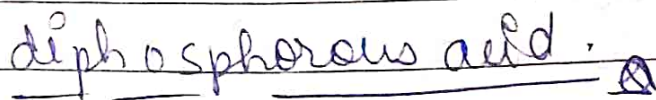
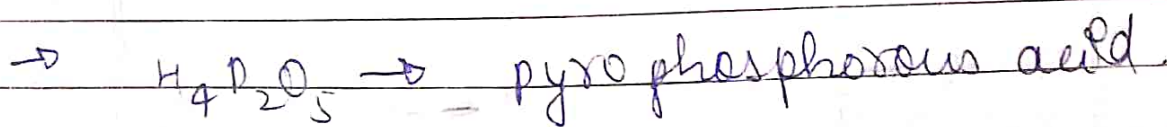
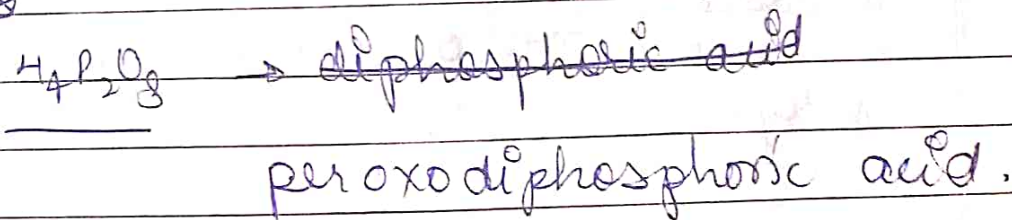
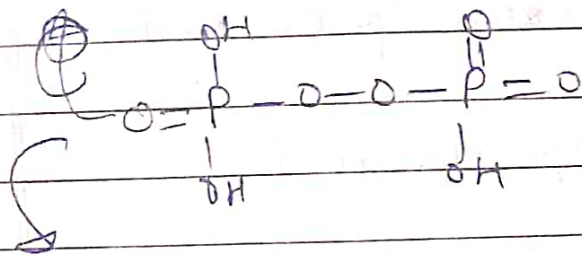
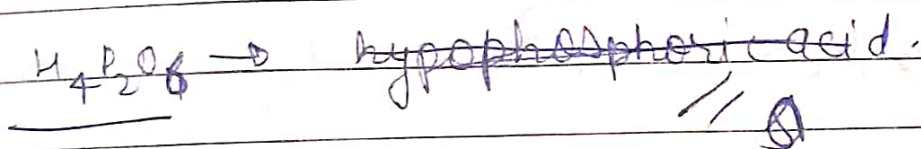
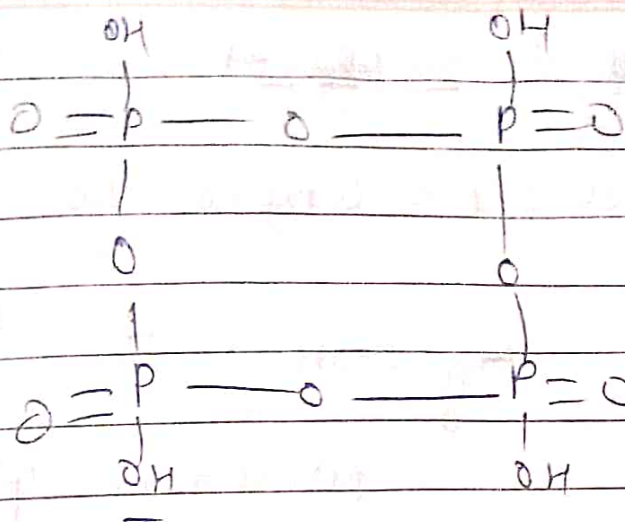
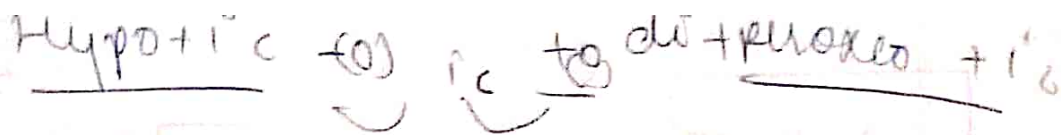
oxoacids of phosphorous →



→ meta phosphonic acid exist in polymeric acid i.e. $(HPO_3)_3$, $(HPO_3)_4$...

→ $(HPO_3)_3 \rightarrow$ trimeta phosphonic acid.

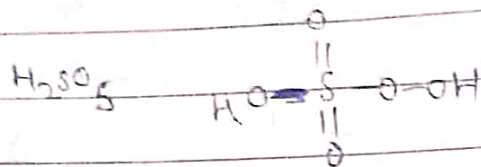




exists \rightarrow 2

Oxoacid of Sulphur →

Highest O.N = Group no - 10.



peroxomonosulphuric acid

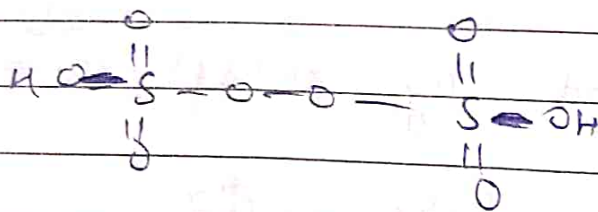
$H_2S_2O_7$ → disulphuric acid / pyrosulphuric acid

~~$H_2S_2O_8$~~ → peroxodisulphuric acid.

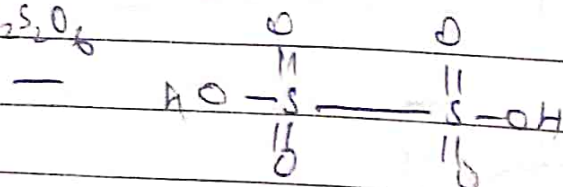
$H_2S_2O_6$ ⇒ hyposulphuric acid.

Series → $H_2S_{n+2}O_6$ $n = 0, 1, 2, \dots, \infty$

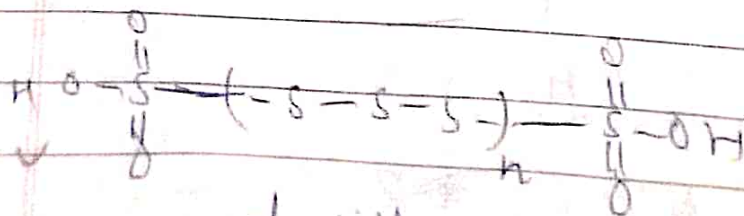
polythionic acid.



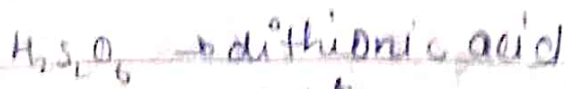
$H_2S_2O_6$



hyposulphuric acid



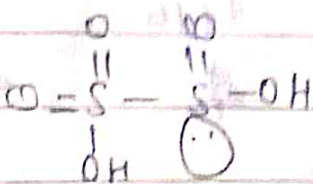
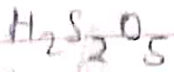
polythionic acid



tetra -



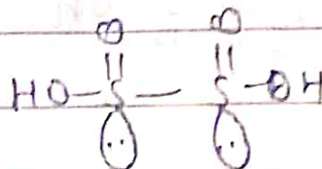
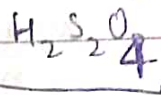
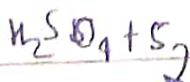
penta -



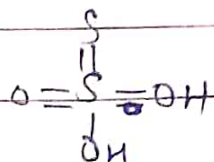
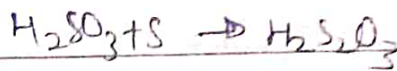
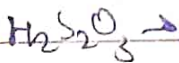
is derivative of sulphuric acid.

pyrosulphuric acid

disulphuric acid.



thiosulphuric acid.



thiosulphuric acid

calculate the value of the expression

$\frac{p^2 + q^2}{R + 1}$ where $p \rightarrow$ total no of species present shows per oxo linkage, oxy

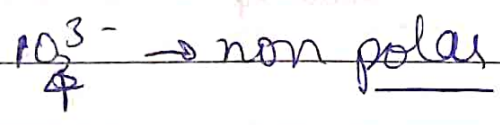
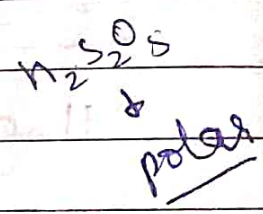
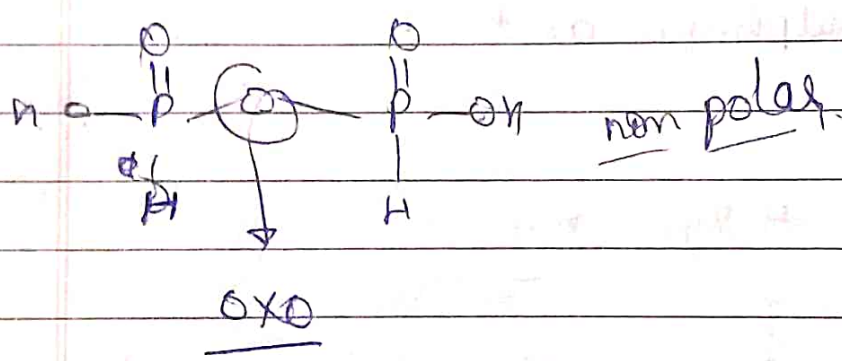
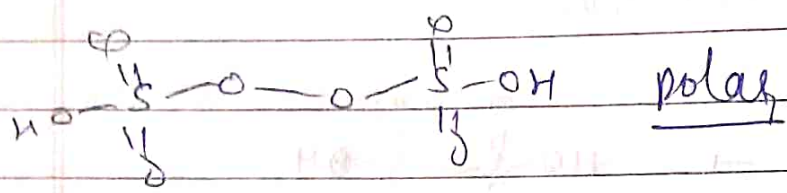
$q \rightarrow$ total no of species shows

basicity greater than 0 and $R \rightarrow$

total no of polar species

$H_2S_2O_8$, $H_9P_2O_5$, $H_4P_2O_7$, H_2SO_5 , ~~H_3PO_4~~
 PO_4^{3-} , $(CN)_2$, $(SCN)_2$

$P \Rightarrow 2$ $\frac{4+16}{4} = \frac{20}{4} = 5$
 $O_n = 4$ $\frac{20}{4} = 5$
 $R = 7$



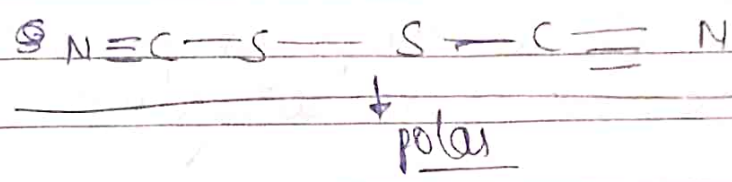
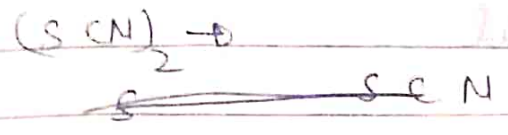
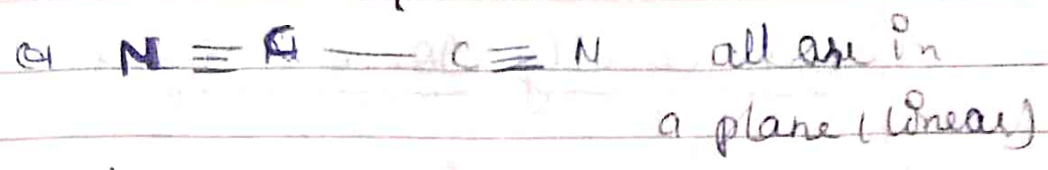
$(CN)_2 \rightarrow$ pseudo halid & halogen structures are written in the same form as written \rightarrow

Pseudohalid \rightarrow polyatomic species containing at least N.



basic acid is not monoprotic but mono basic

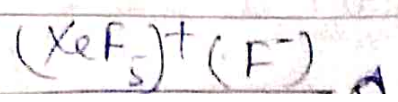
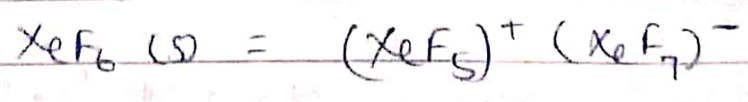
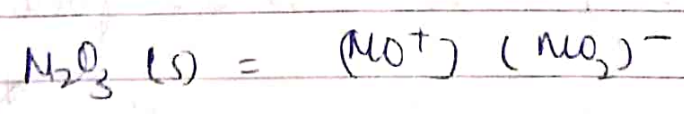
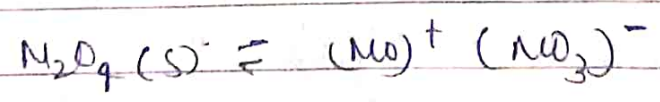
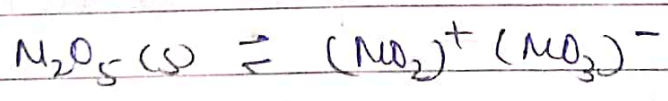
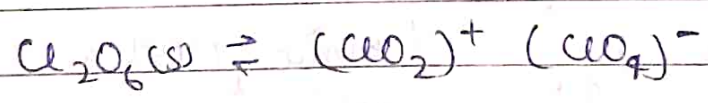
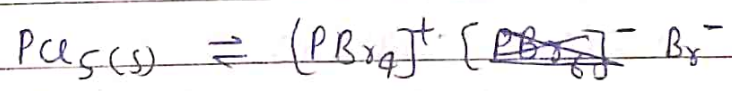
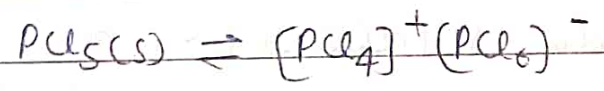
non polar



ionic →

Complete transfer of electron take place between different species.

Non Ionic Solid →



Theoretically Ionic bond →

→ non directional

Fajan's →

Ionic compound possess some covalent character, Qualitatively:

Fajan's explained →

In ideal case (considering compound ionic) ~~the~~ electronic cloud of cation and anion in ionic compound have symmetric distribution. soft sphere

But in real case anionic e^- cloud move towards (diffuse) cationic species (hard sphere) and create directional nature i.e. covalent character.

↘ tendency to attract e^-

polarising power / ionic potential
(define for cation)

+

Polarisability → defined for anion
↗ tendency to diffuse

both process term as polarisation

Factor on which polarisation depends →

* Polarisability = charge ρ / size ρ
(anion)

polarisability

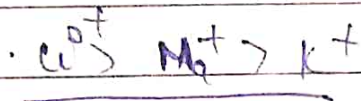
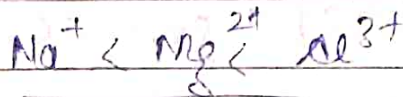


(11) Polarising power / Ionic potential

depends on cationic charge density

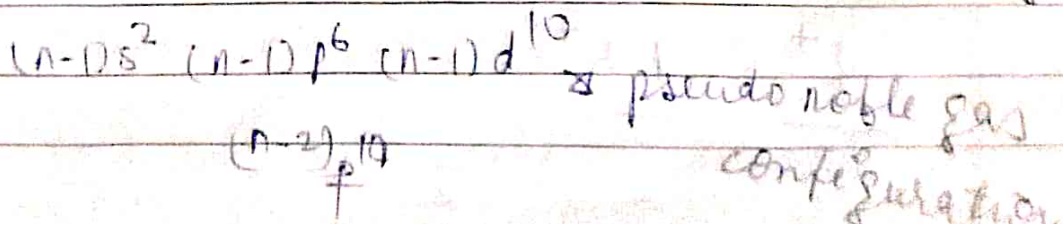
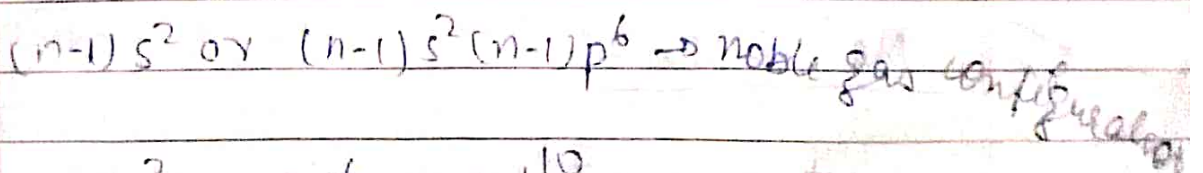
size \rightarrow $\phi = \frac{\text{charge}}{\text{density}}$ $\left(\frac{\text{charge}}{\text{size}} \right)$

polarising power

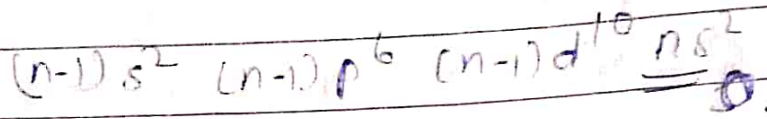


~~data~~

\rightarrow polarising power depend on e⁻ configuration



Non-inert gas configurations



Conclusion of polarising power (Z/r²)

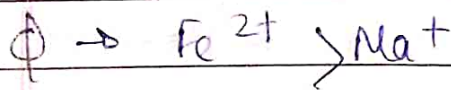
Steps →

1 → Configuration — if different configuration then

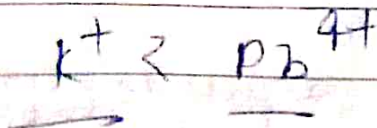
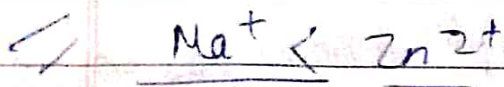
to compare
it look for
charge more
⊕
charge ↑
more
polarising
power ↓

→ pseudo noble gas
→ Non inert.
→ partially filled d } Noble gas configuration

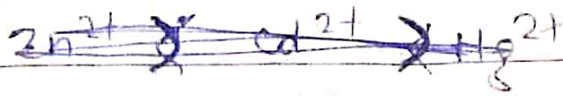
all these will always
win over noble gas configuration
except Al^{3+}, Ac^{2+}



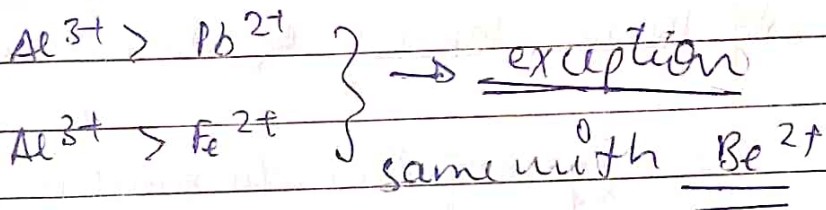
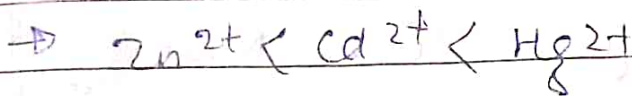
∥ $K^{2+} > Ca^{2+} \rightarrow$ noble gas configuration
partially filled 'd'



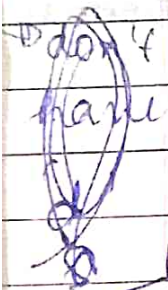
if configuration is same then use
general concept.



→ in d block Zn^{2+} down the group
↑



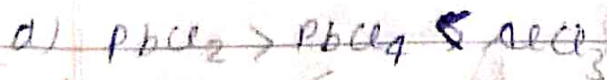
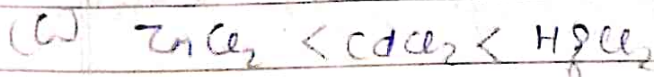
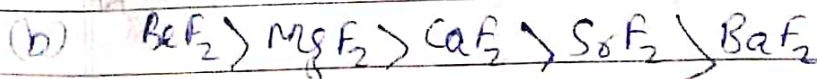
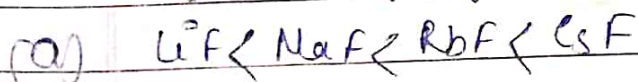
Application of Fajan's rule →

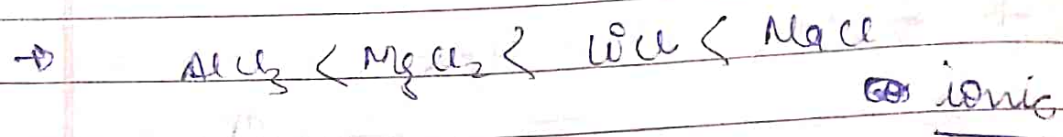
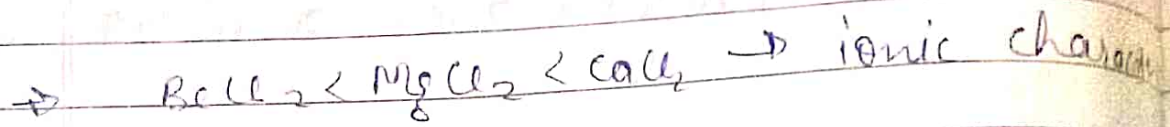
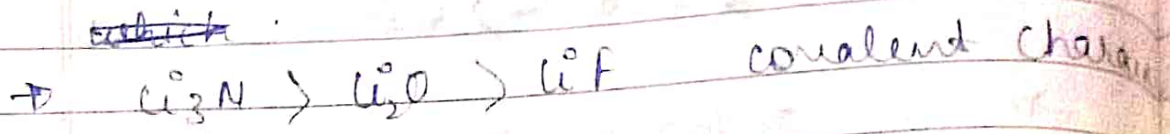


→ covalent and ionic character in ionic
compound →

polarisation & covalent character in
ionic compound.

which of the given order is correct →
in term of covalent character



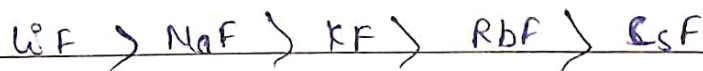


→ thermal stability of ionic compound →

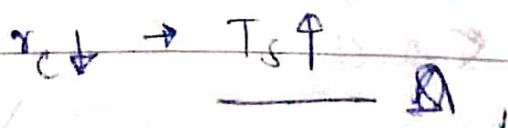
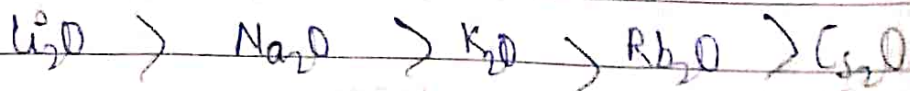
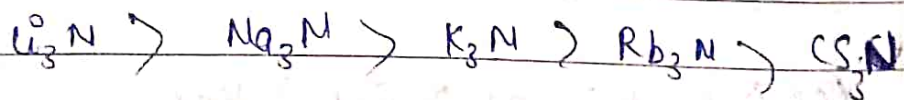
energy required to break bond.

Case-I → Ionic compounds having monoatomic anion.

TS →



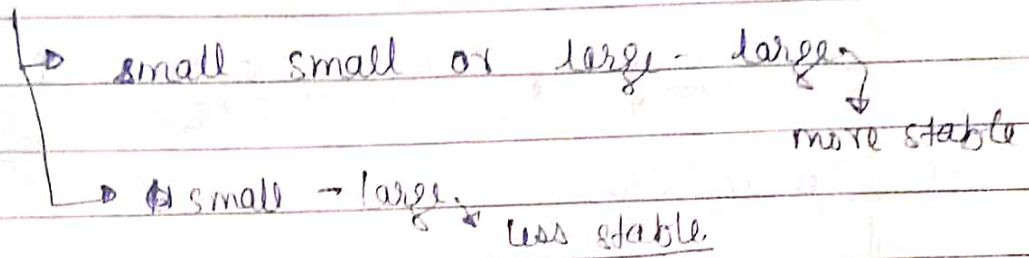
TS \propto L.E $\propto \frac{k_1 q_1 q_2}{r_1 + r_2}$



TS \rightarrow LiI > NaI > KI > RbI > CsI

Trick \rightarrow

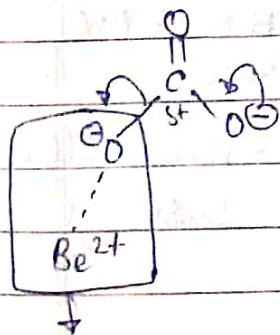
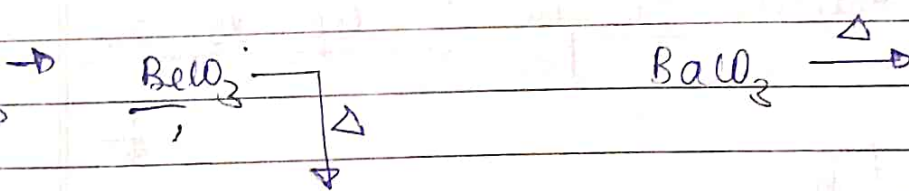
in case of thermal stability (monoatomic anion = small, polyatomic anion = large)



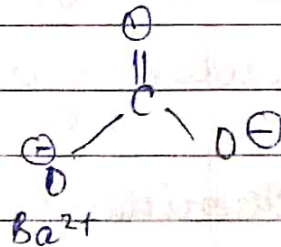
Case-2 \rightarrow Ionic compound possess polyatomic anion
 (CO_3^{2-} , SO_4^{2-} , O_2^{2-} , O_2^- , NO_3^- , ClO_4^- etc.)

TS $\propto \frac{1}{\text{polarisation}}$

MCO_3 (M \rightarrow Group II metal ion)

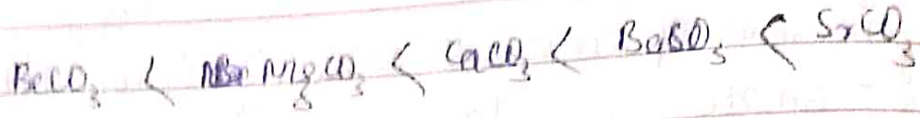


Since polarising power of Be^{2+} is more



Since polarising power of Ba^{2+} is less than Be^{2+} so to break we will need more energy to break BaCO_3 as compared to BeCO_3 .

polyatomic



Solubility of Ionic compound →

→ Solubility →

more K_{sp} → compound more soluble

↑
solubility

Qualitatively, solubility depends upon →

→ various factor like polarisation, C.E., H.E, entropy, etc

majorly Solubility depends on

polarisation

↳ solubility $\propto \frac{1}{I.C.} \propto \frac{1}{C.C.}$
polarisation

dominates

In case of pseudo/d-block element / non inert

H.E + L.E

Block element use it

In case of p/d block element compounds are there use polarisation.

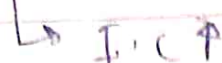
polarisation will not act where noble gas cations are present - (s-block)

Case 1 →

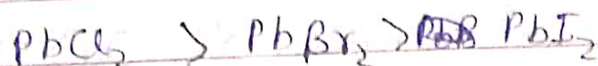
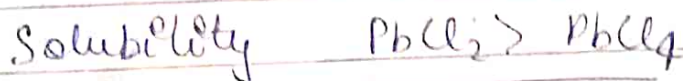
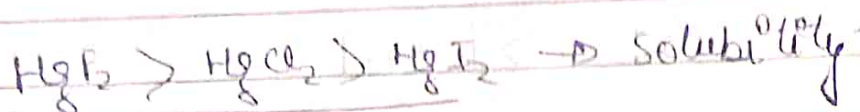
Polarisation is dominating factor →



polarisability ↓



solubility
character ↓



Case-2 → Born-Landé equation for s-block compound →

↓ Trick (only for s block compound)

Small - large or large - small are more soluble than small - small and large - large

$$LE \Rightarrow \frac{r_a r_c}{r_a + r_c}$$

assume anion as large except F^- ΔH_{LE}

$$\Delta H_{total} = \Delta H_{LE} + \Delta H_{HE}$$

$$\Delta H_{total} \propto \frac{1}{r_a + r_c} - \frac{1}{r_a} - \frac{1}{r_c}$$

Spontaneous (solubility) $\propto \Delta G = \frac{\Delta H - T\Delta S}{total}$



Case NO 1 \rightarrow

$$\Delta H_{total} =$$

$$|\Delta H_{LE}| > |\Delta H_{Hyd}|$$

spontaneous \propto solubility

\rightarrow Solubility of compounds $r_a \gg r_c$

$\Rightarrow LiClO_4 > NaClO_4 > KClO_4 > RbClO_4 > CsClO_4$

$$\Delta H_{total} = \frac{1}{r_a} - \frac{1}{r_a} - \frac{1}{r_c} = -\frac{1}{r_c}$$

\downarrow
($r_a \gg r_c$)

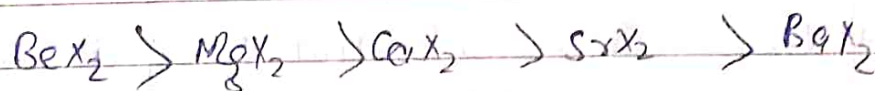
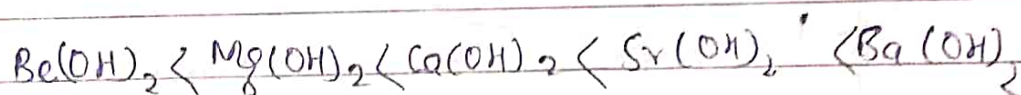
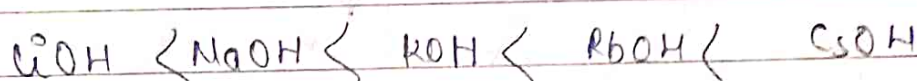
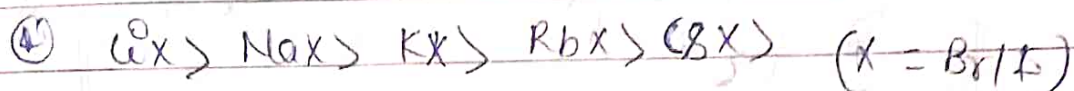
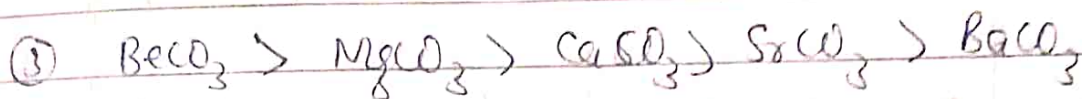
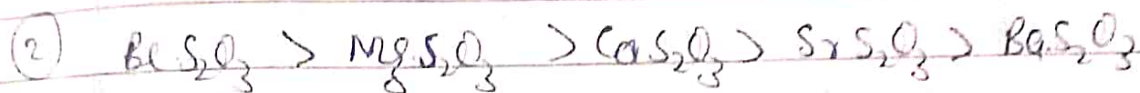
this is from hydration

then we can say that $\Delta H_{Hyd} > \Delta H_{LE}$
in magnitude.

thick \rightarrow for solubility assume all anion to be ~~very~~ large (except OH^-, F^-)

solubility \rightarrow

\downarrow
(smaller anion)



$X = \text{Cl}^-, \text{Br}^-, \text{I}^-$

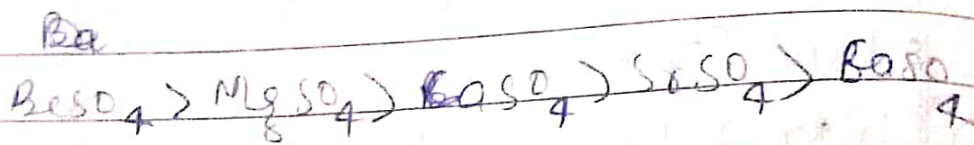
Q \rightarrow incorrect \rightarrow

(a) In alkali metal iodide solubility \uparrow down the group. due to \uparrow in LE.

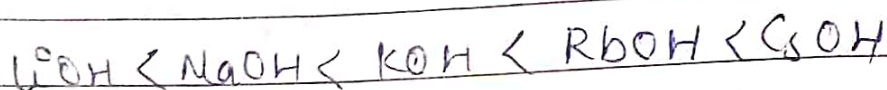
(b) In alkali metal iodide solubility \downarrow due to \uparrow in LE. down the group

(c) In alkali metal iodide solubility \downarrow due to \uparrow in HE.

Q) ~~None~~ all of them



↳ H.E decreasing



$\Delta H_{\text{Hy}} = - \frac{k_1 q_1 q_2}{r_c} \downarrow$ less soluble \ominus ive

$\text{L.E} = \frac{k_1 q_1 q_2}{r_c + r_a} \downarrow$

↳ due to decrease in L.E.

Q) BeSO_4 is soluble and BaSO_4 is insoluble in water at 25°C because -
low H.E of BaSO_4

↳ $\text{LiNO}_3 > \text{CsNO}_3$ solubility

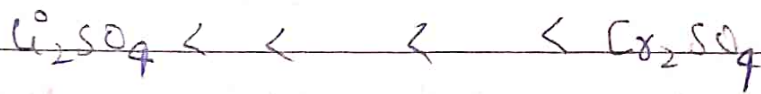
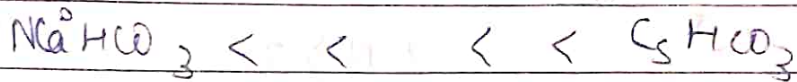
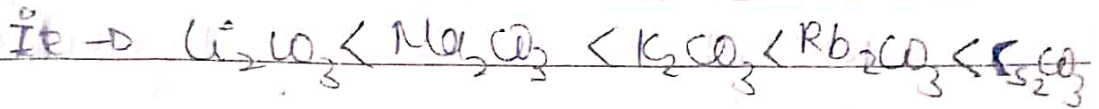
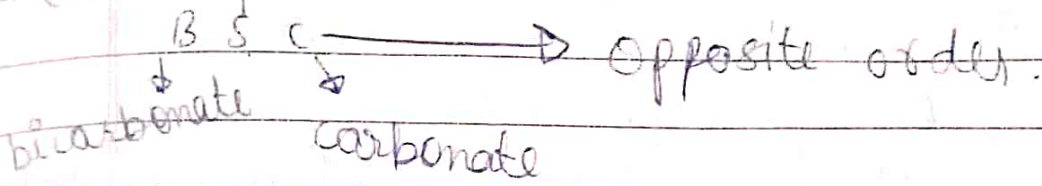
↳ due to decrease in H.E.

exceptions in solubility

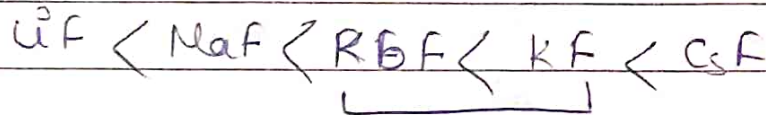
↳ alkali metals compounds

sulphates

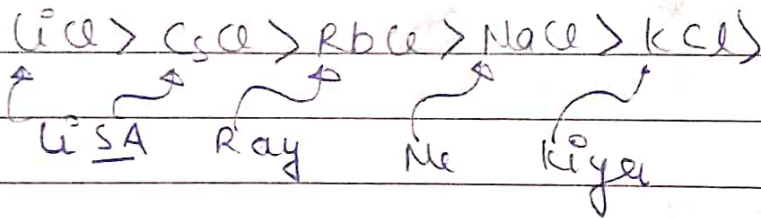
(1) ~~Carbonates~~



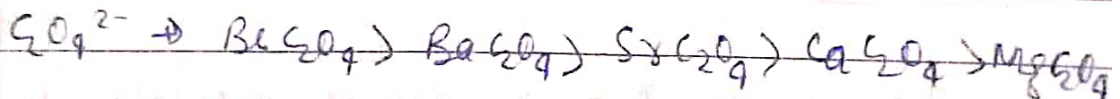
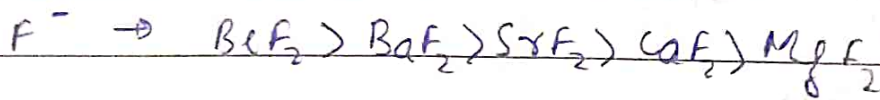
Fluorides \rightarrow

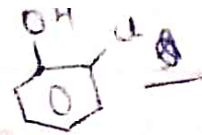


Chlorides \rightarrow



ALKALINE EARTH METAL \rightarrow



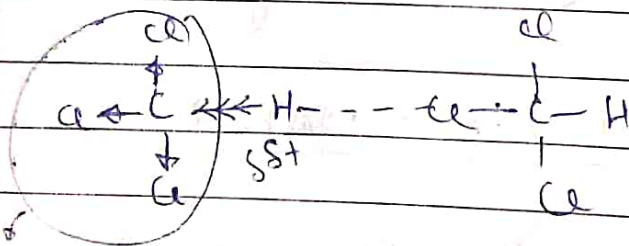
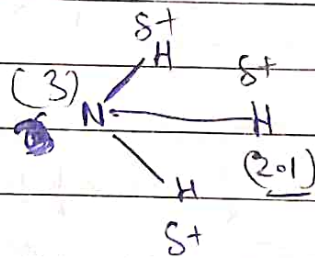


Molecular Forces (Weak Forces) B.E. $\leq 42 \text{ kJ/mol}$

→ HYDROGEN BONDING →

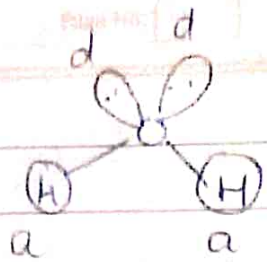
It is a weak interaction b/w H-atom
 $\text{N} | \text{O} | \text{F} | \text{C} \text{Cl}_3 | \text{C} \text{F}_3 | \text{CN} | \text{some time cell (O-hydroxy}$
 pheno)
 $\text{E.N} \geq 3$

According to modern concept →
 H-bonding is defined as weak interaction b/w L-acid and L-base

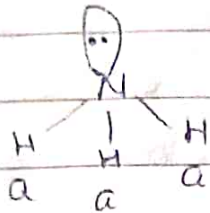


$N = 3 \cdot 14$

No of H-bond → No of acceptor site (H atom)
 + No of donal site (Lone pair)



no of H-bond per H_2O molecule
 $\Rightarrow 4$.



no of H-bond per NH_3 molecule \rightarrow
 $= 2$

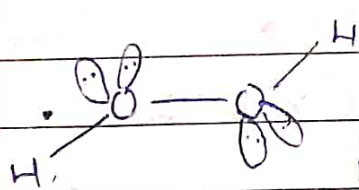
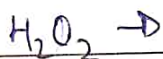
no of acceptor = 3
 no of donor = 3.

since no of donor is less so process will happen according to donor so.

no of H bond = $1+1 = 2$.

no of donor = no of acceptor

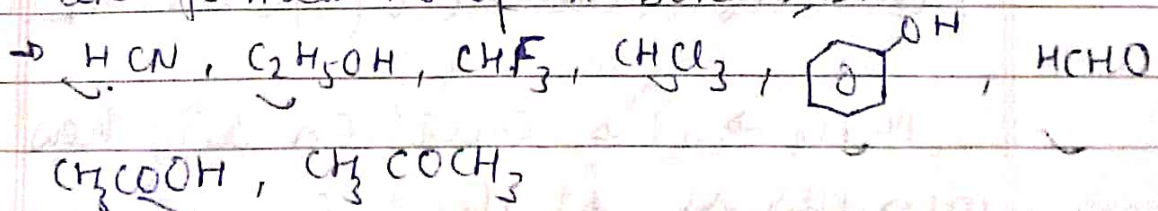
if this is not equal then take ^{min} value of each.



no of donor = 4
 no of acceptor = 2
 no of H-bond = $2+2 = 4$

Ans.

Q- calculate no of molecules undergo H-bonding and formed no of H-bond ≥ 2 .



solⁿ \Rightarrow 6 Ans

sp hybridise (N) ?
 $H-C \equiv N \rightarrow$ will form H-bonding

Types of H-bonding -:

Based on
molecularity

- ↳ Intermolecular H-bonding
- ↳ Intramolecular H-bonding

Based on B.E.

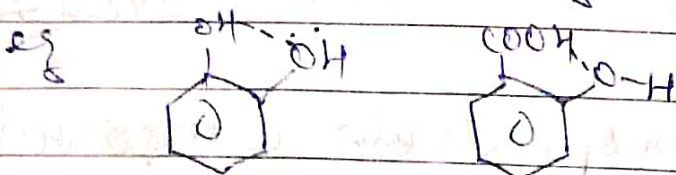
- ↳ Symmetrical H-bonding
($BE > 42$)
- ↳ Unsymmetrical
H-bonding
($8 \leq BE \leq 42$)

* Intermolecular H-bonding \rightarrow

H-bonding take place b/w molecules
 eg $\rightarrow H_2O - H_2O, N_2H_4 - N_2H_4, HClO_4 - HClO_4$ etc.

* Intramolecular H-bonding \rightarrow

H-bonding within molecule.



(condition: chelation (5/6 member))

$N_2H_4 \rightarrow$ it's chelation ring has 4 member so it don't form intermolecular H-bonding

good acceptor & good donor

similarly in solid state H_3BO_3 form intermolecular not intra.

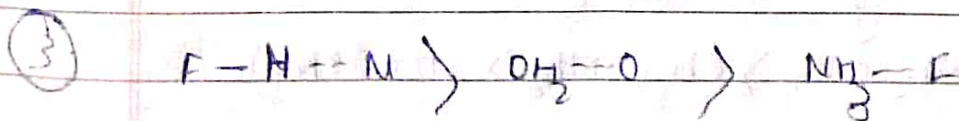
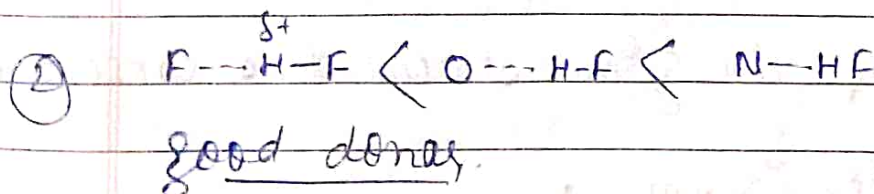
Physical property of molecule affected due to H-bonding \rightarrow

- ① Boiling point
- ② M.P.
- ③ viscosity
- ④ solubility
- ⑤ critical temp
- ⑥ ease of liquification
- ⑦ vapour pressure
- ⑧ from 'i' to 'e' physical property

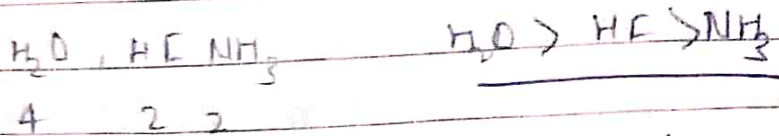
\propto intermolecular

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

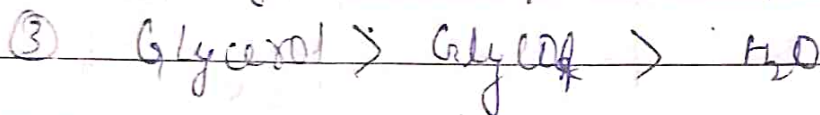
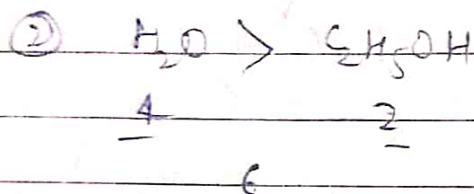
extent of H-bonding \propto (no of H-bonding) \times strength of H-bond



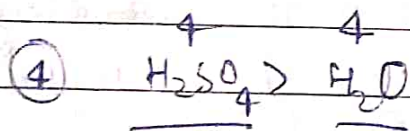
Boiling point \rightarrow



no of H-bond is same then look for strength of H-bond.



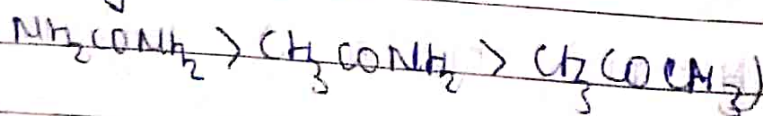
\hookrightarrow here we will look for surface area not strength. this is because H_2O H-bonding H_2O to atom (H₂O) in both of molecules are same.



\hookrightarrow surface area

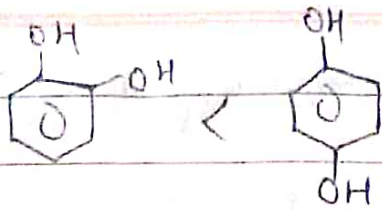
which of the given statement is correct \rightarrow

(a) solubility in water:



(b) ease of liquification

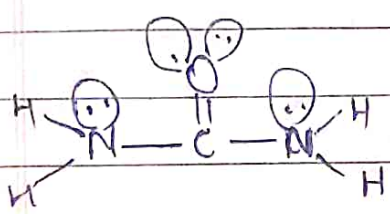




(C) $T_c = H_2O > HF > NH_3$

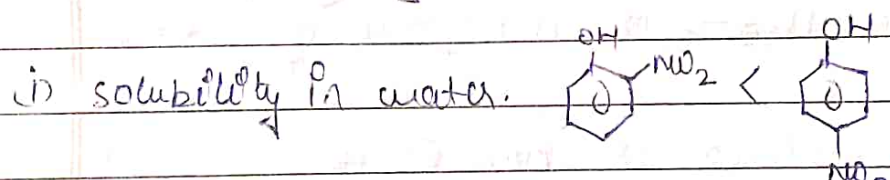
(D) Viscosity $\Rightarrow H_3PO_4 > H_2SO_4 > H_2O$

(E) All of these.



in $H_2O \rightarrow$ 8 - H-bonding
 in Urea \rightarrow 2

Q \rightarrow which of the given option is correct \rightarrow

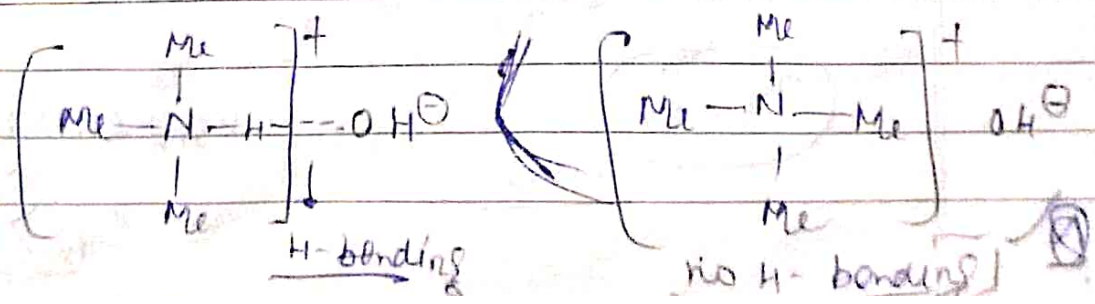


(2) ortho nitrophenol can be separate by p-nitrophenol using steam distillation.

(3) Basic character. $[N(Me)_4]^+ OH^- > [N(Me)_3H]^+ OH^-$

(4) B.P.: o-salicylaldehyde < p-salicylaldehyde.

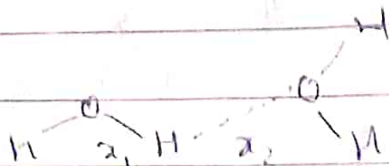
(5) all.



H-bonding based on bond energy

(1) Unsymmetrical H-bonding (p. 8-12 T/J)

when H-atom doesn't lie at mid point w/ different 'O' atom of two molecules



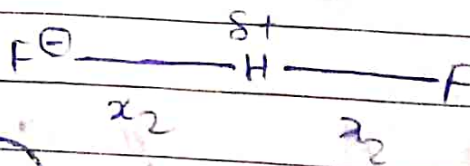
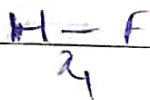
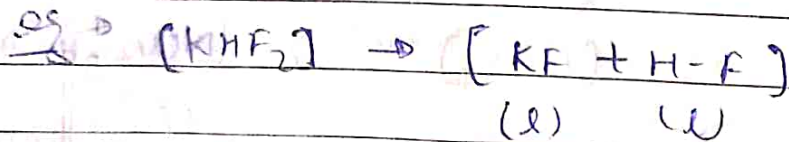
$x_2 < x_1$ unsymmetrical

→ Strong dipole-dipole interaction leads to unsymmetrical H-bonding

eg → H_2O-H_2O , $H_3PO_4-H_3PO_4$ etc

(2) Symmetrical H-bonding

when H-atom lies at mid point w/ two same electronegative atom.



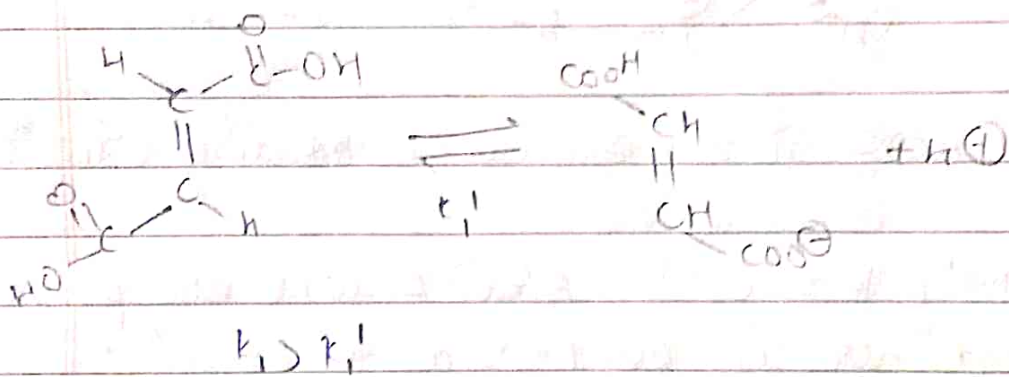
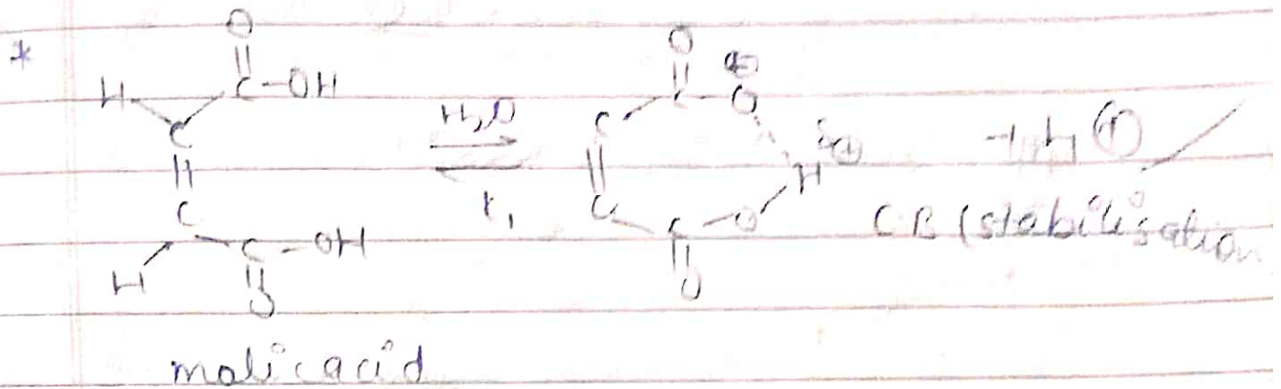
$x_2 > x_1$ Ans

Bond energy

$x_2 > x_1$

Asymmetrical π -bonding observed in ion (π -bond formation) and dipole (π -bond dipole)

Important compounds involved in H-Bonding \rightarrow



H-Bonding in alkali bicarbonates \rightarrow

Solid bicarbonates \rightarrow

$$\frac{\gamma_c}{\gamma_a} = 0.155 - 0.999$$

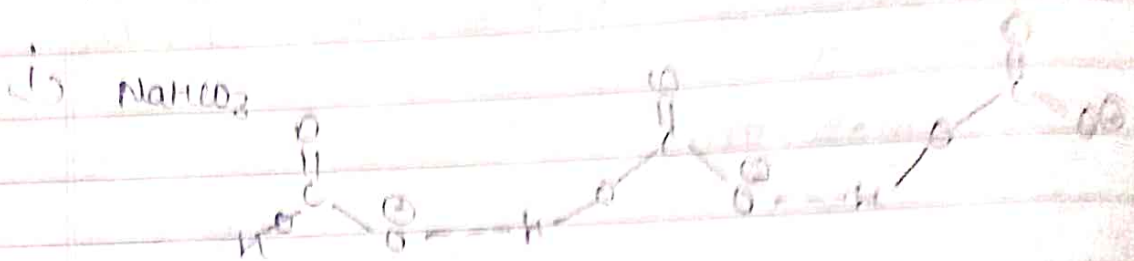
$$\frac{\gamma_w}{\gamma_a} = \text{very small doesn't exist}$$



✓ solid bicarbonates exist as dimeric (in solid)
 bond $(\text{NH}_4)_2\text{HCO}_3$

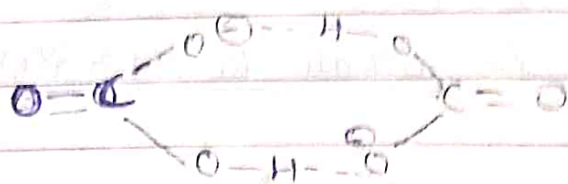
✓ $\text{Ca}(\text{HCO}_3)_2$ (aq) $\text{Ca}(\text{HCO}_3)_2$ (solid) ✓

M^+HCO_3^- (s) ($\text{M} = \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+$)



in HCO_3^- intramolecular H bonding also

(ii) M^+ (K^+ to Cs^+) bicarbonate formed dimer in solid via H-bonding.



best lattice $\rightarrow \text{KHCO}_3 > \text{RbHCO}_3 > \text{CsHCO}_3$

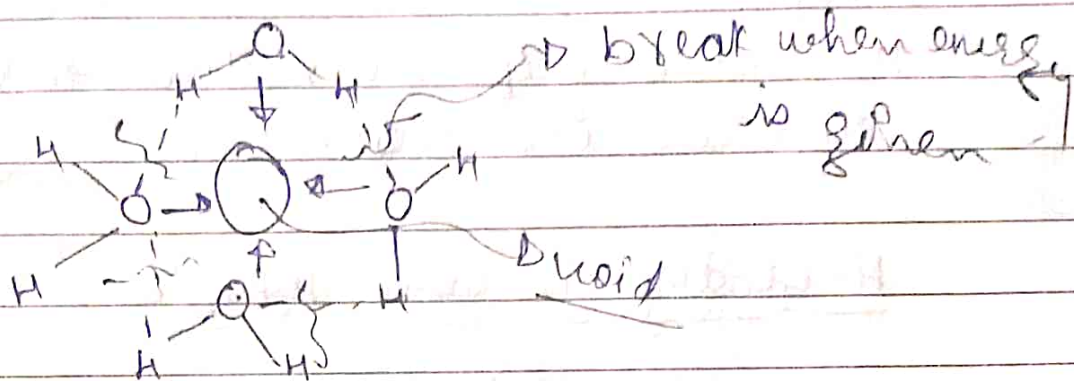
overall order $\rightarrow \text{NaHCO}_3 > \text{KHCO}_3 > \text{RbHCO}_3$

Solubility $\rightarrow \text{CsHCO}_3 > \text{RbHCO}_3 > \text{KHCO}_3 > \text{NaHCO}_3$

(17) ICE (solid H_2O) \rightarrow



ice at low temp exist in HCP (hexagonal closed packing) but it changes to CCP at very low temp.



at $4^\circ C$ density of water max^m

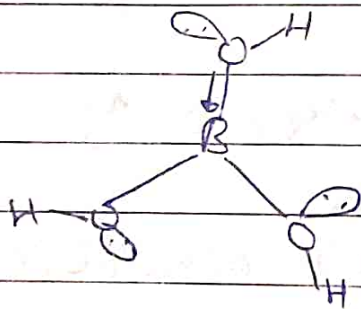
from $0^\circ C$ to $4^\circ C$ \rightarrow H-bond break and H_2O molecule occupied void space that leads to \downarrow in volume and \uparrow in density. till $4^\circ C$.

if temp $> 4^\circ$, H_2O molecule gain thermal energy and start expansion that leads to \uparrow in volume and \downarrow in ρ .

Application of H_2O via H-bond.

- (1) H-bonding helps in sticking of ice on wooden stick (ice cream stick) on stick.
- (2) H-bonding helps in preservation of aquatic life.
- (3) H-bonding helps in making thermal & electrical insulator.

H-bonding in solid H_3BO_3

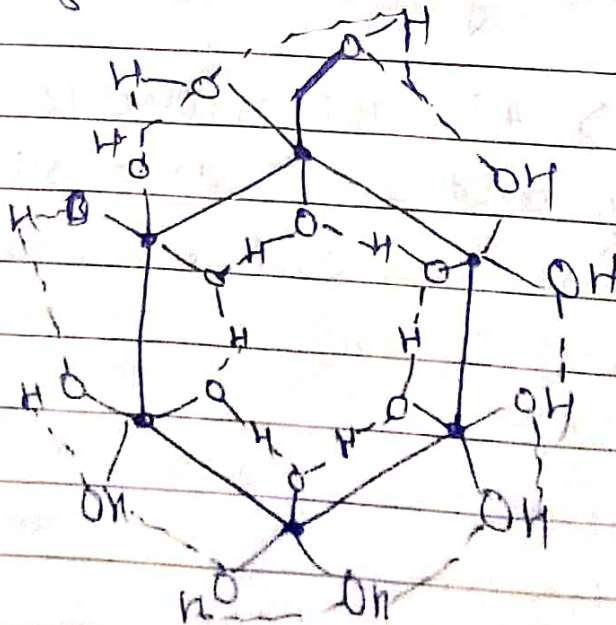


3 lone pair \times 3 H

total

6 H-bonding

One lone pair of each involve in back bonding.



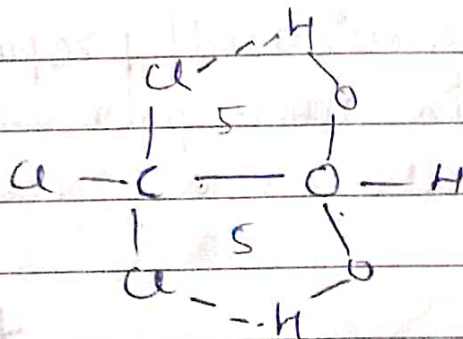
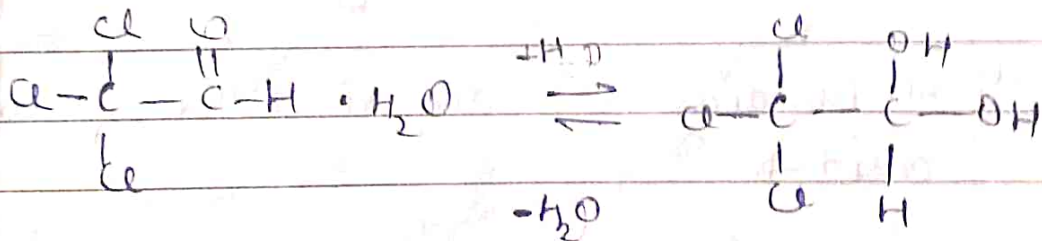
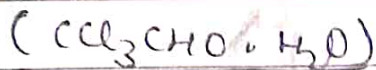
- 12 member ring }
- 8 member ring }

→ No of boron involved in 12 member ring = 0 in $B_2O_3(s)$

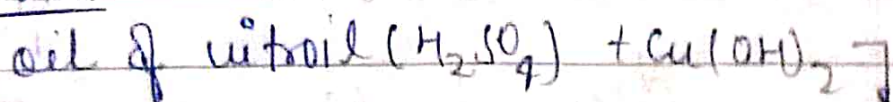
→ No of boron involved in 8 member ring \Rightarrow in $H_3BO_3(s)$

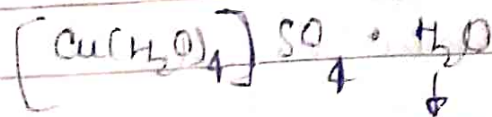
→ No of oxygen atom involved in 12 member ring 6 ✓

→ H-bonding in chloral hydrate \rightarrow

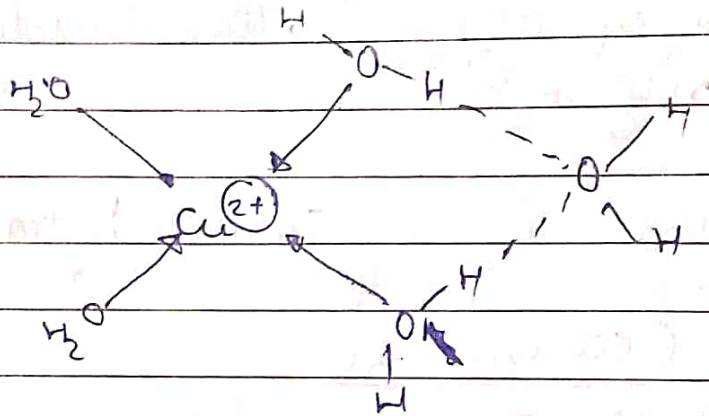
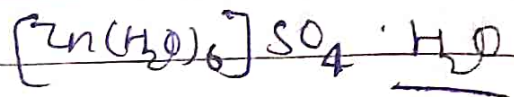
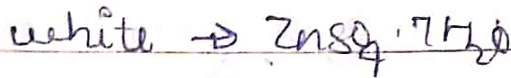
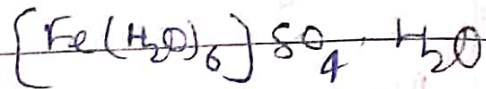
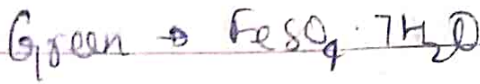


→ vitriol \rightarrow



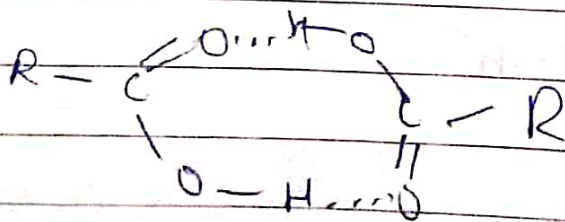


H-bonding



\rightarrow H-bonding in dimerisation of carboxylic acid \rightarrow

Formic acids | Acetic acid | propanoic acid
dimerised in non-polar solvent
Hence molecular mass double.



dimerisation

then can also dimerise in vapour too.

③ ionic solid affected due to polarisation →
 → LiX / MX_2 ($X \rightarrow Cl / Br / I$)

④ Molecular solids →
 eg → $H_2O / HF / CO_2 / P_4 / white / CS_2$ etc
 all van der Waal forces.

order of MP →

→ if ~~the~~ type of solid is different →

eg → Diamond } NaCl } white phosphorous
 ↓ ↓ ↓
 (covalent) (ionic) (molecular solids)
 3D

ca → Black phosphorous } ② CsCl } ③ Dry ice } ④ ice
 (3D-phosphorous } (ionic } (hydrogen }
 covalent } } }
 vanderwaal

1 > 2 > 4 > 3 >

Overall order → 1 > 2 > 3 > 4 of MP

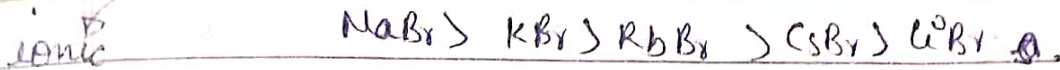
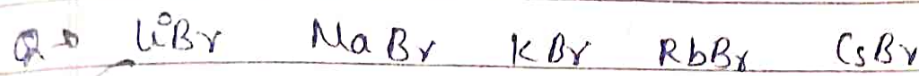
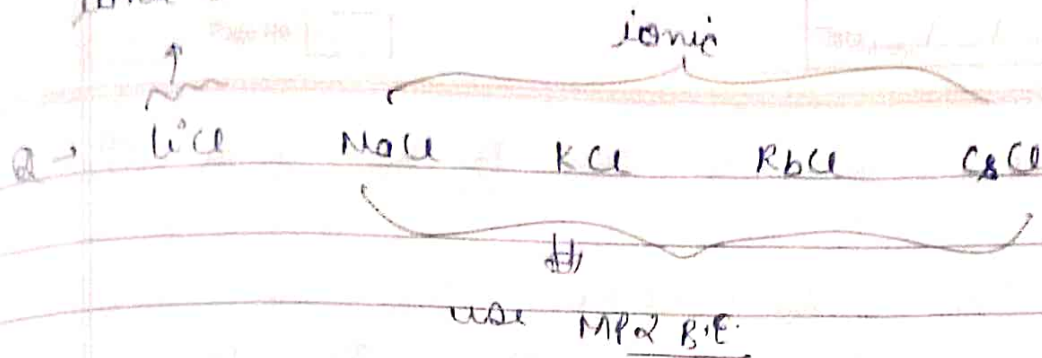
Q → $Li^+F^- > Na^+F^- > K^+F^- > Rb^+F^- > Cs^+F^-$ (all ionic)

if same then look for Lattice energy

LE ∝ MP

($\frac{ka}{r_0} \propto \frac{1}{r_0}$) →

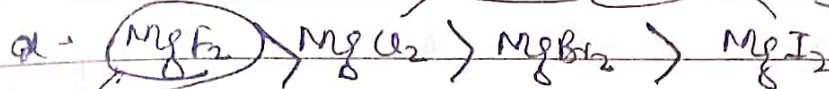
Ionic solid affected due to polarisation



affected due to polarisation

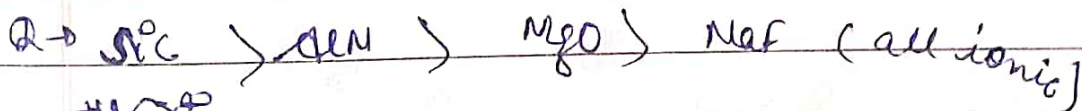
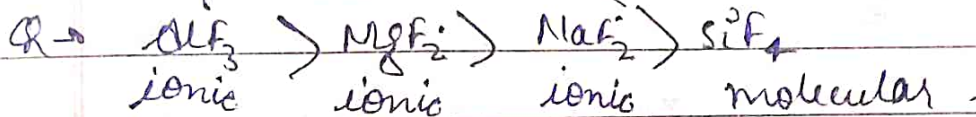
affected due to

polarisation

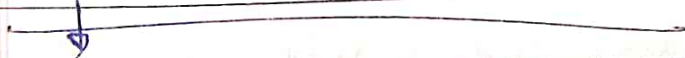


↑
ionic

MP & L.E.



↑
↑
↑



covalent 3D