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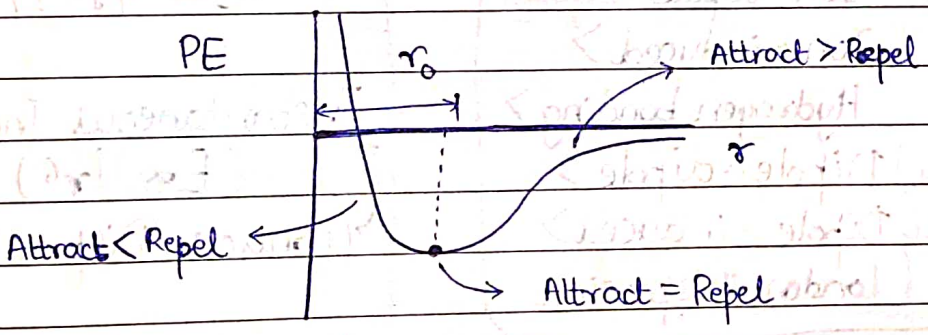
Chemical Bonding

- When two atoms of element approach each other, then ∃ force of attraction & repulsion.
- At min. dist where these two forces become equal, is called bond formation condition (equilibrium condition).
- Min. dist when bond formed is called bond length.



- When Attract > Repel, then PE ↓ (Energy release)
  ⇒ Stability ↑

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Chemical Bond

Inter-atomic (Strong)

- Metallic (b/w Metals)
- Ionic / Electrovalent (b/w Metals & Non Metals)
- Covalent (b/w Non-Metals)
- Coordinate

Intermolecular (Weak)

- Ion - Dipole Interaction ($E \propto 1/r^2$)
- Ion induced Dipole Int. ($E \propto 1/r^4$)
- Dipole Dipole Interraction (Kossem forces) ($E \propto 1/r^3$)
- Dipole induced Dipole Int. ($E \propto 1/r^6$) (Debye forces)
- Instantaneous Induced Dipole Int. ($E \propto 1/r^6$) (London Dispersion forces)
- Hydrogen Bonding

☆ Strength: Ion - dipole > Ion - induced > Van der Wall forces { Hydrogen bonding > Dipole - dipole > Dipole - induced > London Dispersion

Hydrogen Bonding

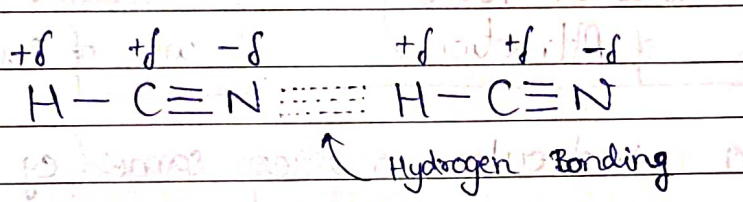
Shown by molecules in which H atom

directly attached with more EN atom. like F, O, N (EN ≥ 3).

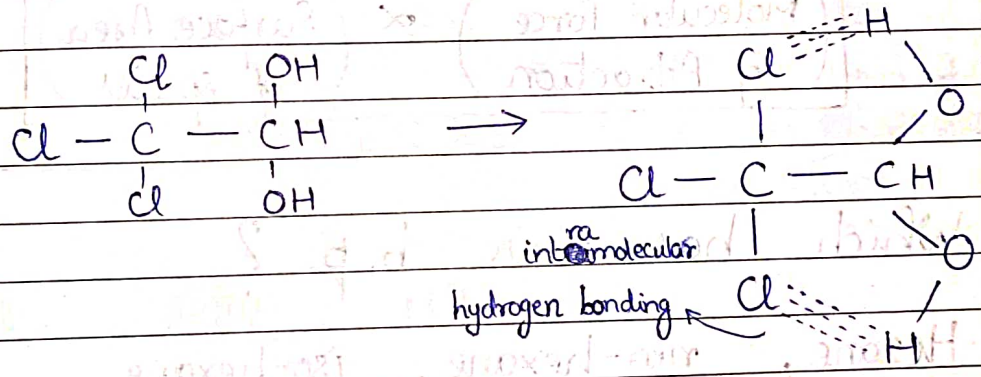
Sometimes, with Cl & sp hybridised C. (≡).

Eg: H−C≡N

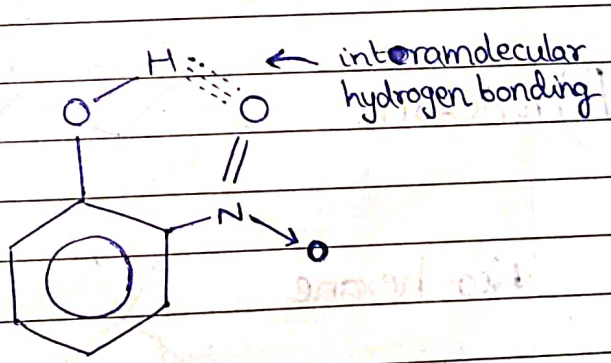
N, C ke ē cheen lega, C, H ke cheen lega.



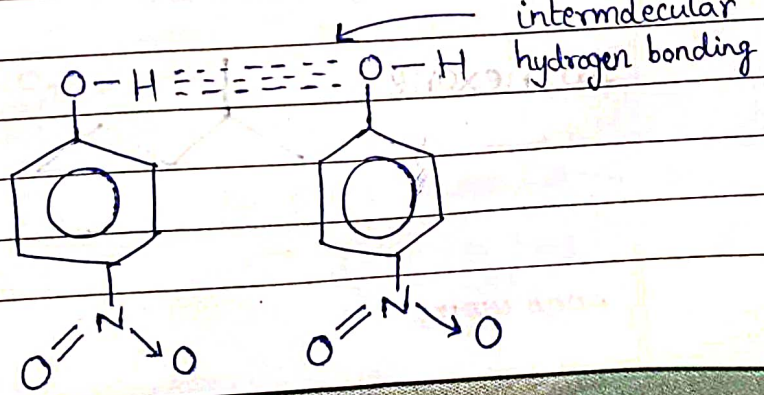
Eg:



Eg: Orthonitrophenol



Eg: Paranitrophenol



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Imp. Pts:

- $\left(\begin{matrix}\text{Boiling Pt.,} \\ \text{Melting Pt.}\end{matrix}\right) \propto$ (Molecular force of Attraction)

- When type of molecular forces same,

$$\left(\begin{matrix}\text{Molecular force} \\ \text{of Attraction}\end{matrix}\right) \propto \left(\begin{matrix}\text{Molecular / At.} \\ \text{wt. of substance}\end{matrix}\right)$$

- When molecular masses same (eg: isomers),

$$\left(\begin{matrix}\text{Molecular force} \\ \text{of Attraction}\end{matrix}\right) \propto \left(\begin{matrix}\text{Surface Area} \\ \text{of species}\end{matrix}\right)$$

Q) Which has max. b.p. ?

n-Hexane, neo-hexane, iso-hexane

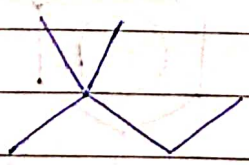
A) n-Hexane 

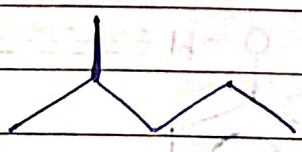
Max surface area

⇓

n-Hexane

max. b.p.

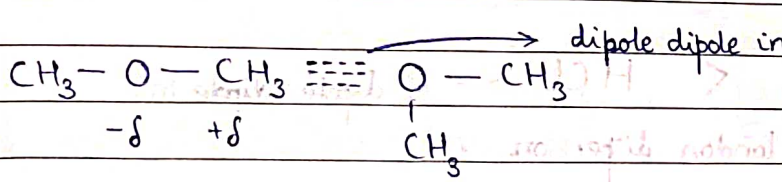
Neo-hexane 

Iso-hexane 

Q) Compare b.p. of CH_3-CH_2-OH & CH_3-O-CH_3.

A) $CH_3-CH_2-\underset{\text{causes hydrogen bonding}}{OH}$

$\Rightarrow$ B.P. : $CH_3-CH_2-OH > CH_3-O-CH_3$



Q) Compare force of intermolecular attraction in —

1) He, Ne, Ar, Kr, Xe

A) He < Ne < Ar < Kr < Xe — All forces london dispersion

$\Rightarrow$ Force $\propto$ Mass

2) HCl, HBr, HI, HF

A) HCl < HBr < HI < HF

(HCl, HBr, HI: Dipole-Dipole; HF: hydrogen bonding)

3) H_2S, H_2Se, H_2Te, H_2O

A) $H_2S < H_2Se < H_2Te < H_2O$

(H_2S, H_2Se, H_2Te: Dipole-Dipole; H_2O: hydrogen bonding)

4) F_2, Cl_2, Br_2, I_2

A) $F_2 < Cl_2 < Br_2 < I_2$ — All forces london dispersion

$\Rightarrow$ Force $\propto$ Mass

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5) CH_4, SiH_4, GeH_4, SnH_4

A) $CH_4 < SiH_4 < GeH_4 < SnH_4$ All forces london dispersion.
⇒ (force ∝ Mass)

★ 6) Cl_2 HCl

A) Cl_2 < HCl — dipole-dipole int.
└ london dispersion

★ 7) PH_3, AsH_3 NH_3 SbH_3 BiH_3

A) $PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$

In SbH_3 & BiH_3, mass ↑ ⇒ forces ↑.

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Ionic Bond

Whenever chem. bond formed by complete transfer of e^- from valence shell of 1 atom to valence shell of another atom.

Ionic bond is NON-DIRECTIONAL.

Eg: $Na(s) + \frac{1}{2} Cl_2(g) \longrightarrow NaCl(s)$

Born Haber Cycle

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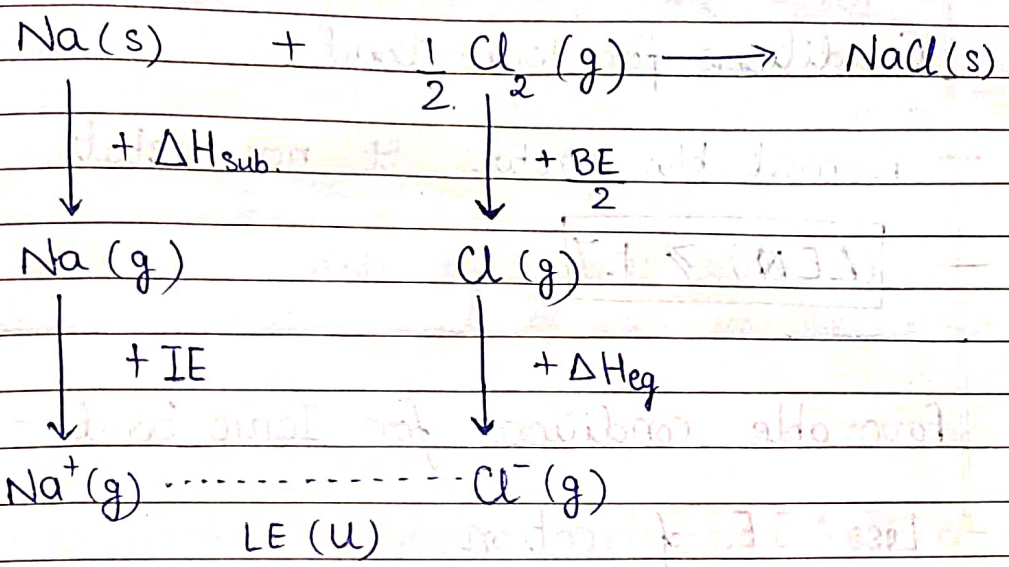

$$\Delta H_{rxn} = \underbrace{\Delta H_{sub} + IE + \tfrac{1}{2}BE}_{(+ve)} + \underbrace{\Delta H_{eg} + U}_{(-ve)}$$

- Lattice Energy (U) is calced. by Born Haber Cycle & E.A.

Q) Calc. L.E. of KCl given that. —

$\Delta H_{sub}(K) = 89$ kJ/mol, BE of $Cl_2 = 244$ kJ/mol,

IE of K = 425 kJ/mol, $\Delta H_{eg}(Cl) = -355$ kJ/mol,

Enthalpy of formation of KCl = −438 kJ/mol.

A) Just like NaCl,

$$\Delta H_{rxn} = \Delta H_{sub} + IE + \frac{BE}{2} + \Delta H_{eg} + U$$

$U = -719 \frac{kJ}{mol}$

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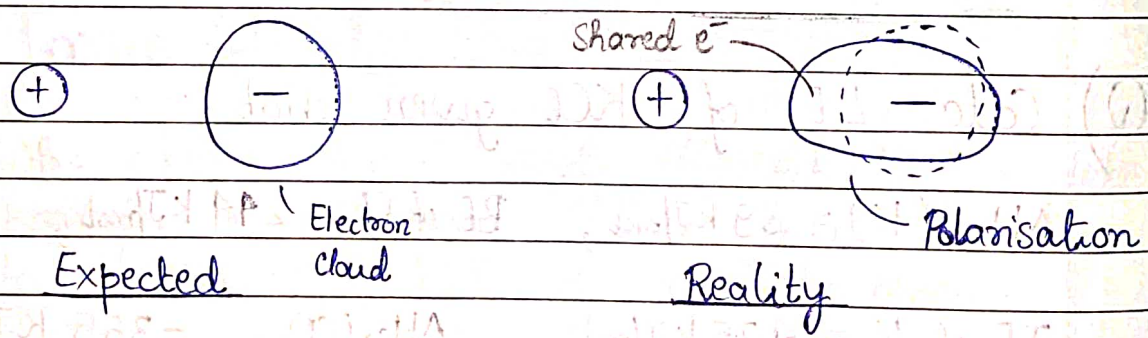
Conditions for Ionic Bond –

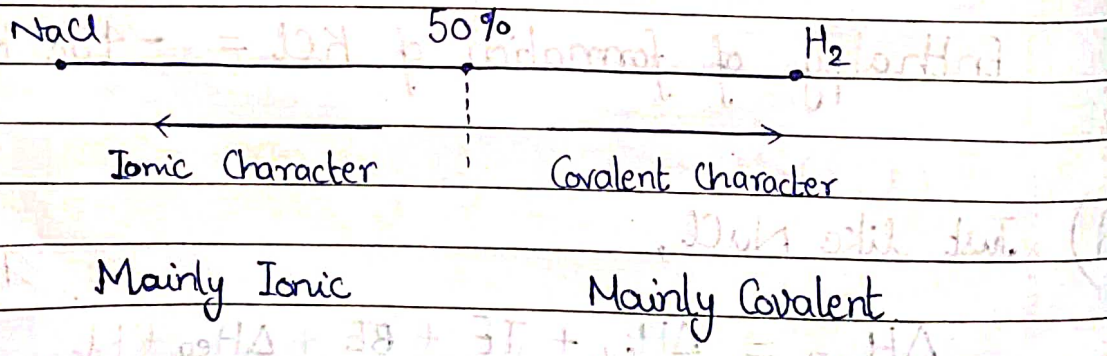
- formed b/w metals & non metals.
- $\boxed{(\Delta EN) \geq 1.7}$

Favorable conditions for Ionic Bond –

- Less IE of cation
- More |EA| of anion
- More |LE|

Covalent Nature in Ionic Bond –





If each ion (cation & anion) does NOT disturb the distr. of electron cloud of other ion, then it is said to be NON POLARISED.

In an ionic comp., upto some extent, the distr. of electron cloud of ion is disturbed by cation.

Polarisation: Distortion of electron cloud of anion due to cation.
(Ionic Potential)

Cation → Polarising Power (ability to polarise)

Anion → Polarisability (ability to get polarised)

Factors affecting Polarisation (Fajan's Rule) –

- Size of Cation: $\boxed{\text{Pol.} \propto \left(\frac{1}{\text{Size of Cation}}\right)}$

- Size of Anion: $\boxed{\text{Pol.} \propto (\text{Size of Anion})}$

- Charge on Ions: $\boxed{\text{Pol.} \propto (\text{Charge on Cation/Anion})}$

- Type of Cation (based on e^- config.):

• Noble gas EC – $\boxed{EC = ns^2np^6}$

Eg: Na^+, Mg^{2+}, Al^{3+}, Be^{2+}, K^+, Rb^+, ...

(18 valence e^-)

- Pseudo Noble Gas EC — $EC = ns^2np^6nd^{10}$

Eg: Zn^{2+}, Cd^{2+}, Hg^{2+}, Cu^+, Ag^+, Au^+, Pb^{4+}, ...

- (18+2) valence e^- — $EC = (n-1)s^2(n-1)p^6(n-1)d^{10}ns^2$

☆ Polarising Power of Cation

(Pseudo Noble gas config.) > (18+2 valence e^-) > (Noble gas config.)

Application —

- Polarisation $\propto$ (Covalent Character) $\propto$ $\left(\frac{1}{\text{Melt Pt.}}\right)$ $\propto$ $\left(\frac{1}{\text{Solubility in } H_2O}\right)$ $\propto$ (Color in sol^n)

Q) Arrange in order of inc. covalent character —

1) LiCl NaCl KCl RbCl CsCl

A) LiCl > NaCl > KCl > RbCl > CsCl
(Anion same, Cation Small ⇒ Pol. ↑)

2) BeF_2 MgF_2 CaF_2 SrF_2 BaF_2

A) BeF_2 > MgF_2 > CaF_2 > SrF_2 > BaF_2
(Anion same, Cation Small ⇒ Pol.↑)

3) Na_2O MgO Al_2O_3

A) $Na_2O < MgO < Al_2O_3$

Charge: $Na^+ < Mg^{2+} < Al^{3+}$

Size: $Na^+ > Mg^{2+} > Al^{3+}$

$\Rightarrow$ Pd.: $Na_2O < MgO < Al_2O_3$

4) $NaCl$ $AgCl$

A) $NaCl < AgCl$ (Ag $\rightarrow$ Pseudo Noble gas config.)

5) $CaCl_2$ $SnCl_2$ $CdCl_2$

A) $CaCl_2 < SnCl_2 < CdCl_2$ (Cd^{2+} $\rightarrow$ Pseudo Noble gas config; Sn^{2+} $\rightarrow$ 18+2, Ca^{2+} $\rightarrow$ Noble gas config.)

☆6) $ZnCl_2$ $CdCl_2$ $HgCl_2$

A) $ZnCl_2 < CdCl_2 < HgCl_2$ (Hg^{2+} $\rightarrow$ Pseudo Noble; Cd^{2+} ↗ Zn^{2+} ↗) Can't compare

(Z_{eff}: Hg > Cd > Zn)

7) $SnCl_4$ $SnCl_2$

A) $SnCl_4 > SnCl_2$ (Sn^{4+} $\rightarrow$ PNGC; Sn^{2+} $\rightarrow$ (18+2) config.)

8) LiI NaI

A) $LiI > NaI$ (Size: Li < Na)

☆9) AlF_3 $AlCl_3$

A) $AlF_3 < AlCl_3$ (Size: Cl > F)

GOOD WRITE VERY ionic.

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Q) Compare solubility in H_2O —

1) $LiCl$ $BeCl_2$ BCl_3

A) $LiCl$ > $BeCl_2$ > BCl_3 (Charge: $B^{3+} > Be^{2+} > Li^+$; Size: $B^{3+} < Be^{2+} < Li^+$; Pol.: $B^{3+} > Be^{2+} > Li^+$)

★ 2) LiI NaI

A) $LiI < NaI$ (Exception: as solubility of s block salts dec. down group generally)

3) Ag_2O Ag_2S

A) $Ag_2O > Ag_2S$ (Size: S > O; Pol.: S > O)

4) BeF_2 $BeCl_2$ $BeBr_2$ BeI_2

A) $BeF_2 > BeCl_2 > BeBr_2 > BeI_2$

5) AgF $AgCl$ $AgBr$ AgI

A) $AgF > AgCl > AgBr > AgI$ (Size of Anion ∝ Pol.)

6) PbF_2 $PbCl_2$ $PbBr_2$ PbI_2

A) $PbF_2 > PbCl_2 > PbBr_2 > PbI_2$ (Size of Anion ∝ Pol.)

7) $HgCl_2$ $HgBr_2$ HgI_2

A) $HgCl_2 > HgBr_2 > HgI_2$ (Size of Anion ∝ Pol.)

GOOD WRITE

★ • Predominantly Ionic Comp. conduct ↯ in both AQUEOUS & MOLTEN FORM

• Polar Covalent Comp. conduct ↯ only in AQUOUS.

— Thermal Stability :

1 element/atom

Cl- ~~Monoatomic~~ Anion.

$$\left(\frac{\text{Therm.}}{\text{Stab.}}\right) \propto LE \propto \left(\frac{\text{Charge}}{\text{Size}}\right)$$

Eg: Therm. Stab. : $LiF > LiCl > LiBr > LiI$

" : $NaF > NaCl > NaBr > NaI$

" : $LiF > NaF > KF > RbF > CsF$

★ " : $BeF_2 > MgF_2 > CaF_2 > SrF_2 > BaF_2$

VERY covalent

" : $Li_2O > Na_2O > K_2O > Rb_2O > Cs_2O$

" : $Li_3N > Na_3N > K_3N > Rb_3N > Cs_3N$

" : $LiH > NaH > KN > RbH > CsH$

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C2 – Multi element/Anion (atom)

$$\left(\text{Therm. Stab.}\right) \propto \left(\frac{1}{\text{Polarisation}}\right)$$

Eg: Therm. Stab: $Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$

" : $BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$

" : $Li_2SO_4 < Na_2SO_4 < K_2SO_4 < Rb_2SO_4 < Cs_2SO_4$

Be^{2+} $[O-O]^{2-}$ ← Multi atoms

" : $BeO_2 < MgO_2 < CaO_2 < SrO_2 < BaO_2$

" : $Ag_2CO_3 < Li_2CO_3 < Na_2CO_3$

– Solubility : (for p block : HE > LE dominant ; for d block : Fajan's Rule dominant)

Generally, $$\left(\text{Solubility in } H_2O\right) \propto \left(\frac{1}{\text{Polarisation}}\right)$$

Exceptions :

- On moving down group in s block, solubility of most salt dec. (HE becomes dominant factor over polarisation).
- But in alkali metals, solubility of fluorides (F^-), OH^-, HCO_3^- & CO_3^{2-} inc. down the group.
- But in alkali earth metals, solubility of F^-, OH^- & HCO_3^- inc. down the group.

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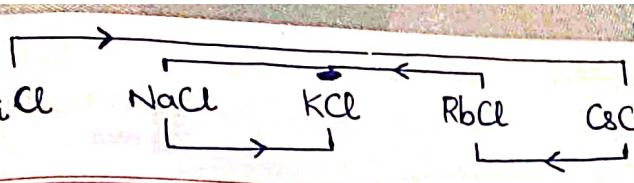

- In alkali earth metals, among fluorides, BeF_2 has highest solubility (due to high HE)

Q) Compare solubility —

1) $LiNO_3 > NaNO_3 > KNO_3 > RbNO_3 > CsNO_3$
(Generally solubility dec.)

2) $LiClO_4 > NaClO_4 > KClO_4 > RbClO_4 > CsClO_4$
(Generally solubility dec.)

3) $LiOH < NaOH < KOH < RbOH < CsOH$
(Exception in Alkali Metal Salts)

4) $Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$
(Exception in Alkali Metal Salts)

5) $NaHCO_3 < KHCO_3 < RbHCO_3 < CsHCO_3$
(Exception in Alkali ~~Earth~~ Metal Salts)

6) $LiF < NaF < KF < RbF < CsF$
(Exception in Alkali Metal Salts)

7) $BeCO_3 > MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$
(NOT an exception)

8) $LiBr > NaBr > KBr > RbBr > CsBr$
(Generally solubility dec.)

9) $BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$
(Generally solubility dec.)

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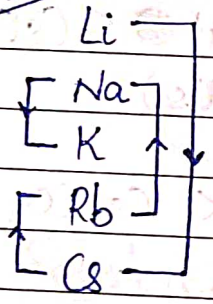
10) $Be(NO_3)_2 > Mg(NO_3)_2 > Ca(NO_3)_2 > Sr(NO_3)_2 > Ba(NO_3)_2$
(Generally solubility dec.)

☆ 11) $MgF_2 < CaF_2 < SrF_2 < BaF_2 < BeF_2$
(Exception in Alkali Earth Metals)

☆ 12) $NaI > LiI > KI > RbI > CsI$
Exception (Generally solubility dec.)

☆ 13) $LiCl > CsCl > RbCl > NaCl > KCl$

Chlorides



Covalent Bond

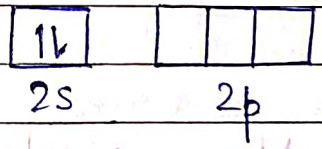
Bond formed b/w atoms by mutual sharing of e^- is known as covalent bond.

- It is formed b/w 2 non-metals.
- $(\Delta EN) \leq 1.7$

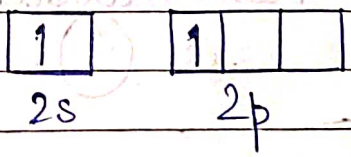
Covalency : (# Covalent bonds) + (# Coordinate bonds).

★ (# simple covalent bonds) = (# unpaired e^- in ground/excited state)

Eg – 1) Be = $[He]\,2s^2$



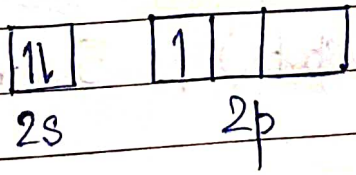
$Be^* = [He]\,2s^1\,2p^1$



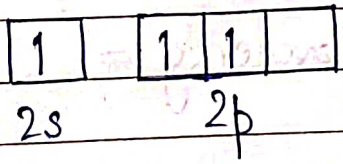
Covalency = 2 (in excited state)

Max. Covalency = 4 (2 vacant orbitals can make coordinate bonds)

2) B = $[He]\,2s^2\,2p^1$



$B^* = [He]\,2s^1\,2p^2$



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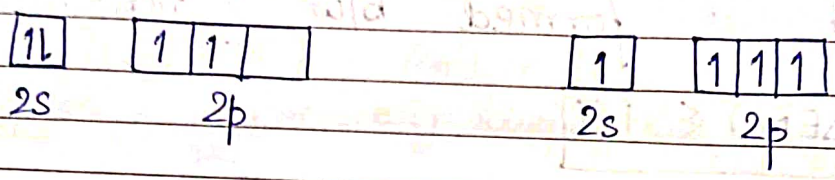
Covalency = 3 (in excited state), 1 (in ground state)

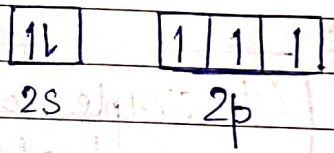
Max. Covalency = 4 (1 vacant orbital can make coordinate bond)

3) $C = [He]\ 2s^2\ 2p^2$ $\quad C^* = [He]\ 2s^1\ 2p^3$



Covalency = 2 (in ground state), 4 (in excited state)

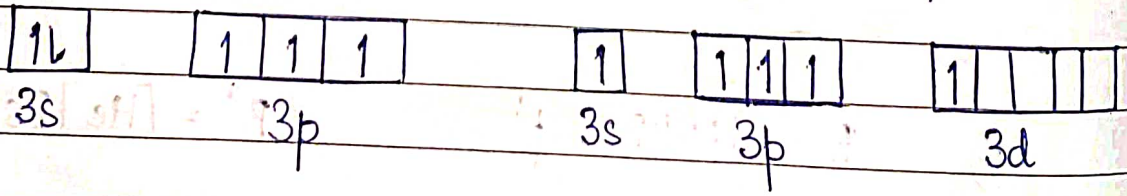
4) $N = [He]\ 2s^2\ 2p^3$



Covalency = 3 (in ground state) $\quad$ Max. Covalency = 4 (can donate 1 lone pair)

★ Max. covalency of 2nd period elements is (4).

5) $P = [Ne]\ 3s^2\ 3p^3$ $\quad P^* = [Ne]\ 3s^1\ 3p^3\ 3d^1$



Covalency = 3 (in ground state), 5 (in excited state)

(First e^- from 3p excites, then e^- from 3s excites)

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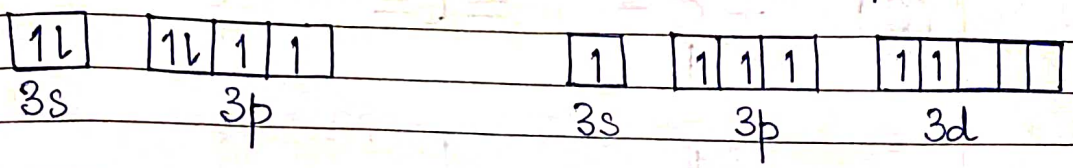
6) $S = [Ne]\,3s^2\,3p^4$ $\qquad$ $S^{**} = [Ne]\,3s^1\,3p^3\,3d^2$



Covalency = 2 (in ground state), 4 (in 1st exited state), 6 (in 2nd excited state).

7) $Cl = [Ne]\,3s^2\,3p^5 \Rightarrow$ Covalency = 1 (Ground), 3 (1st), 5 (2nd), 7 (3rd).

Lewis Octet Theory

It disscusses concept of shared pair (bond pair) and unshared pair (lone pair) of valence e^-s.

It states that any atom completes it octet (or duplet for H), anyhow.

Simple Covalent Bond

- Single Covalent Bond (Eg: HCl, Cl_2, NH_3, ...)
- Double Covalent Bond (Eg: O_2, CO_2, ...)
- Triple Covalent Bond (Eg: N_2, C_2H_2, ...)

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(C) $-\overset{|}{\underset{|}{C}}-$ $=C=$ $\equiv C-$ $-C\equiv$

(N) $-\overset{|}{N}-$ $N=$ $N\equiv$

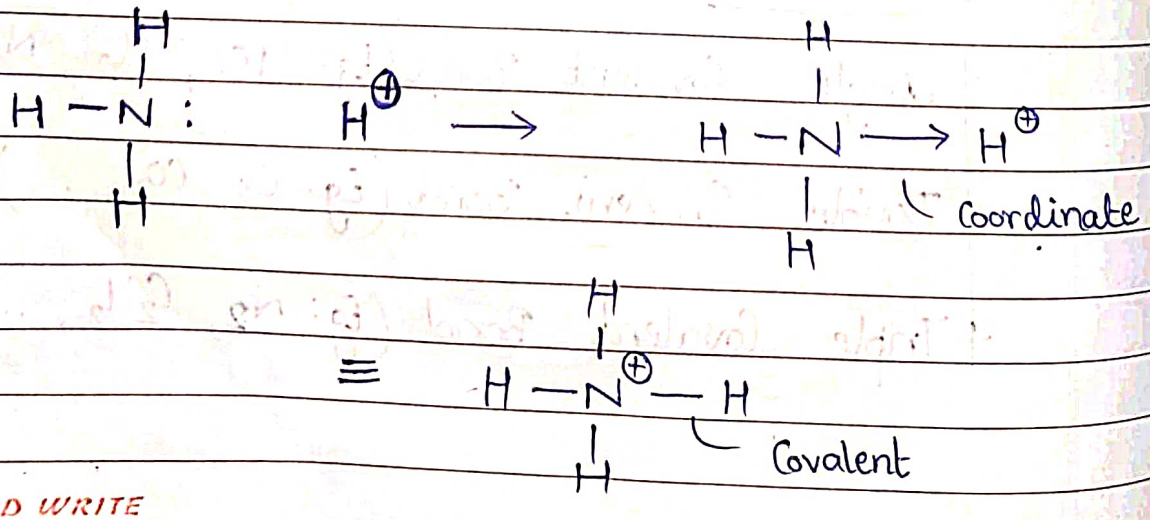
(O) $-O-$ $O=$

(F) $F-$

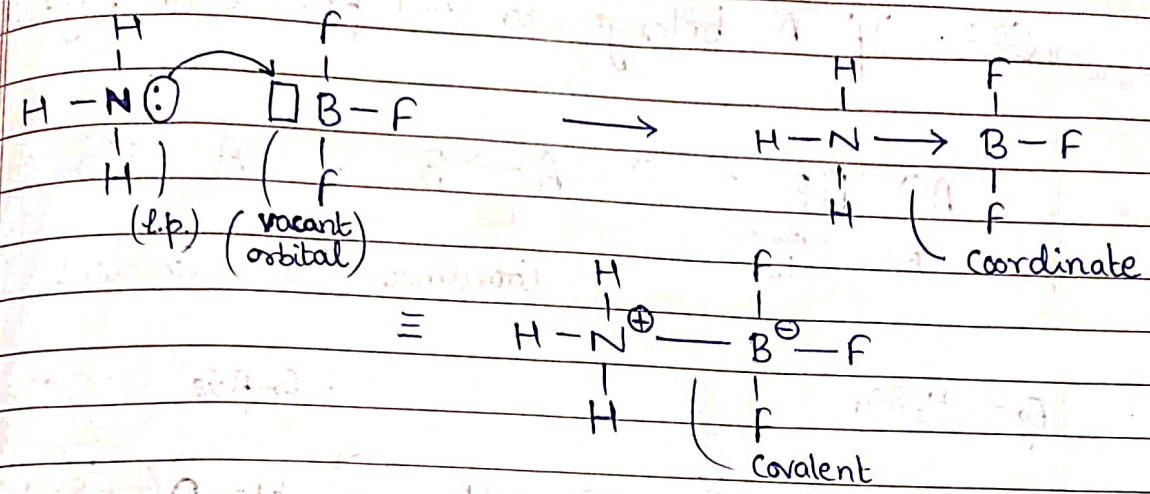
Coordinate Bond

During formation of bond, the $\bar{e}$ pair (lone pair) is donated by 1 atom and shared by both atoms, so as each atom completes its octet. It is ALWAYS a σ bond.

Eg: NH_4^+



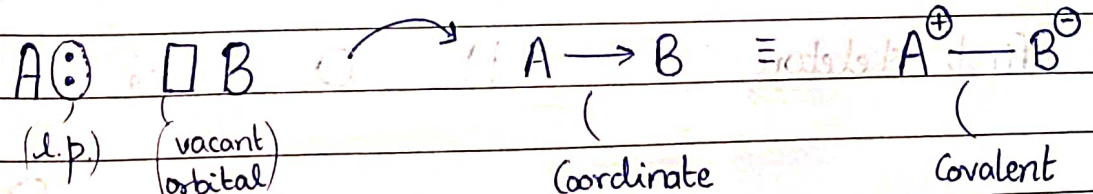
H_3NBF_3



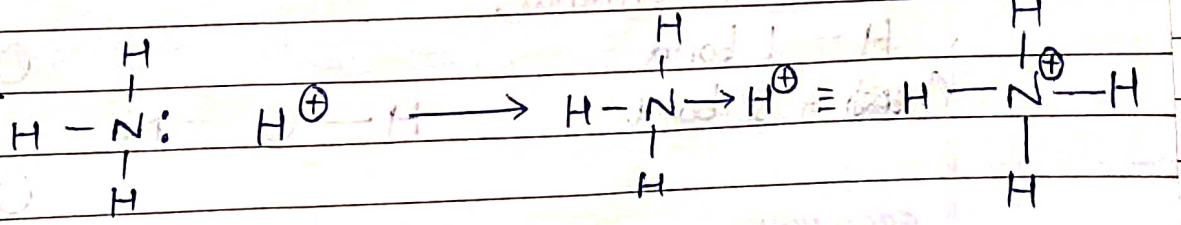
Conversion of Coordinate Bond into Simple Covalent Bond —

A (must have l.p. of e^-s) B (Incomplete Octet & Vacant Orbital)

Cl: If A belongs to 2nd period.



Eg - NH_3



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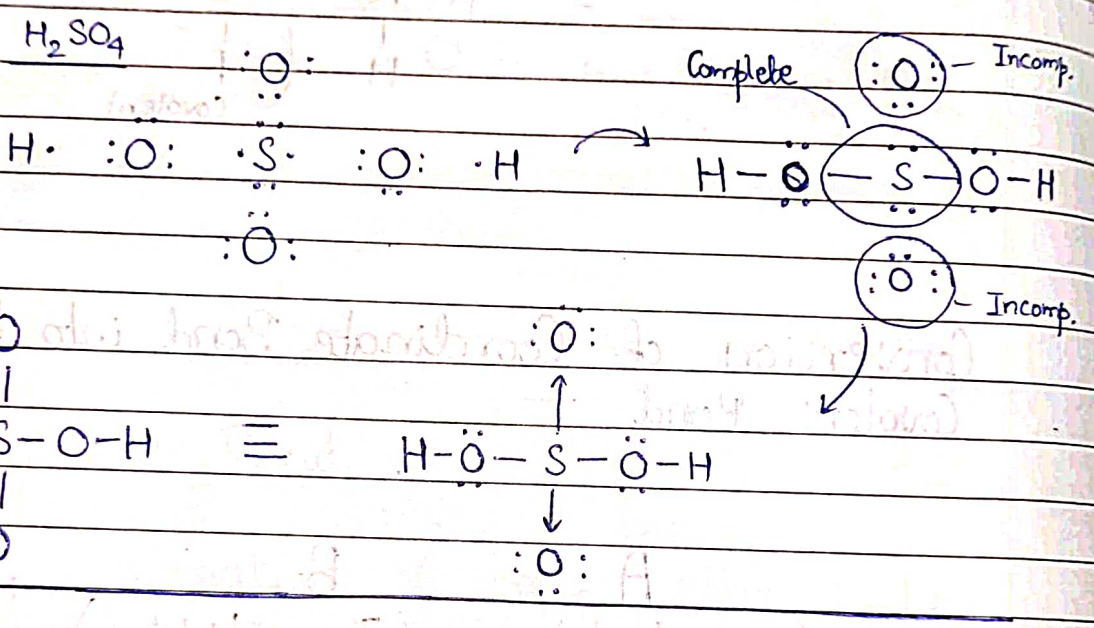
C2: If A belongs to 3rd period or higher.

A(:) □B → A → B ≡ A = B

(l.p.) (vacant orbital) (Coordinate) (Covalent)

Eg- H_2SO_4



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How to draw Lewis Dot Structure

Eg: HNO_3

First skeleton, H O N

Start with terminal,

H — 1 bond

O — 2 bond

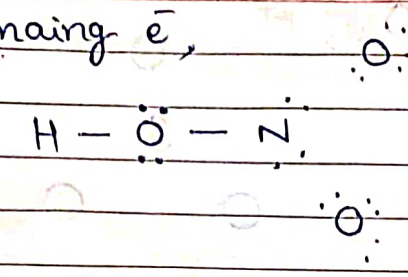
H — O — N

O

O

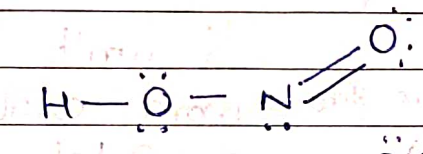
O

Now write remaing $\bar{e}$,

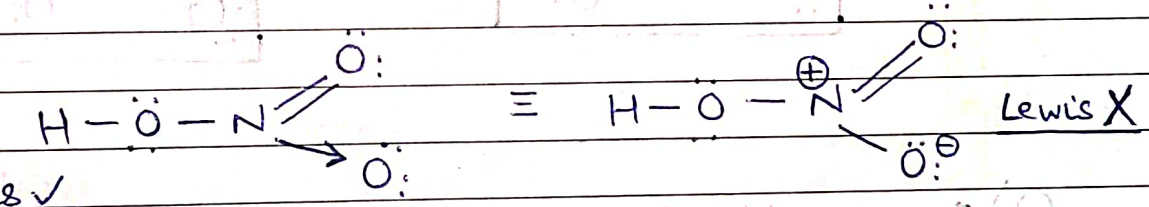


N can't make single bond with remaing O atom, as O req. 2 bonds.

Hence,



Since remaining O incomplete octet, and all others have complete octet; N gives its l.p.



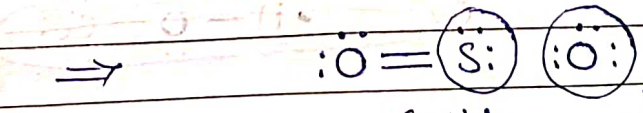
Lewis ✓ ≡ Lewis X

Q) Draw SO_2

A) Skeleton, O S O

O double bond with S as it can't have 1 bond

$O=S\ O \Rightarrow$



Complete Octet — Incomplete octet

$\Rightarrow$ $:\ddot{O}=\ddot{S}\rightarrow\ddot{O}:$ Lewis ✓ ≡ Lewis X $:\ddot{O}=\ddot{S}=\ddot{O}:$

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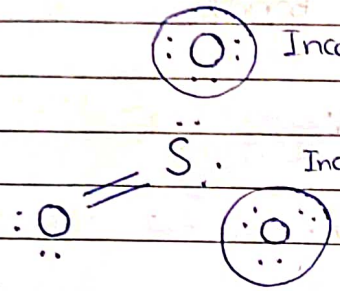
Q) Draw SO_3.

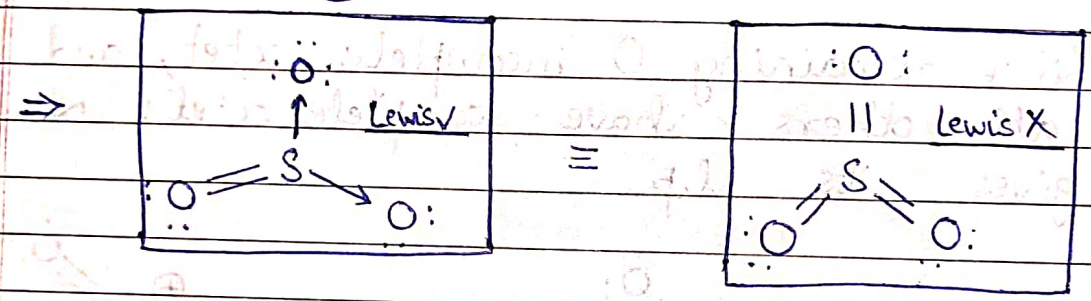
A) Skeleton,

O
S
O O

O makes 2 bonds with S as O can't have 1 bond.



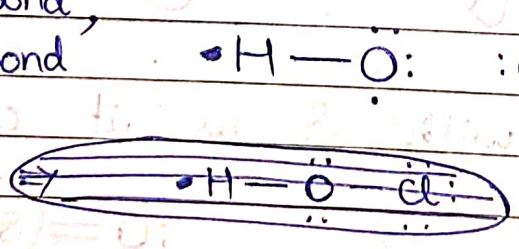
S can't make any more covalent as ⇒ Octet expand.

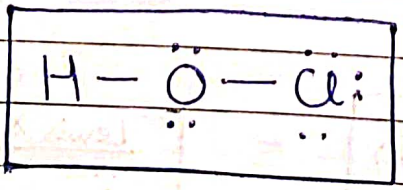


Q) Draw HClO.

A) Skeleton, H O Cl

H – 1 bond,
Cl – 1 bond



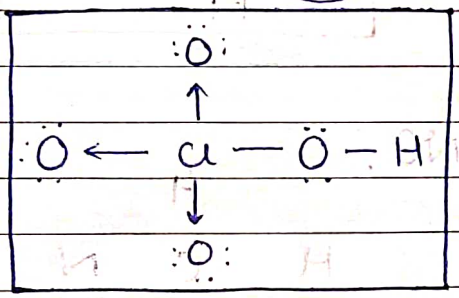


Q) Draw $HClO_4$.

A) Skeleton,

H – 1 bond,
O – 2 bonds,

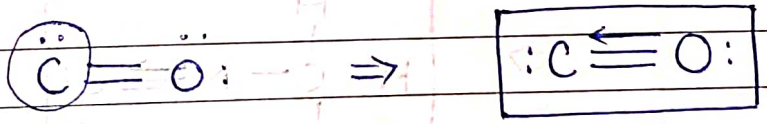
⇒



Q) Draw CO.

A) Skeleton,

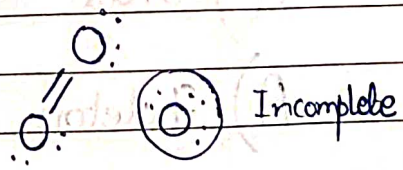
O – 2 bonds,



Incomplete

Q) Draw O_3.

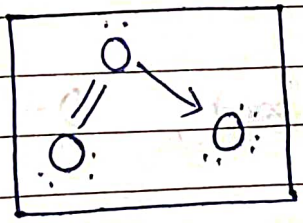
A) Skeleton,



Incomplete

O – 2 bonds,

⇒



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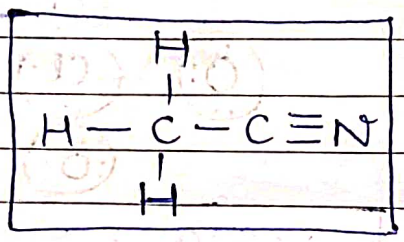
Q) Draw CH_3CN.

A) Skeleton,

H C C N

H

H – 1 bond,
N – 3 bond,
C – 4 bond,



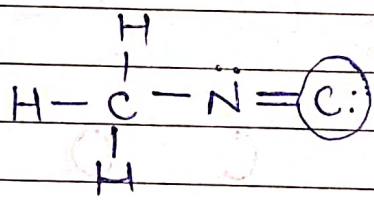
Q) Draw CH_3NC.

A) Skeleton,

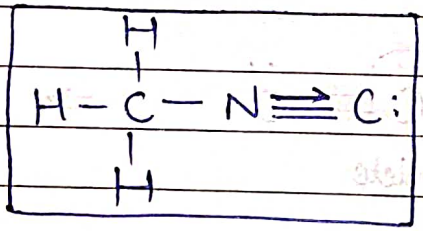
H C N C

H

H – 1 bond,
N – 3 bond,
C – 4 bond,



⇒



Q) Draw H_2CO_3.

A) Skeleton,

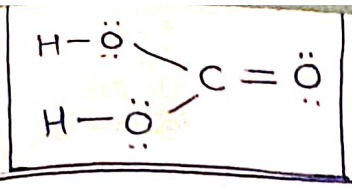
O H

O C

O H

H – 1 bond, O – 2 bond, C – 4 bond

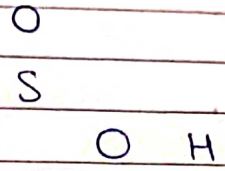
GOOD WRITE



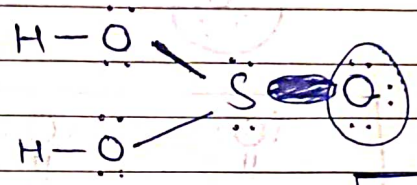
Q) Draw SO_3^{2-}

A) ☆ Draw H_2SO_3 & remove H

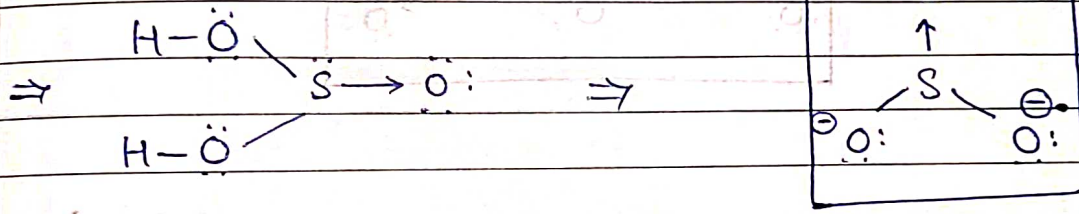
Skeleton,



H – 1 bond,
O – 2 bond,

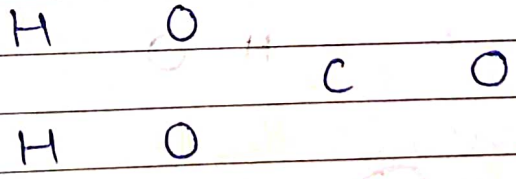


Incomplete

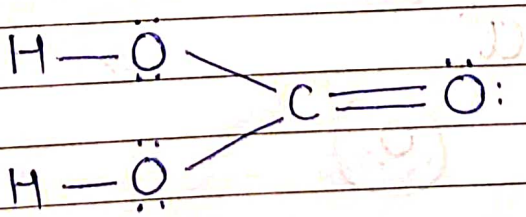


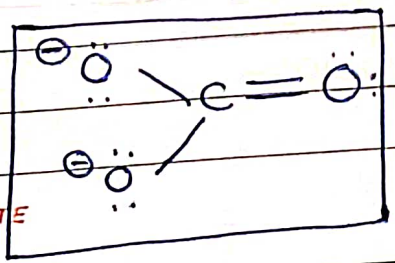
Q) Draw CO_3^{2-}

A) Skeleton,



H – 1 bond,
O – 2 bond,





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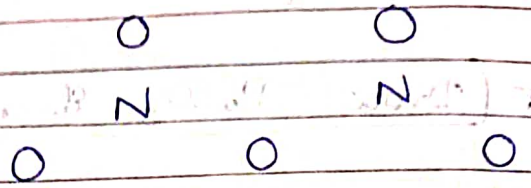
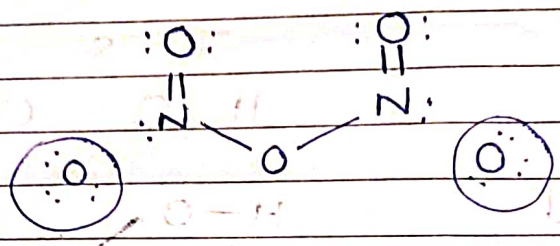
☆Q) Draw N_2O_5

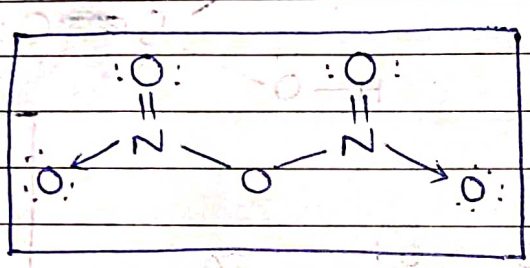
A) Skeleton,



O-2 bond,

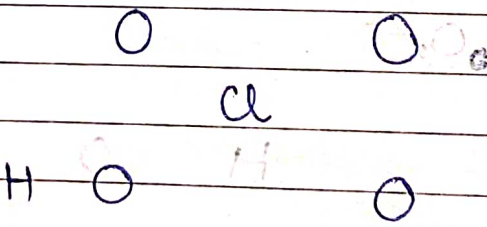


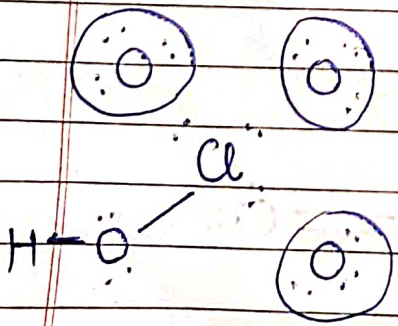
⇒



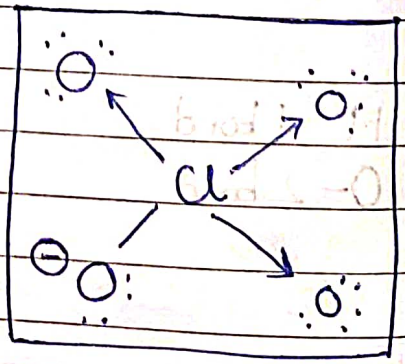
Q) Draw ClO_4^-

A) Skeleton,





⇒



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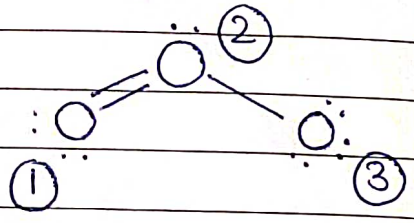
Formal Charge –

$$F.C. = \left(\#\ \text{valence } e^-\right) - \left(\#\ \text{unshared } e^-\right) - \frac{1}{2}\left(\#\ \text{bond pair } e^-\right)$$

Eg – O_3

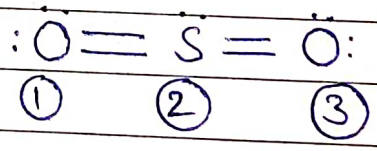


① F.C. = 6 – 4 – 4/2
⇒ F.C. = 0

② F.C. = 6 – 2 – 6/2 ⇒ F.C. = 1

③ F.C. = 6 – 6 – 2/2 ⇒ F.C. = (–1)

Eg – SO_2



① F.C. = 6 – 4 – 4/2
⇒ F.C. = 0

② F.C. = 6 – 2 – 8/2 ⇒ F.C. = 0

③ F.C. = 6 – 4 – 4/2 ⇒ F.C. = 0

Limitations of Lewis Octet Theory —

1) Existence of hypovalent molecules. ($< 8e^-$) [Lewis Acids]

Eg - $AlCl_3$, BCl_3, BBr_3, BrI_3, $BeCl_2$, ...

★ AlF_3 is NOT hypovalent.

It is Very Ionic ⇒ AlF_3 ≐ Al^{3+} $3F^-$ (Complete Octet)

2) Existence of hypervalent molecules. ($> 8e^-$) [Superoctet]

Eg - PCl_5, IF_7, H_2SO_4, $HClO_4$, ...

3) Existence of comp. of Kr & Xe.

Eg - XeF_2, XeF_4, XeF_6, KrF_2, $XeOF_2$, ...

4) Existence of odd e^- molecule.

Eg - NO, NO_2, ClO_2, ClO_3, ...

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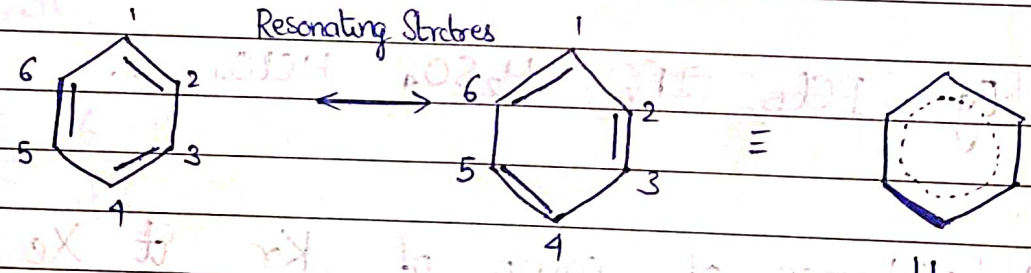
5) Couldn't explain the complete structure of molecule (Bond length, bond strength, ...).

6) Couldn't explain stability of molecules.

Resonance

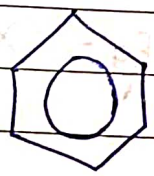
For certain molecules, it is not possible to explain all propts of molecule with help of a single structre. More than one structure is req. to explain all propts.

Eg- Take Benzene



Theoretically, double bonds must be smaller than single bonds.

But practically all bonds identically & no bond purely single or double.



Resonance Hybrid

Def^n: Delocalisation of πe^- is known as resonance

Imp. Pts:

- During resonance, atoms don't move.
- Resonance $\Rightarrow$ Energy $\downarrow$ $\Rightarrow$ Stability $\uparrow$
- Resonance occurs only in conjugated system (double bond in alternate post.) or (double bond, single bond, charge (+) or (-)).

Conj. System

$H_2C=CH-CH=CH_2$ ✓ | $H_2C=CH-CH-CH=CH_2$ X

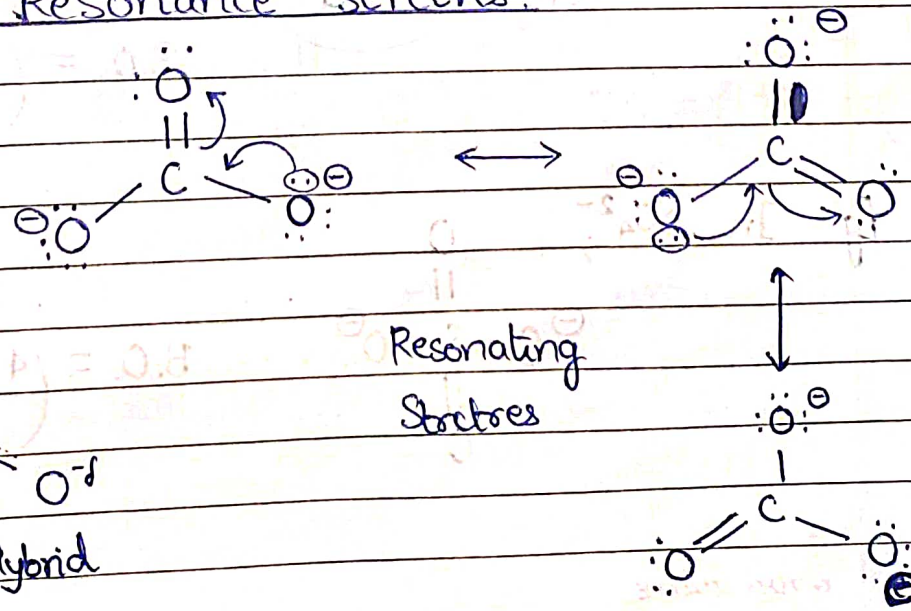
$H_2C=CH-\overset{\oplus}{C}H_2$ ✓ | $H_2C=CH-CH_2-\overset{\oplus}{C}H_2$ X

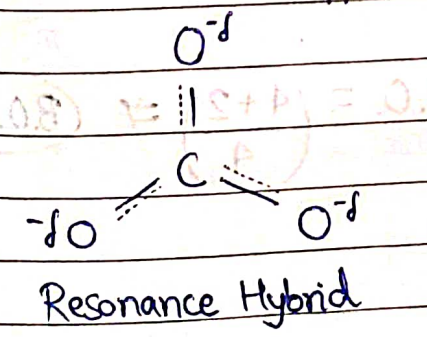
$H_2C=CH-\overset{\ominus}{C}H_2$ ✓ | $H_2C=CH-CH_2-\overset{\ominus}{C}H_2$ X

- Vacant Orbital ⇄ l.p. (Eg: BF_3)

Making Resonance Strctres.

CO_3^{2-}





Resonance Hybrid

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☆ (Bond Order) = $\frac{\Sigma(\#\text{ bonds b/w 2 atoms in all res. structures})}{(\#\text{ Resonating Structures})}$

(Nb. of bonds b/w 2 atoms)

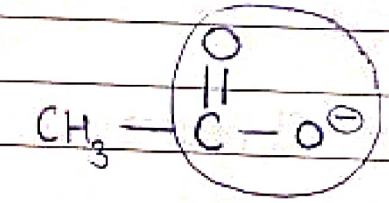
Eg- In CO_3^{2-}, (B.O. of C-O) = $\left(\frac{2+1+1}{3}\right)$

$\Rightarrow$ (B.O. of C-O) = 1.33

☆ Short Trick:

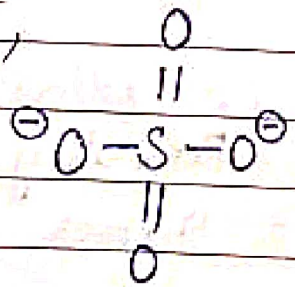
$$\boxed{B.O. = \left(\frac{\sigma + \pi}{\sigma}\right)}$$

Jiska bond order calc. karna hai, usi ke σ aur π count karo.

Eg- In 

This is resonating part.

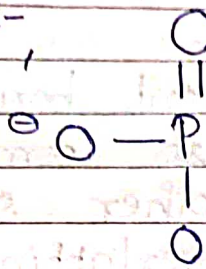
B.O. = $\left(\frac{3}{2}\right)$ $\Rightarrow$ B.O. = 1.5

Eg- In SO_4^{2-}, 

B.O. = $\left(\frac{4+2}{4}\right)$ $\Rightarrow$ B.O. = 1.5

★ (Bond Order) $\propto$ (Bond Strength) $\propto \left(\frac{1}{\text{Bond Length}}\right)$

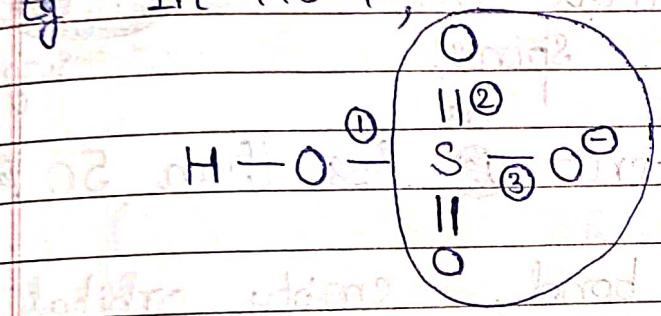
Eg - In PO_4^{3-},



$$B.O. = \left(\frac{4+1}{4}\right)$$

$$\Rightarrow \boxed{B.O. = 1.25}$$

Eg - In HSO_4^-,



This is resonating part.

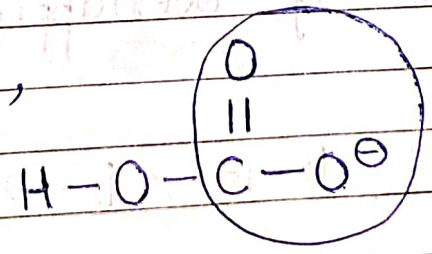
$$B.O. = \left(\frac{3+2}{3}\right) \Rightarrow \boxed{B.O. = 5/3}$$

Now, $BO(2) = BO(3) = 5/3$ and $BO(1) = 1$

$5/3 > 1 \Rightarrow$ Bond Length : $2 = 3 < 1$

$BO(3) = BO(2) > BO(1) \Rightarrow$

Eg - In HCO_3^-,



This is resonating part.

$$B.O. = \left(\frac{1+2}{2}\right) \Rightarrow \boxed{BO = \frac{3}{2}}$$

2/8/22

Valence Bond Theory (VBT)

Postulates –

- To form a covalent bond, at. orbitals of 2 atoms must come sufficiently close to each other so that they can start overlapping.
- Overlapping orbitals must have single e⁻, with opp. spin's.
- Overlapping extent is less than 50 %.
- In coordinate bond, empty orbital of one atom will overlapp with full filled orbital of another atom.
- Closer the valence shell of one atom to other atom's nucleus, larger the extent of overlapping. ⇒ Stronger Bond

Eg – Overlapping : 1s-1s > 1s-2s > 2s-2s > 2s-3s > 3s-3s

- For same shell, order of extent of overlapping

p-p > s-p > s-s

because 'p' is dirx^{n}al.

(In extent of overlapping, dist. to nucleus dominant factor)

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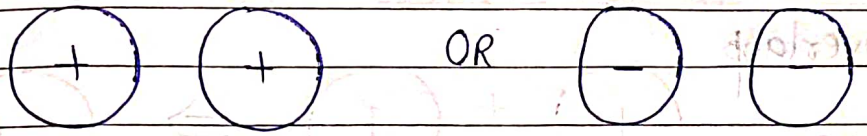
★Q) Arrange in order of σ bond strength

1) 1s-1s > 1s-2p > 1s-2s > 2p-2p > 2s-2p > 2s-2s

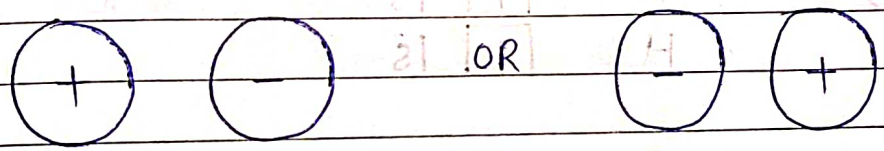
1s-2p: dirxal; 1s-2s: non dirxal; Dist. from nucles

2p-2p > 2s-2p > 2s-2s: Extent of overlapping

★ 

Bond ✓

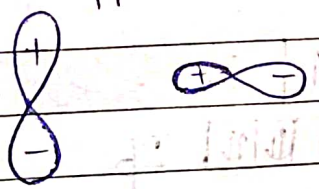
Positive Overlapp. ⇒ Same phase overlapp ⇒ Stability Inc.



Bond X

Negative Overlapp. ⇒ Diff. phase overlapp. ⇒ Stability Dec.

-If no overlapp. due to orientation ⇒ No bond form

Eg: 

⇒ No overlapp
No bond.

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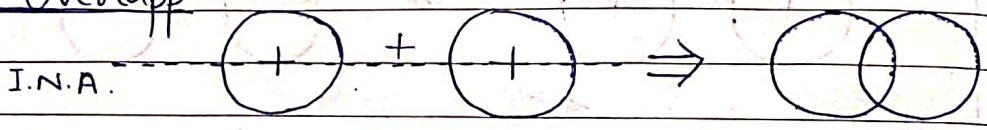
i) Types of Overlapping –

1) **Axial / Head On**: Overlapping along internuclear axis.

σ bond will form.

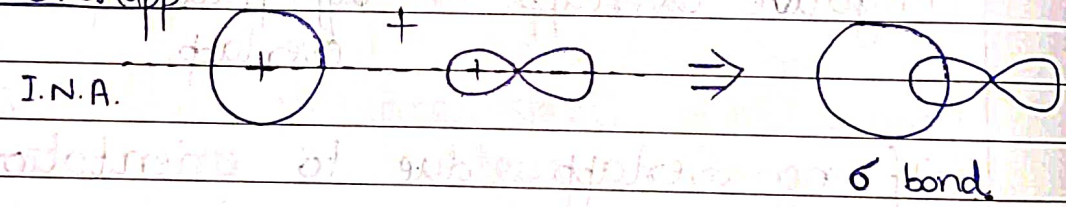
– S-s Overlapp



Eg – H_2

H	1	1s
H	1	1s

– S-p Overlapp

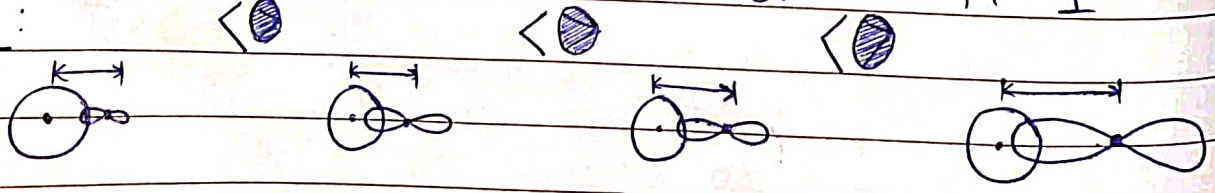


Eg – HF

H	1	1s
f	1 ↿⇂ ↿⇂	2p

★ (Q) Compare bond length and acidic character

H – F H – Cl H – Br H – I

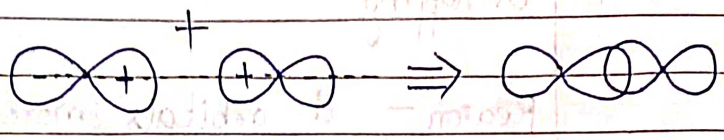
B.L: 

p orbital size inc.

Acidic Strength : < < <

HI easily lose H^+

- p-p Overlapp



σ bond

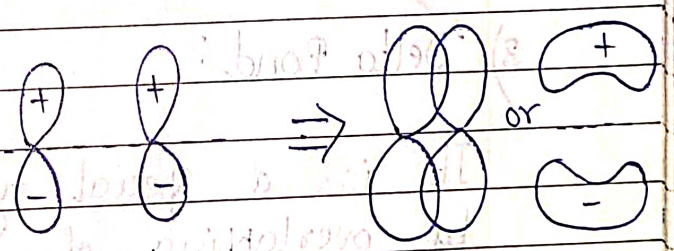
Eg- F_2

F	↿⇂	↿⇂	1	2p
F	↿⇂	↿⇂	1	2p

2) Sidewise / Lateral : Overlapping above and below internuclear axis.

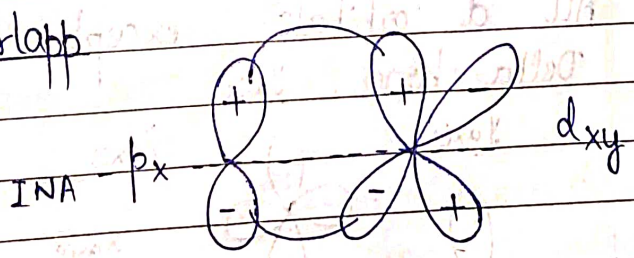
π bond will form.

- $p_\pi - p_\pi$ Overlapp

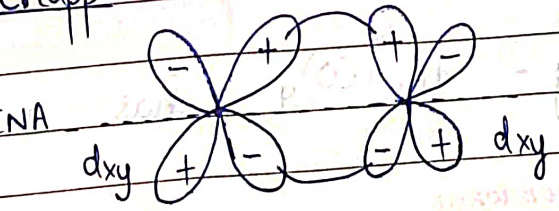


p_x p_x π bond

- $p_\pi - d_\pi$ Overlapp



- $d_\pi - d_\pi$ Overlapp



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for same shell,

☆ Extent of Overlapping : $d_\pi - d_\pi > p_\pi - d_\pi > p_\pi - p_\pi$

Reason – d orbitals more inclined ⇒ more overlapping.

☆ Q) Compare bond strength –

Strength: $2p_\pi - 2p_\pi$ > $2p_\pi - 3d_\pi$ > $2p_\pi - 3p_\pi$ > $3p_\pi - 3p_\pi$

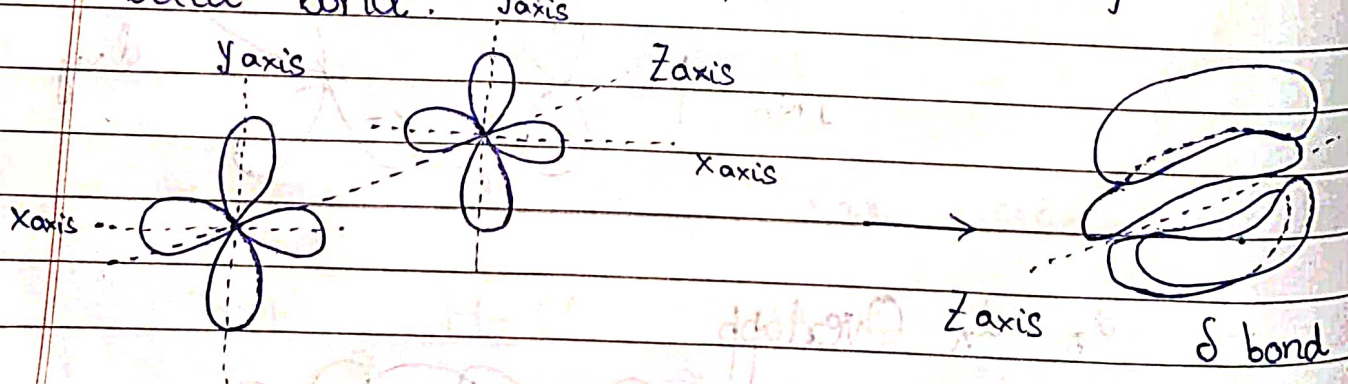
($2p_\pi - 3d_\pi$: dirxal)

Dist. Dist.

3) Delta Bond :

It is a special type of bond formed by overlapping of all 4 lobes of d orbital with those of another d orbital.

All d orbitals, except d_{z^2}, can form Delta bond.



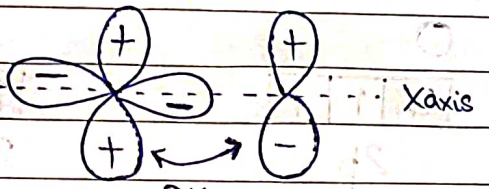
Eg – $Fe_2(CO)_9$ has a delta bond.

★ s, $d_{x^2-y^2}$ & d_{z^2} CAN'T form π bonds

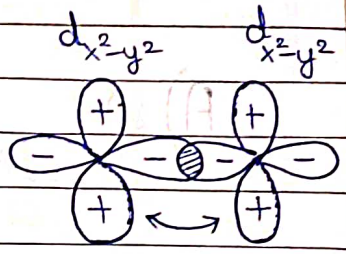
Reason:

– s is non-dirx^{n}al

– $d_{x^2-y^2}$

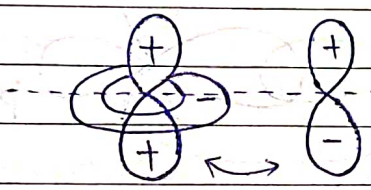


$d_{x^2-y^2}$ Opp. by $d_{x^2-y^2}$

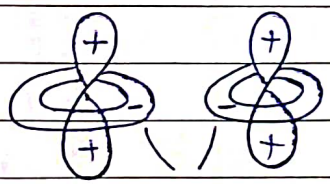


Can't π as σ > 50% then.

– d_{z^2}



Opp.



Same sign, repulsion

Can't π as σ > 50% then

σ bond	π bond
Axial/Head on overlap	Sidewise/Lateral overlap
Bond is strong, so less reactive.	Bond is weak, so more reactive
Free rotation around the bond is possible.	Rotation around the bond restricted
Determines the geometry of molecule	No role in determining Geometry

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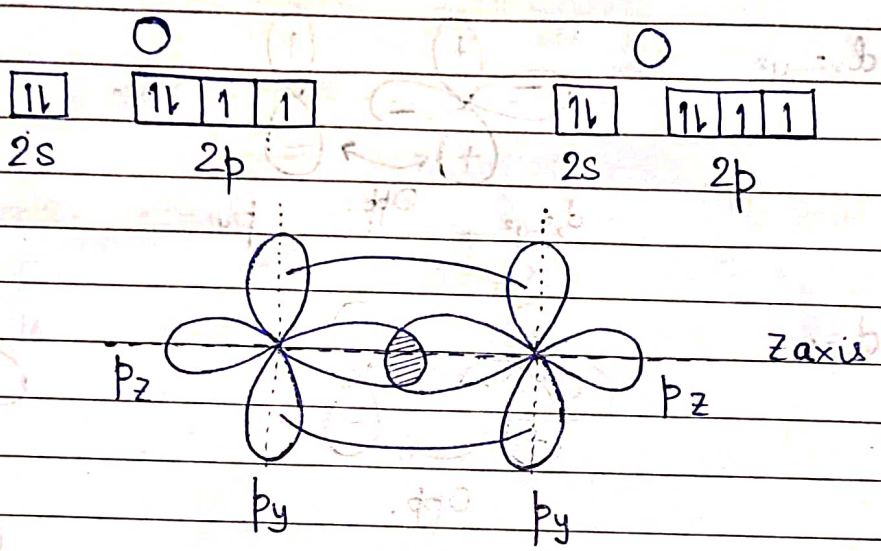
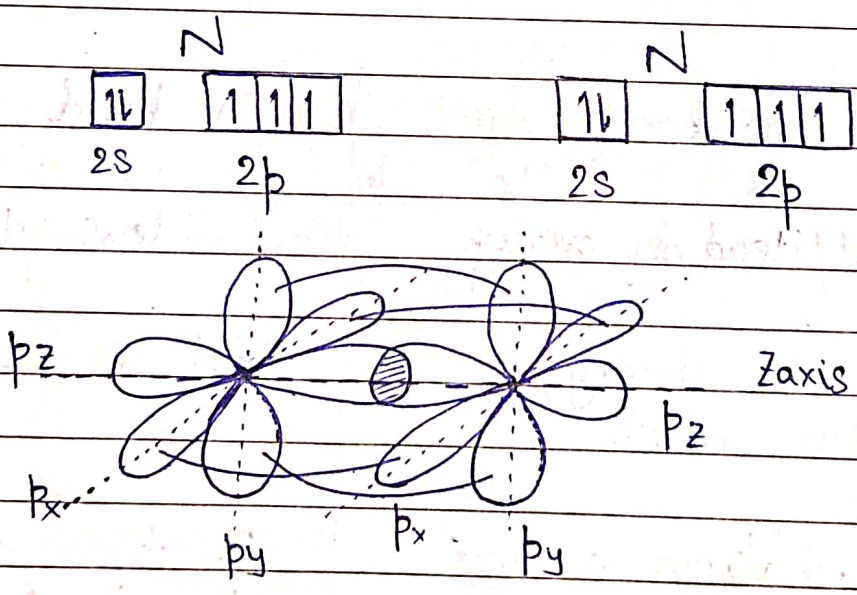
Q) Draw molecular orbital diagram for –

1) O_2 2) N_2

A) 1)

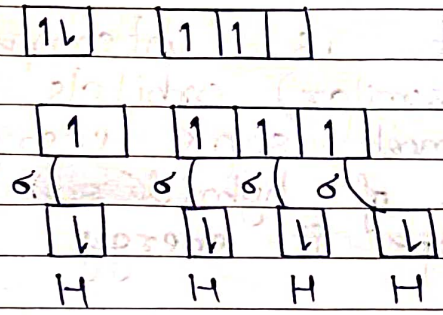


2)



ii) Drawbacks of V.B.T. –

CH_4 :



Acc. to V.B.T all 4 C–H bonds should NOT be identical.

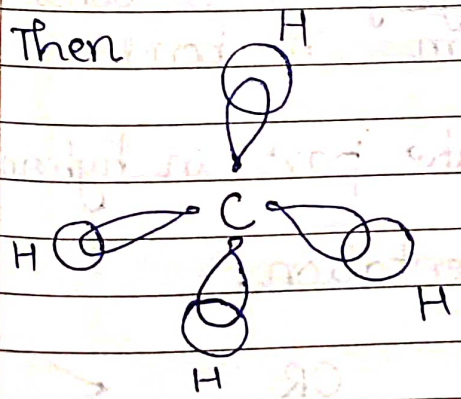
But experimentally it was found that all four C–H bonds are identical in size & strength.

So to explain this a new concept of Hybridisation was introduced.

If 2s + 2px + 2py + 2pz ⇒ 4 sp^3

hybridised orbital

Then



All 4 bonds s – sp^3.

⇒ Identical bonds

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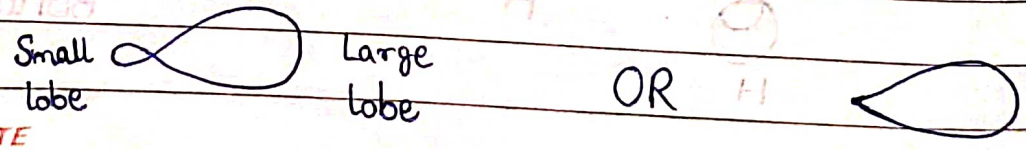
Hybridisation

It is intermixing of s, p, d (dissimilar) orbitals of same atom having almost same energy, to form equal no. of hybrid orbitals of identical shape & energy.

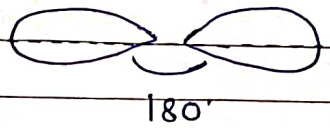
- It is a hypothetical concept.
- (No. of hybrid orbitals) = (No. of pure orbitals)
- Hybrid orbitals are identical in size, shape & energy.
- Intermixing orbitals should have nearly same energy. (Eg: 2s & 1p can't intermix.)
- Hybridisation occurs before bonding.
- Empty, half & full orbitals can participate in hybridisation.
- Hybrid orbitals always form σ bond. They can NOT form π bond.
- Lone pairs also take part in hybridisation.
- Hybrid Orbital representation,



i) Types of Hybridisation –

1) $s + p \Rightarrow 2\ sp$

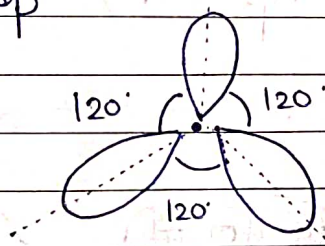
Geometry:



Linear

2) $s + 2p \Rightarrow 3\ sp^2$

Geometry:

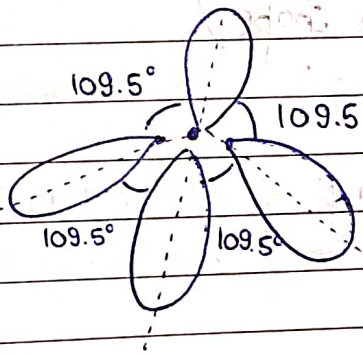


Triangular Planar

[2D]

3) $s + 3p \Rightarrow 4\ sp^3$

Geometry:

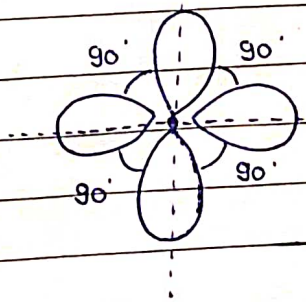


Tetrahedral

[3D]

4) $(n-1)\ d_{x^2-y^2} + ns + np_x + np_y \Rightarrow 4\ dsp^2$

Geometry:



Square Planar

[2D]

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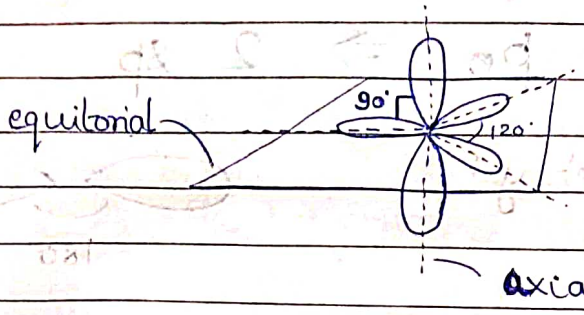
5) $ns + 3np + nd_{z^2} \Rightarrow 5\ sp^3d$

Geometry:

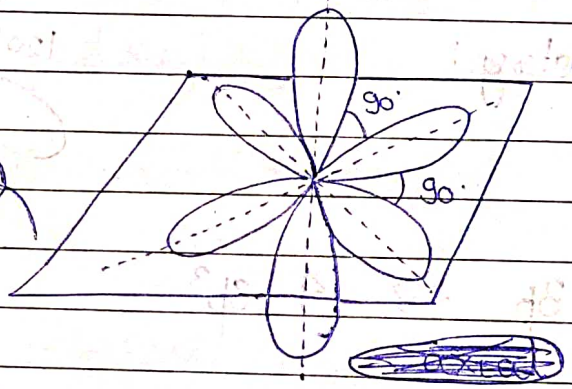


Trigonal Bipyramidal

[3D]

6) $ns + 3np + nd_{z^2} + nd_{x^2-y^2} \Rightarrow 6\ sp^3d^2$

Geometry:



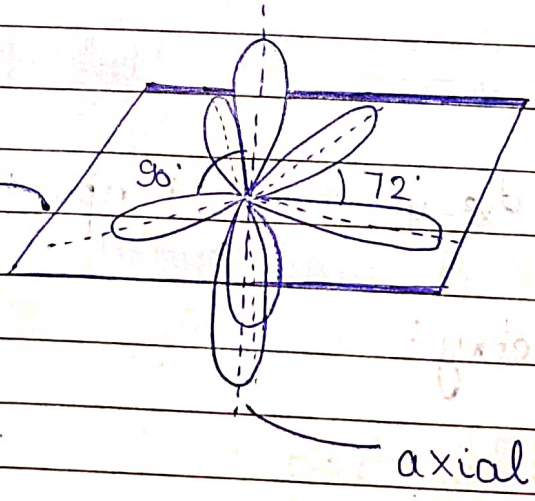
(Octahedral) Square Bipyramidal

[3D]

(No equi or axial post. as regular shape)

7) $ns + 3np + nd_{z^2} + nd_{x^2-y^2} + nd_{xy} \Rightarrow 7\ sp^3d^3$

Geometry:



Pentagonal Bipyramidal

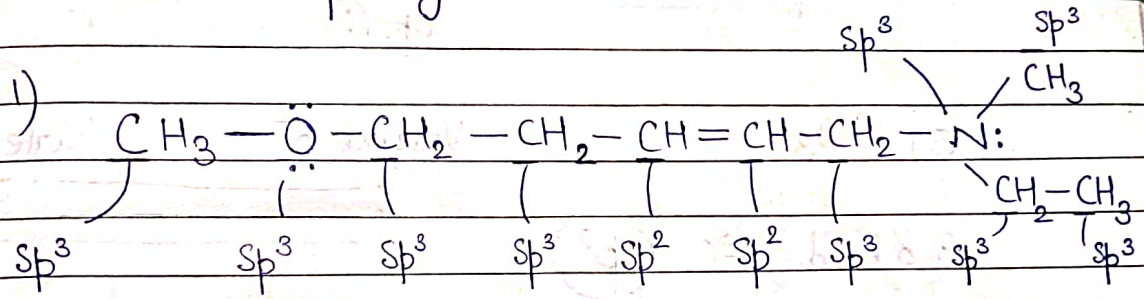
[3D]

ii) Finding Hybridisation

$$\left(\begin{matrix}\text{Steanic}\\ \text{No.}\end{matrix}\right) = \left(\begin{matrix}\text{No. of}\\ \text{hybrid orbitals}\end{matrix}\right) = \left(\begin{matrix}\#\sigma\\ \text{bond}\end{matrix}\right) + \left(\begin{matrix}\#\\ \text{l.p.}\end{matrix}\right)$$

- If structure if given :

Eg- 1)



- If molecular formula is given :

Eg- 1) BF_3

Write valence e⁻ for central atom

3 σ bonds

Write valency of surrounding

⇒ Sp^2

2) $BF_4^{\ominus}$

4 σ bonds

Valence e⁻	Valency
:	× → σ
:	× → σ
:	× → σ
Add le⁻ due to ⊖ ⊙	× → σ

⇒ Sp^3

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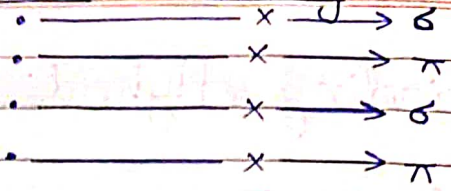
3) CO_2

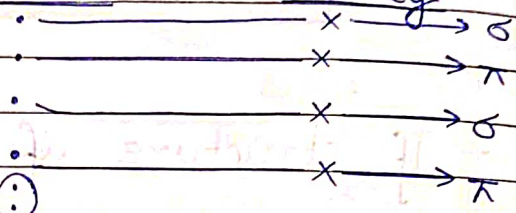
Valence e^- | Valency



2 σ bonds ⇒ (Sp)

4) SO_2

Valence e^- | Valency

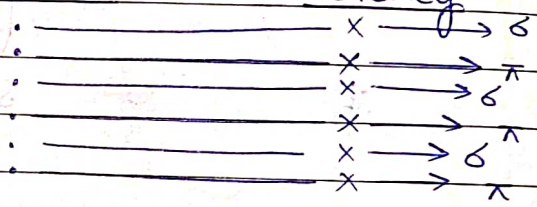


2 σ bonds ⇒ (Sp^2)
+1 l.p.

l.p. ⊙

5) SO_3

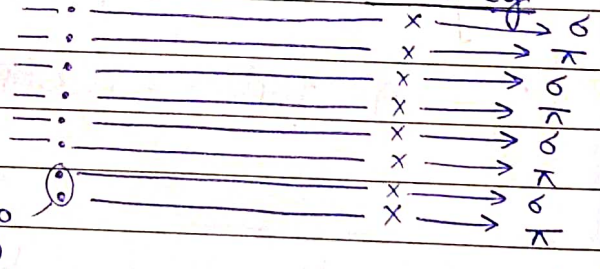
Valence e^- | Valency



3 σ bonds ⇒ (Sp^2)

6) SO_4^{2-}

Valence e^- | Valency

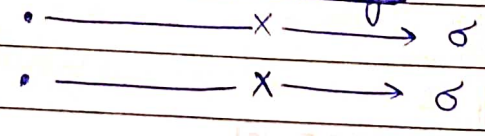


4 σ bonds
⇒ (Sp^3)

due to 2⊖

7) $BeCl_2$

Valence e^- | Valency



2 σ bonds ⇒ (Sp)

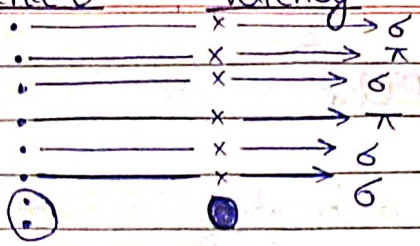
8) XeO_2F_2

(Xe)

Valence e^- → Valency

4 σ bonds + 1 l.p.

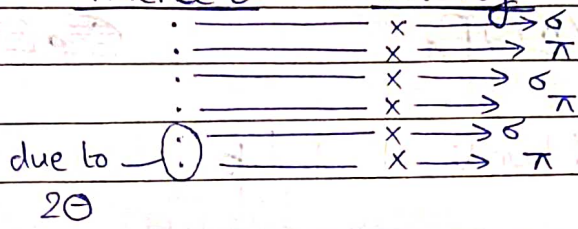
⇒ sp^3 sp^3d



9) CO_3^{2-}

3 σ bonds

⇒ sp^2

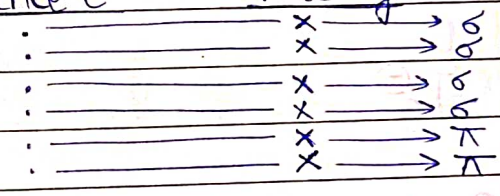


(S)

10) SNF_3

4 σ bonds

⇒ sp^3



11) PCl_5

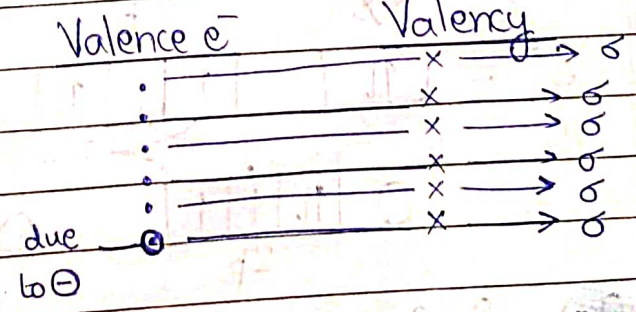
5 σ bonds

⇒ sp^3d

12) $PCl_6^{\ominus}$

6 σ bonds

⇒ sp^3d^2



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13) $PCl_4^{\oplus}$

Valence e^-	Valency
⋮	× → σ
⋮	× → σ
⋮	× → σ
⋮	× → σ
due to ⊕	×

4 σ bonds
⇒ sp^3

14) $XeOF_4$ (Xe)

~~XeOF~~ Valence e^-	Valency
⋮	× → σ
⋮	×
⋮	× → σ
⋮	×
⋮	× → σ
⋮	× → σ
l.p. — ⋮	× → π

5 σ bonds + 1 l.p.
⇒ sp^3d^2

15) $I_3^{\ominus}$

Valence e^-	Valency
⋮	× → σ
⋮	× → σ
⋮	= l.p.
due to ⊖	⋮

2 σ bonds + 2 l.p.s
⇒ sp^3d

★ Q) Find no. of $p_\pi - p_\pi$ & $d_\pi - p_\pi$ bonds in SO_2

A) $S^* =$ 3s: ↑↓ | 3p: 1 1 1 | 3d: 1

O: ↑↓ 1 1 (2p) — O: 1 1 ↑↓ (2p)

$p_\pi - p_\pi = 1$
$p_\pi - d_\pi = 1$

2) 2 3p orbitals of S make σ bond with 1 2p orbitals from 1 O each.

⇒ π bonds : $3p_\pi - 2p_\pi$ & $3d_\pi - 2p_\pi$

GOOD WRITE

VSEPR Theory

(Valence shell e^- pair repulsion)

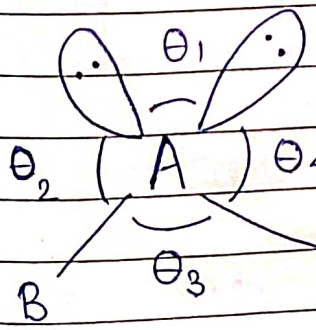
Postulates

- Geometry & Shape of molecule is decide by no. of σ bond & # L.p. available with central atom.

- If central atom has only b.p, then its shape = geometry. But if it has l.p., then shape is distorted.

- Since b.p. under influence of 2 nuclei, hence it occupies less space.
  Since l.p. under influence of 1 nucleus, hence it occupies more space, & creates repulsion.

- Repulsion : (lp - lp) > (lp - bp) > (bp - bp)



$\theta_1 > \theta_2 = \theta_4 > \theta_3$

Repulsion in Bonds : (Multiple - Multiple) > (Multiple - Single) > (Single - Single)

~~(2 triple bond) (triple-double)~~

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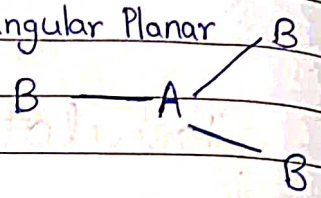
i) Shapes of Molecules

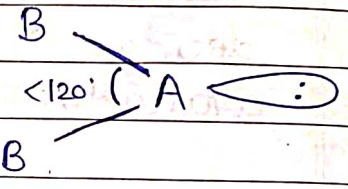
1) Steric No. = 3 (sp^2)

i) AB_3 (b.p. = 3, l.p. = 0) Triangular Planar



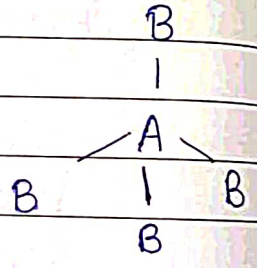
ii) $:AB_2$ (b.p. = 2, l.p. = 1)

Bent / Angular

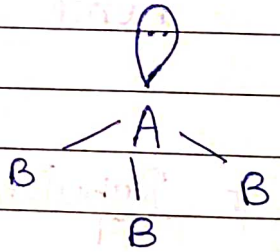


2) Steric No. = 4 (sp^3)

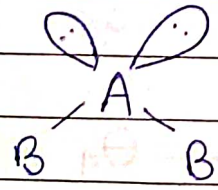
i) AB_4 (b.p. = 4, l.p. = 0) Tetrahedral



ii) $:AB_3$ (b.p. = 3, l.p. = 1) Trigonal Pyramidal



iii) $:\ddot{A}B_2$ (b.p. = 2, l.p. = 2)



Bent / Angular

ii) Bent Rule –

- Higher EN atom tends to attach with hybrid orbitals having less % s character (Axial Post.) generally
- Lone pair and Multiple bonds occupy that post. with more % s character (Equitorial Post.) generally

Bond Angle (θ) : $\cos(\theta) = \left(\frac{s}{s-1}\right)$ s = s character (Valid for hybrid with only s & p)

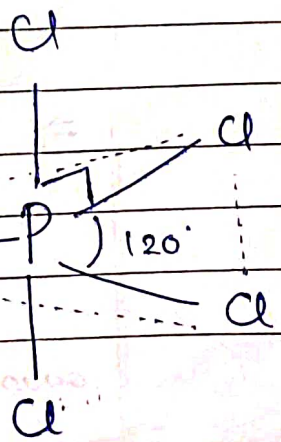
	Sp	Sp^2	Sp^3
(% s character) :	50%	33.3%	25%

(% s character) ∝ (Closeness of e^- to nucleus)

∝ (E.N. of Central Atom) ∝ $\left(\frac{1}{\text{Bond Length}}\right)$ ∝ (Bond Angle)

Explanation of Bent Rule –

✓ Take PCl_5 for eg.



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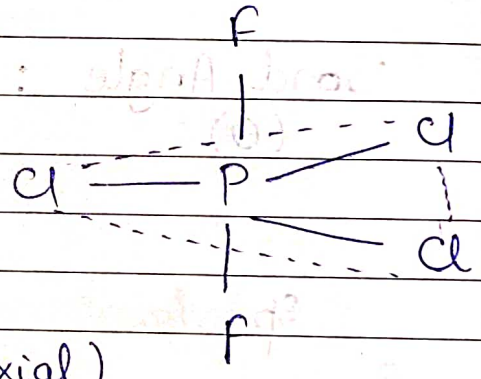
(% character in equitorial P–Cl) = 33.3% ⇒ sp^2

(% character in axial P–Cl) = 0

for Molecule $sp^3d = sp^2 + (pd)$

⇒ Generally, [(Axial Bond Length) > (Equitorial Bond Length)]

✓ Now ~~assume~~ consider : PCl_3F_2.



We know,

(EN of P observed from axial)
∧
(EN of P observed from equitorial)

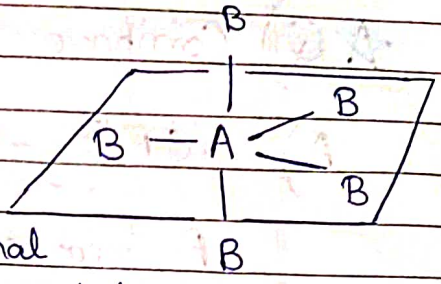
for stronger bond, F prefers axial post.
[F high EN good bond P low EN]

✓ for l.p., it wants to remain close to nucleus ⇒ wants more EN of central atom.

⇒ l.p. occupies equitorial post.

3) Steric No. = 5 (sp^3d)

i) AB_5 (b.p. = 5, l.p. = 0)



Trigonal Bipyramidal

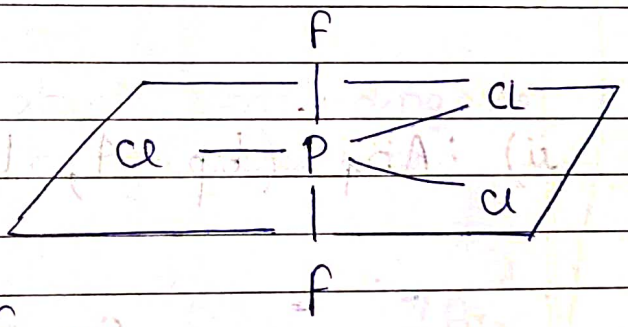
★Q) Compare bond length in PCl_3F_2.

A)

★ (Bond Length) = (Size of hybrid orbital) + (Size of side atom)

B.L

(Equitorial P–Cl) > (Axial P–F)

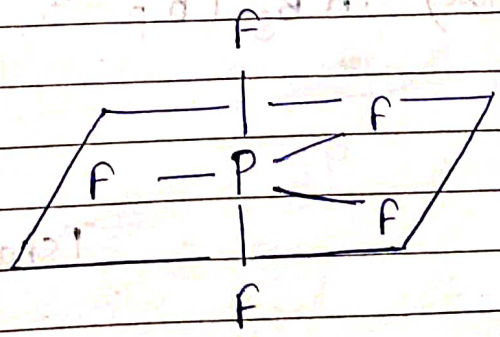


Bcoz, Size: Cl > F

★Q) Compare bond length in PF_5

A) B.L

Equitorial = Axial.



Acc. to Pseudo Berry Rotation, axial & equitorial bonds inter-changable as F keep rotating.

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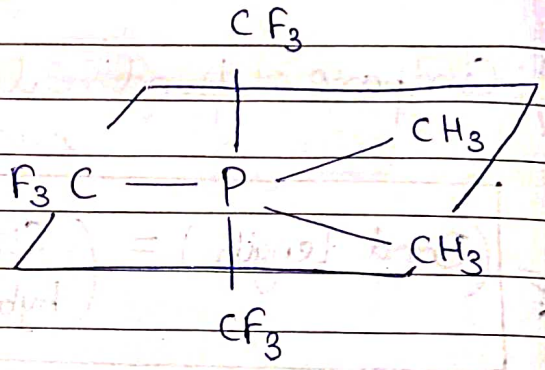
☆Q) Compare bond length in $P(CH_3)_2(CF_3)_3$

A) $CF_3^{\ominus}$ carbon more EN than $CH_3^{\ominus}$ as, F carbon ke e^- kheench leta hai

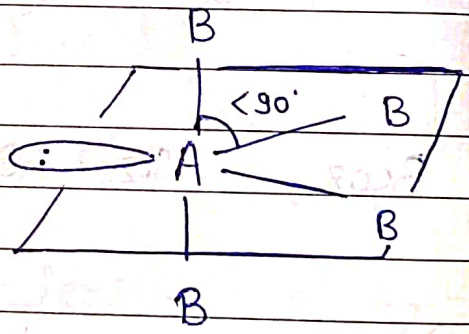
B.L.

(Axial) F_3C-P > (Equi.) H_3C-P > (Equi) F_3C-P



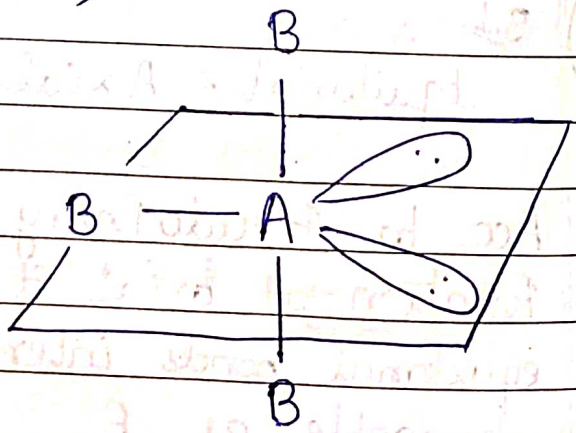
ii) : AB_4 (b.p. = 4, l.p. = 1)

See-saw



iii) : $\ddot{A}B_3$ (b.p. = 3, l.p. = 2)

T shape



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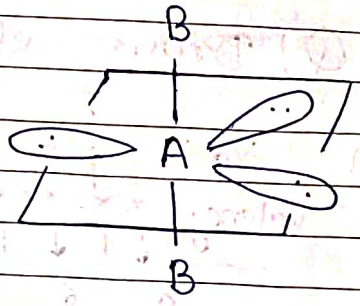
iv) $:\ddot{A}B_2$ (b.p. = 2, l.p. = 3)



★ In case of ANY molecule with ANY hybridisation with Central Atom and surrounding atoms all Halogens, size of central atom should be greater than surrounding atoms.

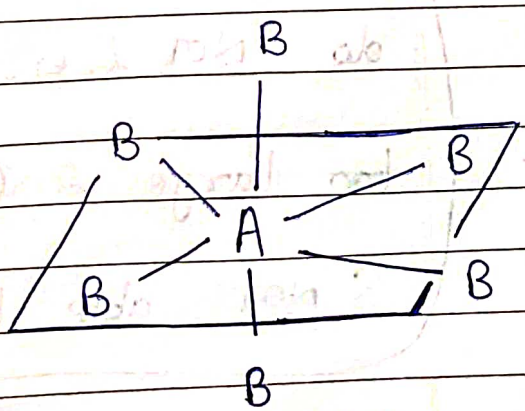
Reason: If Central atom < Surrounding atom, Central atom doesn't get space to make bonds.

Eg: BrF_3 ✓, ICl_3 ✓, ClF_3 ✓, $ClBr_3$ ✗

4) Steanic No. = 6 (sp^3d^2)

i) AB_6 (b.p. = 6, l.p. = 0)

Octahedral



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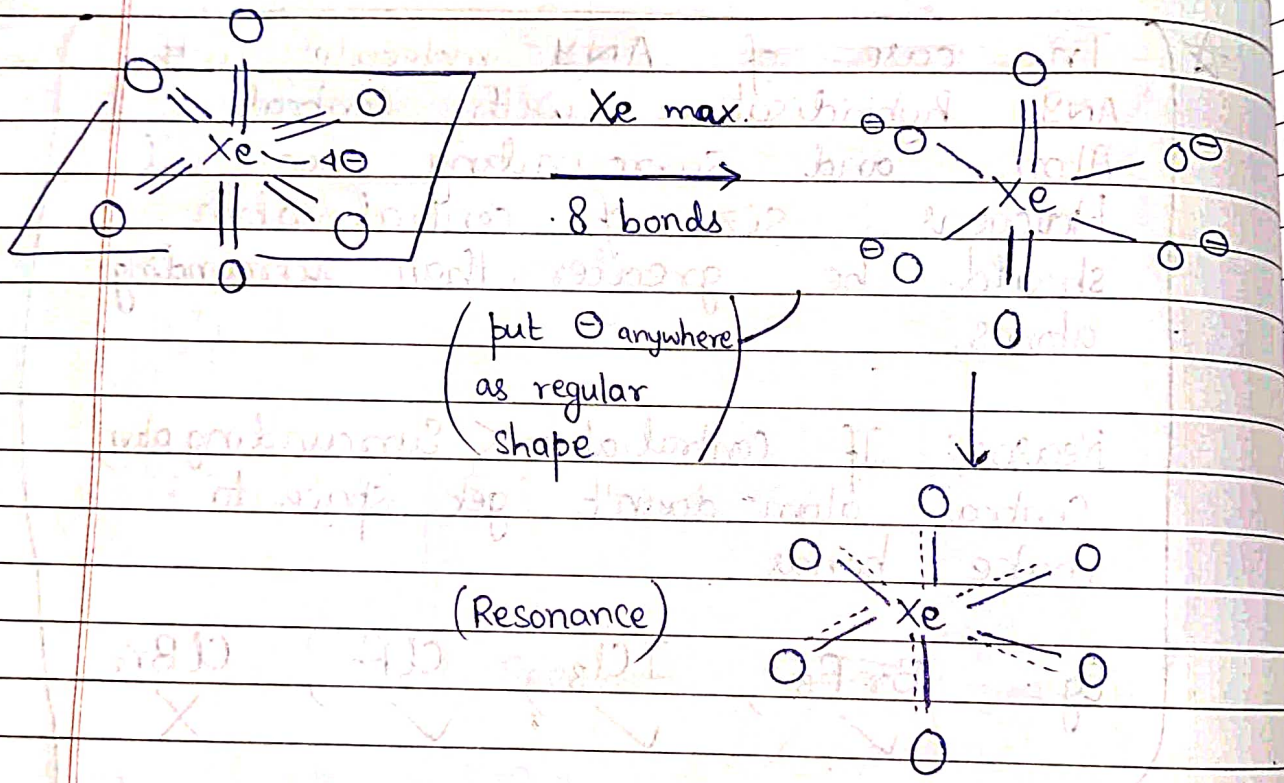
★ Q) Draw structure of XeO_6^{4-} (per Xenate ion)

A) Xe : ↑ ↑ ↑ ↑ ↑ ↑ due to 4⊖

Valency : × × × × × × × × × × × ×

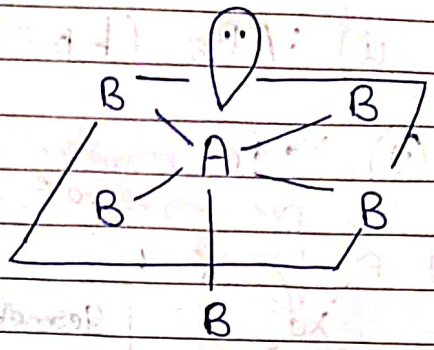
σ σ σ σ σ σ



★ SF_6 (Very inert as F cover S from all sides) exists. But SCl_6, SBr_6, ... do NOT exist because Cl, Br, ... too Large. Cover space around S. S NOT able to form bonds.

ii) $:AB_5$ (b.p. = 5, l.p. = 1)

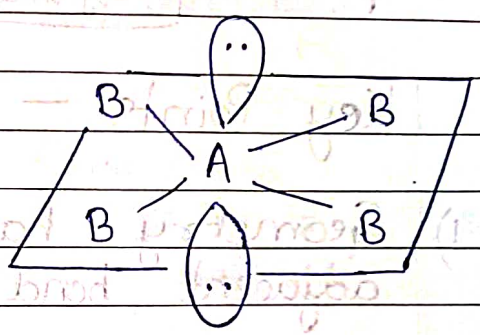
Square Pyramid



iii) $:AB_4$ (b.p. = 4, l.p. = 2)

(l.p. repulsion ⇒ farthest apart)

Square Planar



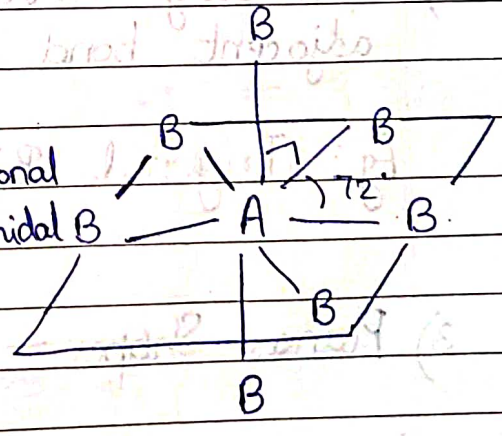
5) Steanic No. = 7 (sp^3d^3)

i) AB_7 (b.p. = 7, l.p. = 0)

In this case,

72° < 90°

Pentagonal Bipyramidal



⇒ (% s character) : Equitorial < Axial

⇒ (Bond Length) : Equitorial > Axial (in sp^3d^3)

(Stereochemical Active / l.p. change geometry/shape)

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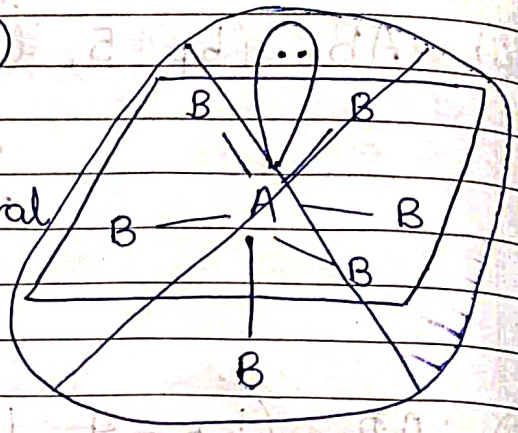
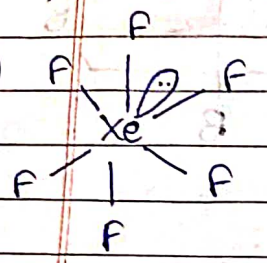
ii) : AB_6 (b.p. = 6, l.p. = 1)



☆ Q) XeF_6

Shape { Capped Octahedral

A)



Geometry ≠
Pentagonal
Bipyramidal

Key Points –

1) Geometry having only 1 type of adjacent bond angle is called Regular

Eg: Linear, Trigonal Planar, Tetrahedral, Square Bipyramidal

2) Geometry having more than 1 type of adjacent bond angle is called Irregular

Eg: Trigonal Bipyramidal, Pentagonal Bipyramidal

3) Planar Shapes –

Linear, V shape, T shape, Trigonal planar, Square planar, Pentagonal planar.

Explanation –

1) Since bonded to high EN atom, EN of Central atom inc. Unpair e^- firmly held ⇒ Hybridisation ✓

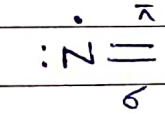
2) Central atom tries to hold l.p. first.

(iii) Hybridisation in Odd e^- Species –

1) If side atoms high EN (mainly F, O, N, Cl), then unpaired e^- will participate in hybridisation.

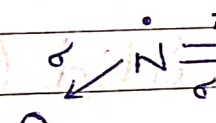
2) If lone pair & unpaired e^- present, then only l.p. will participate in hybridisation.

Eg – NO



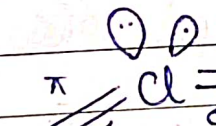
(σ)
1 + 1 = 2 (sp)
(l.p.)

Eg – NO_2



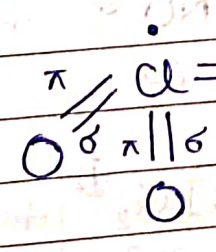
(e⁻)
1 + 2 = 3 (sp^2)
(σ)

Eg – ClO_2



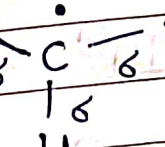
(σ)
2 + 1 = 3 (sp^2)
l.p.

Eg – ClO_3



(σ)
3 + 1 = 4 (sp^3)
(e⁻)

Eg – $\dot{C}H_3$



3 (sp^2)

EN of H low.

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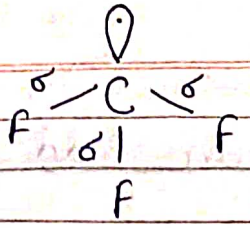
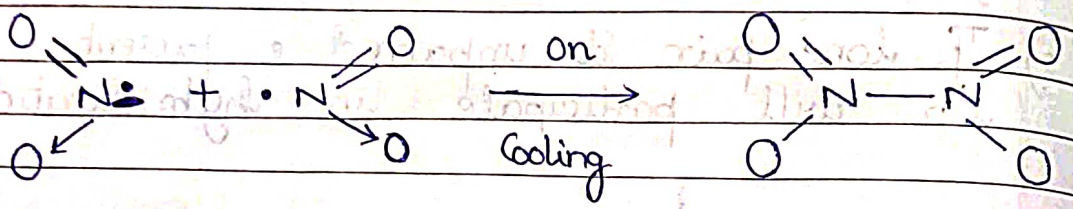
Eg - $\dot{C}F_3$



(σ)
3+1 = 4 (sp^3)
(e^-)

★ Compounds having only 1 e^- unpaired tend to dimerise.



Paramagnetic (Brown Color)

Diamagnetic (Colorless)

(iv) Hybridisation in Solid Compounds

Some covalent compounds exist in Ion pairs in Solid state. ($2n \rightarrow (n-1)^{\oplus} + (n+1)^{\ominus}$)

$N_2O_4(s) \longrightarrow \underset{sp}{:NO^{\oplus}} + \underset{sp^2}{NO_3^{\ominus}}$

$N_2O_5(s) \longrightarrow \underset{sp}{NO_2^{\oplus}} + \underset{sp^2}{NO_3^{\ominus}}$

$I_2Cl_6(s) \longrightarrow \underset{sp^3}{:\ddot{I}Cl_2^{\oplus}} + \underset{sp^3d^2}{:\ddot{I}Cl_4^{\ominus}}$

$I_2O_4(s) \longrightarrow IO^{\oplus} + IO_3^{-}$

$Cl_2O_6(s) \longrightarrow ClO_2^{\oplus} + ClO_4^{\ominus}$

$SF_6(s) \rightarrow SF_5^{\oplus} + F^{\ominus}$

$2PCl_5(s) \rightarrow PCl_4^{\oplus} + PCl_6^{\ominus}$

$PBr_5(s) \rightarrow PBr_4^{\oplus} + Br^{\ominus}$

Drago's Rule

- If Stearic No. = 4 and Central Atom has min. 1 l.p.
- Central atom is of 3rd or higher period
- Side atom EN < 2.5 (generally H atom)

if all these conditions true simultaneously

⇒ No hybridisation!

- Bond angle ≈ 90°

Eg –

CH_4	NH_3	H_2O	HF
SiH_4	PH_3	H_2S	HCl
GeH_4	AsH_3	H_2Se	HBr
SnH_4	SbH_3	H_2Te	HI

No hybridisation

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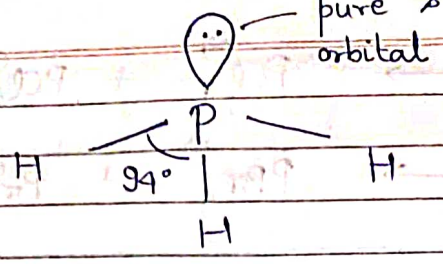
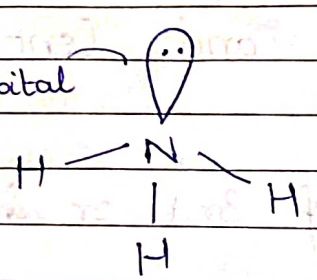
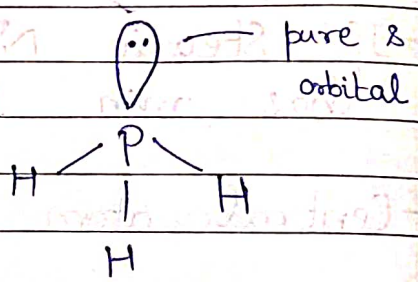
Eg - PH_3



Q) Explain why Ammonia (NH_3) better base that Phosphine (PH_3) gas.

A)





(l.p. in sp^3) farther from Central atom than (l.p. in pure s)

$\Rightarrow$ NH_3 easily donate L.p. than PH_3.

Bond Parameters –

1) Bond Angle :

– Check hybridisation, $\boxed{B.A. \propto (\% \text{ s character})}$

Eg: Bond Angle : $\underset{Sp}{BeCl_2} > \underset{Sp^2}{BCl_3} > \underset{Sp^3}{CCl_4}$

Dominance –

Hybridisation > l.p. > Bulky group > EN

- If hybridisation is same, check (# l.p.)

$$B.A \propto \left(\frac{1}{\#\,l.p.}\right)$$

Eg: B.A: CH_4 > NH_3 > H_2O

CH_4: 0 l.p. ; NH_3: 1 l.p. ; H_2O: 2 l.p.

- If both hybridisation & (# l.p.) same, check EN of atoms.

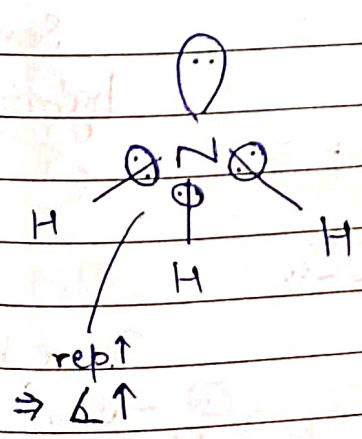
$$B.A. \propto (EN)_{\text{central Atom}} \propto \frac{1}{(EN)_{\text{side atom}}}$$

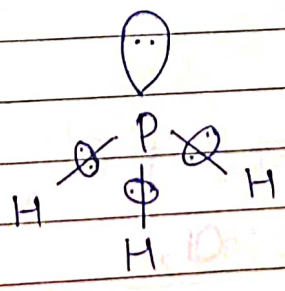
★ If side atom is large, then due to steanic repulsion (b/w e^- clouds) bond angle increases very much in irregular geometry/shape

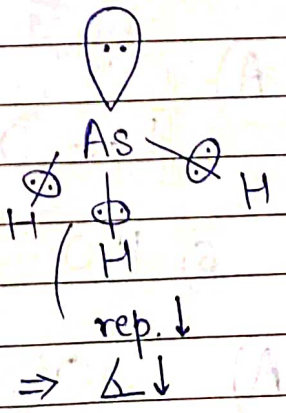
← No hybridisation →

Eg: B.A: NH_3 > PH_3 > AsH_3 > SbH_3

NH_3: sp^3 ; EN: P > As > Sb







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Q) Compare bond angle —

1) CCl_4 $NO_2^{\oplus}$ ClF_3

A) $NO_2^{\oplus}$ > CCl_4 > ClF_3 B.A. $\propto$ (% s char.)
(sp) (sp^3) (sp^3d)

2) BF_3 BCl_3 BBr_3 BI_3

A) " = " = " = "
Regular Shape

3) CCl_4 $SiCl_4$ $GeCl_4$ $SnCl_4$

A) " = " = " = "
Regular Shape

4) CCl_4 NH_3 H_2O

A) " > " > "
l.p. = 0 l.p. = 1 l.p. = 2
Same hybridisation.

5) $NH_4^{\oplus}$ NH_3 $NH_2^{\ominus}$

A) " > " > "
l.p. = 0 l.p. = 1 l.p. = 2
Same hybridisation

6) H_2O OF_2 OCl_2

A) OCl_2 > H_2O > OF_2
Size large EN: F > H
Same hybridis-ation & # l.p.

GOOD WRITE

7) NH_3 NF_3 NCl_3 NBr_3

A) $NBr_3 > NCl_3 > NH_3 > NF_3$

(large size) (EN: F > H) Same hybridis-ation & #l.p.

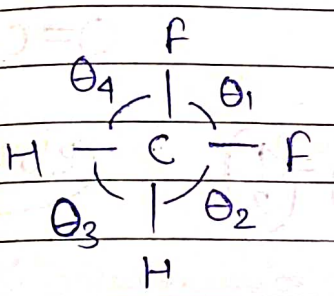
8) H_2O CH_3OH CH_3OCH_3

A) " < " < "

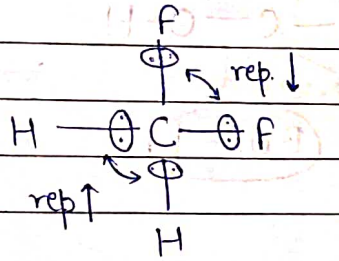
Same hybrid. & #l.p.

CH_3 is bulky group, large size.

9)

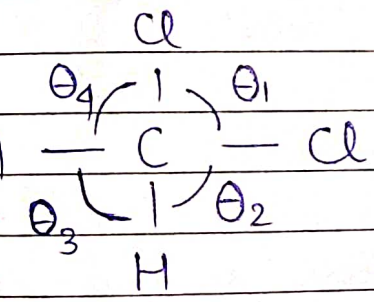


A)



$\theta_3 > \theta_2 = \theta_4 > \theta_1$

10)



A) Cl very large size.

$\theta_1 > \theta_2 = \theta_4 > \theta_3$

11) NH_3, PH_3, NF_3, OCl_2, ClO_2, CO_2, PF_3

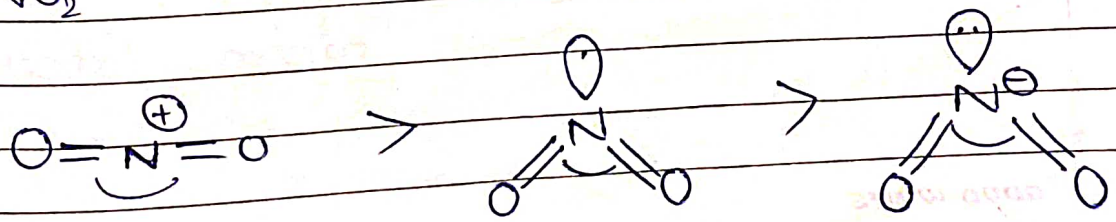
(EN: F > H) (BA: $sp^2 > sp^3$)

A) $PH_3 < PF_3 < NF_3 < NH_3 < OCl_2 < ClO_2 < CO_2$

No hybrid. EN: N > P #l.p.: 2 > 1 BA: $sp > sp^2$

12) $NO_2^{\oplus}$ NO_2 $NO_3^{\ominus}$

A)



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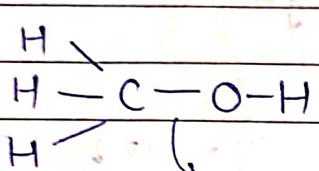
2) Bond Order : $\left(\text{Bond Order}\right) \propto \left(\text{Bond Energy}\right) \propto \left(\frac{1}{\text{Bond Length}}\right)$

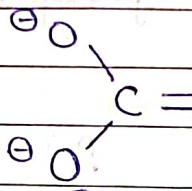
Q) Compare bond order of C–O bond.

CH_3-OH CO_3^{2-} CO_2 CO

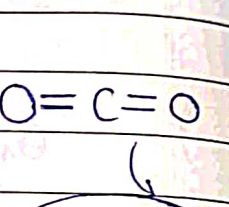
A)



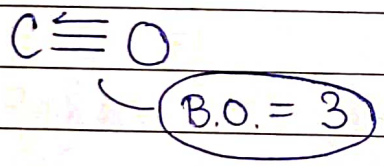
B.O. = 1



$B.O = \left(\frac{1+3}{3}\right) = \frac{4}{3}$



B.O. = 2



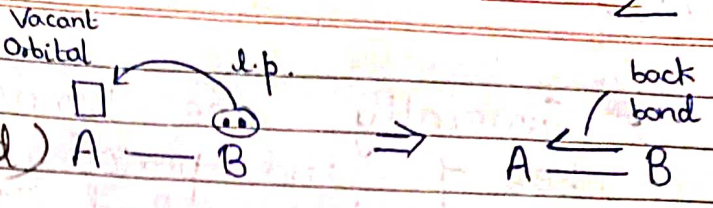
B.O. = 3

Bonding in e⁻ deficient Molecules

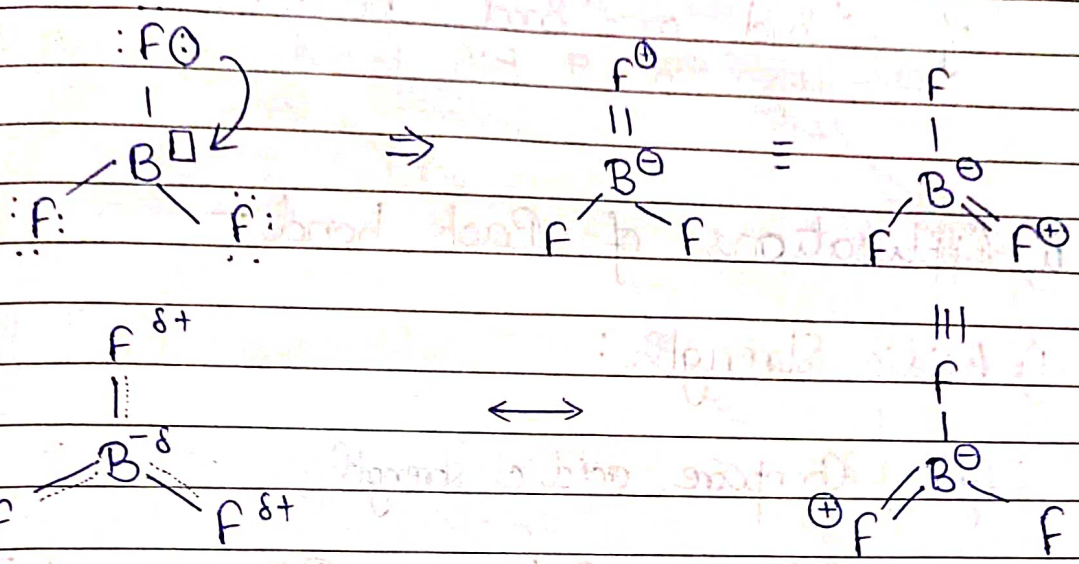
e⁻ deficient molecule can minimise their e⁻ deficiency either by effective Back Bond or by undergoing Dimerisation thru Bridge Bonding.

1) Back Bonding :

(Make only 1 back bond)



Eg :



Resonance hybrid.

Eg : $H_3N : \square BF_3 \Rightarrow H_3N \longrightarrow BF_3$

(Coordinate bond (Not Back bond)

It is a weak π bond which is formed within same molecule by sidewise overlapping of at. orbitals of bonded atom.

i) Conditions for Back bond —

1) One atom has l.p. & other has vacant orbital.

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2) Generally, one bonded atom should be of 2nd period & other atom of 2nd or 3rd period.
(Also in 4th & 5th period, but weak)

ii) Applications of Back bond –

1) Acidic Strength :

Eg: Compare acidic strength,

BF_3 BCl_3 BBr_3 BI_3

(Effective Back Bonding) : " > " > " > "

($2p_\pi$-$2p_\pi$) ($2p_\pi$-$3p_\pi$) ($2p_\pi$-$4p_\pi$) ($2p_\pi$-$5p_\pi$)

⇒ (e^- deficiency of B) : " < " < " < "

⇒ (Acidic Strength) : $BF_3 < BCl_3 < BBr_3 < BI_3$

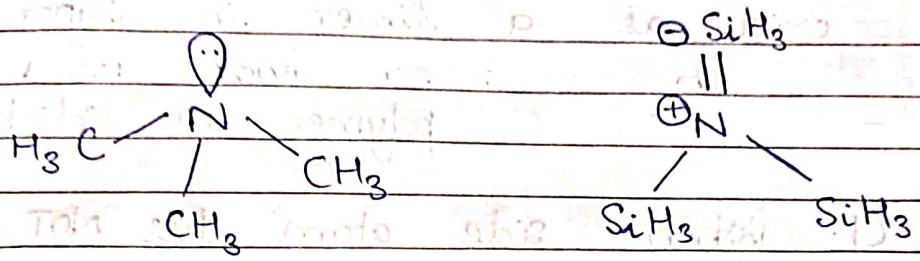
2) Basic Strength :

Eg: Compare basic strength

$N(CH_3)_3$ ● $N(SiH_3)_3$

C has No vacant orbital ⇒ No back bond.

Si has vacant orbital ⇒ Back bond



l.p. available — No L.p. available.

⇒ Basic Strength: $N(CH_3)_3 > N(SiH_3)_3$

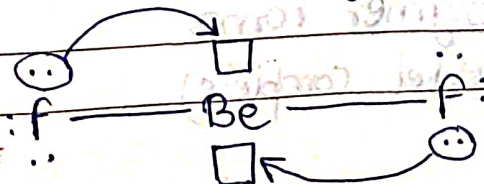
☆ If l.p. of Central atom make back bond, then Steanic No. --
(no back bond)

If side atom Cl, Br, I then hybridisation won't change, as they have weak back bond.

2) Bridge Bonding:

i) for (Be).

- BeF_2 does NOT for bridge bond. It forms 2 strong back bonds.



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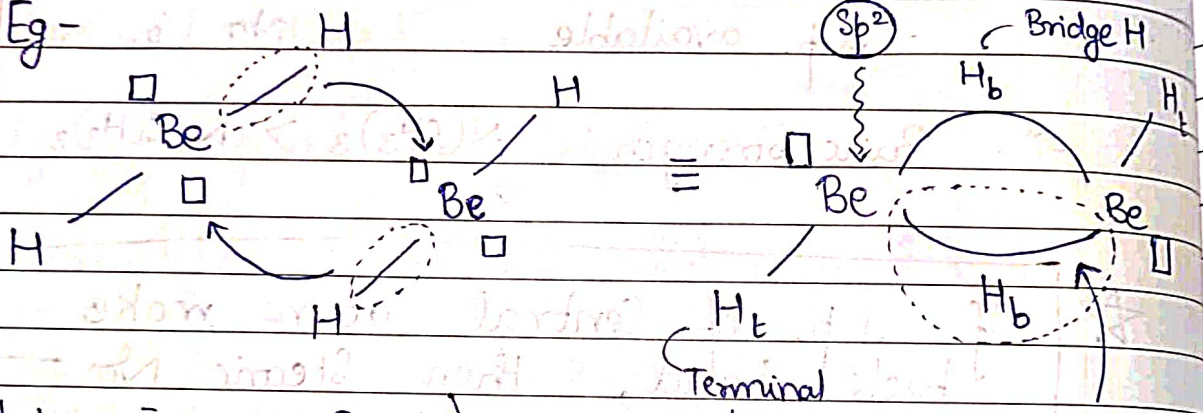
- BeX_2 ($X = Cl, Br, I$) & BeH_2

— exist as a dimer in vapor phase.

— " " " polymer in solid state.

Cl: When side atom does NOT have l.p.

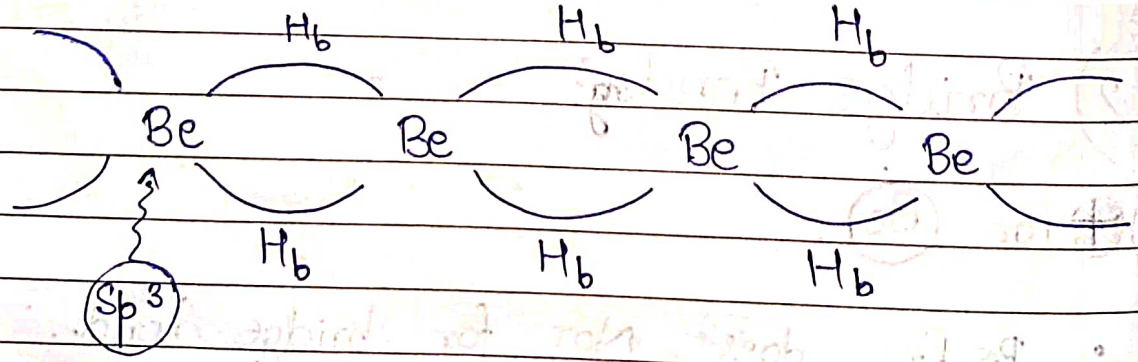
Eg-



(b.p. e^- in Be–H bond are shared b/w 3 atoms)

Dimer form
(Octet not complete)

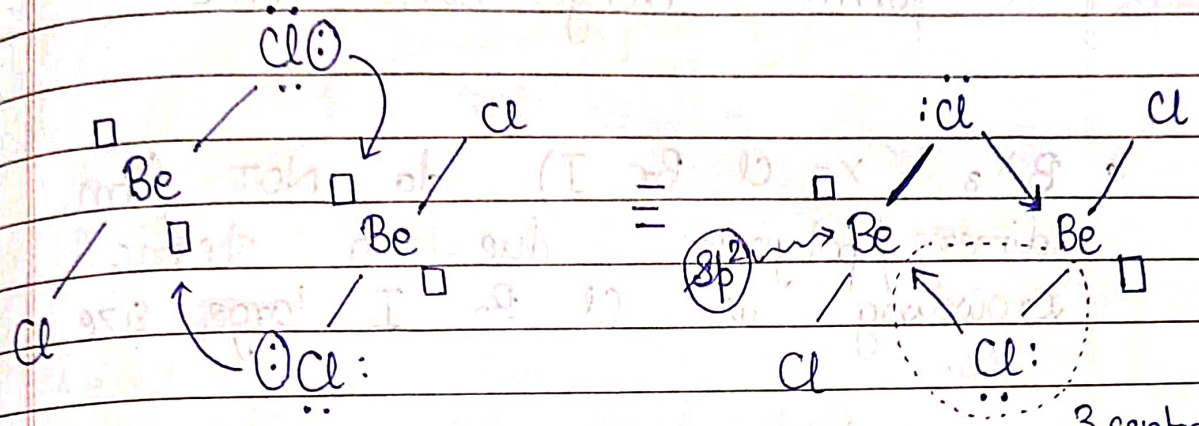
Bond Length: $Be-H_b > Be-H_t$



Polymer form
(Octet complete)

C2: When side atom has l.p.

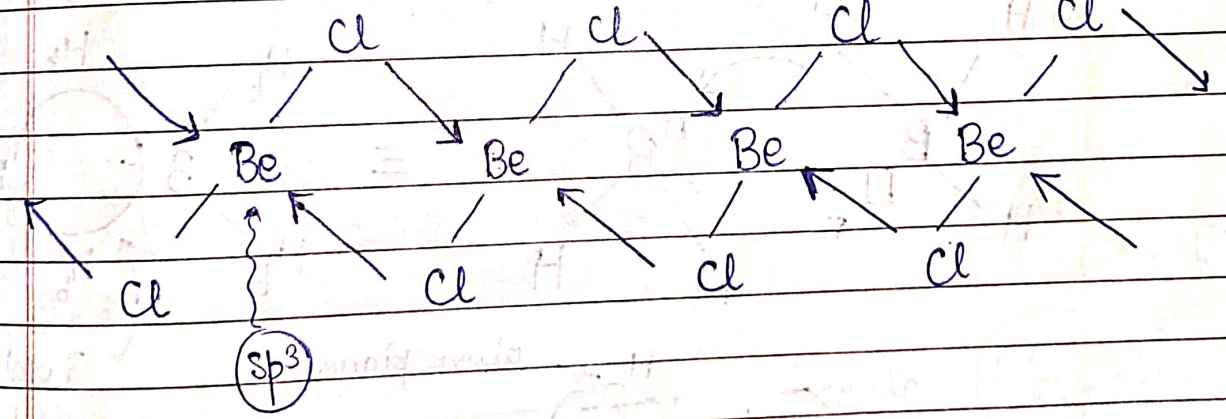
Eg - $BeCl_2$ Cl's coordinate bond stronger than back bond.



3 centre 4e⁻ bond

(Cl gives l.p. to Be. ⇒ Coordinate Bond.)

Dimer form
(Octet not complete)



Polymer form
(Octet complete)

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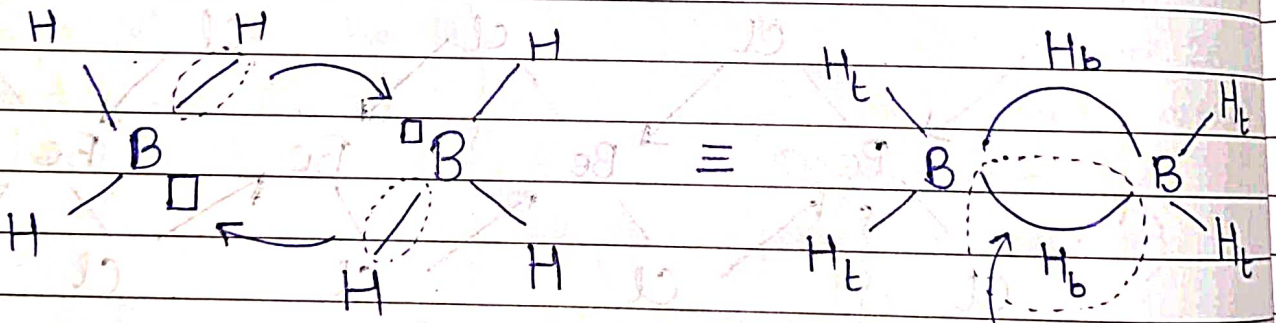
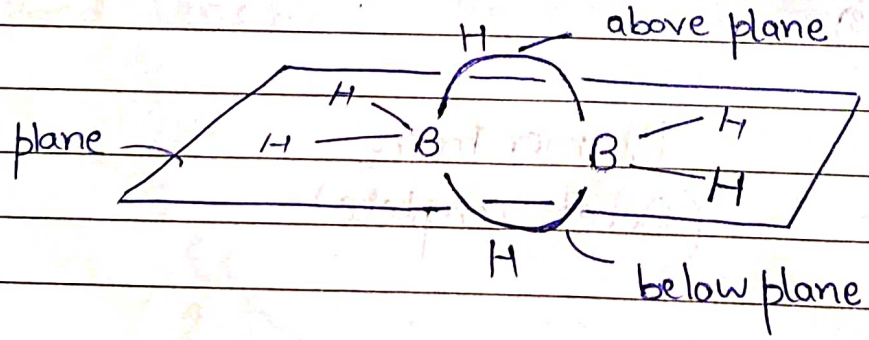
ii) for (B).

- BF_3 does NOT form bridge form. It forms strong back bond.

- BX_3 ($X = Cl, Br, I$) do NOT form dimers / polymer due to steric crowding as Cl, Br, I large size.

- BH_3 forms dimer in vapor phase. Can't form polymer as only 1 vacant orbital.





Dimer form

* B still e⁻ deficient as this dimer breaks, then forms, then breaks, ...

(iii) For (Al)

- AlF_3 is predominantly ionic ⇒ Octet Complete.

$$AlF_3 \longleftrightarrow Al^{+3} \; 3F^-$$

- $AlCl_3$, AlH_3, $Al(CH_3)_3$ exist as dimers in vapor state, and as polymer in solid state.

- $AlBr_3$, AlI_3 can form dimer, but can't form polymer.

(i) Find molecules which have 3 centre $2e^-$ bond.

Al_2H_6 B_2H_6 BeH_2 Be_2Cl_4 Al_2Cl_6 $Al_2(CH_3)_6$

A) Side atom NOT L.p. for 3 centre $2\bar{e}$ bond.

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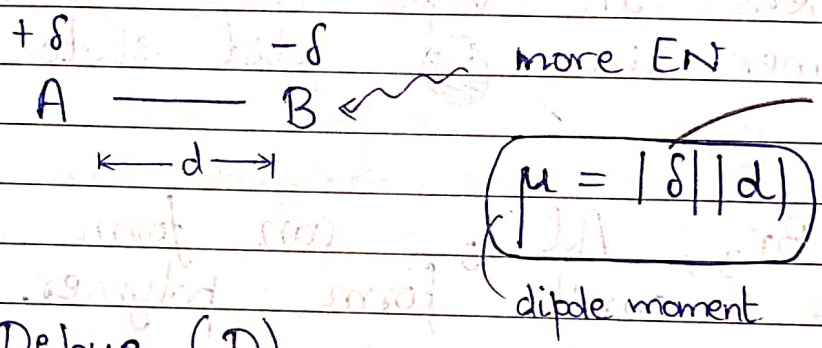
Dipole Moment

It measures ionic character in polar covalent molecules.

Defⁿ: It is product of magnitude of charge and interatomic dist. b/w atoms.

Eg:

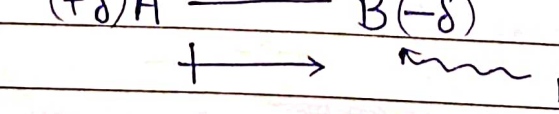


Unit: Debye (D)

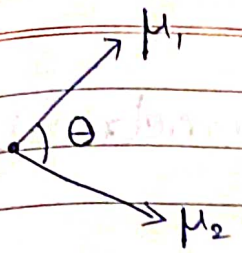
$1\ D = 3.3 \times 10^{-30}\ Cm = 10^{-18}$ esu - cm
(electrostatic unit

$1\ e^- = 1.6 \times 10^{-19}\ C = 4.8 \times 10^{-10}$ esu

Dirxⁿ: Diople Moment is vector qty.



From less EN atom to more EN atom.



* $\mu_{net} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos(\theta)}$

$\Rightarrow$ $\boxed{\mu_{net} \propto 1/\theta}$

* $\mu = 0 \Rightarrow$ Non Polar ; $\mu \neq 0 \Rightarrow$ Polar.

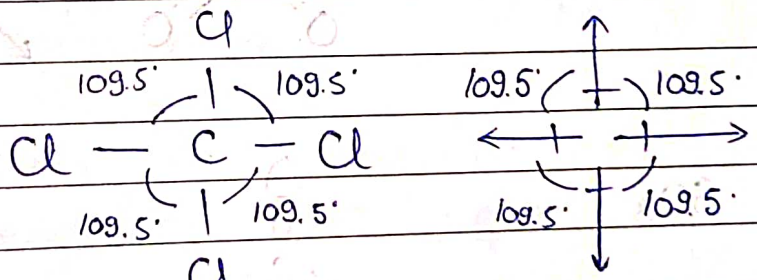
i) Comparison of μ

- Symmetrical molecular species in which l.p. & b.p. are symmetrically placed, their ($\mu = 0 \Rightarrow$ Non polar)

Eg : CCl_4

$\mu = 0$

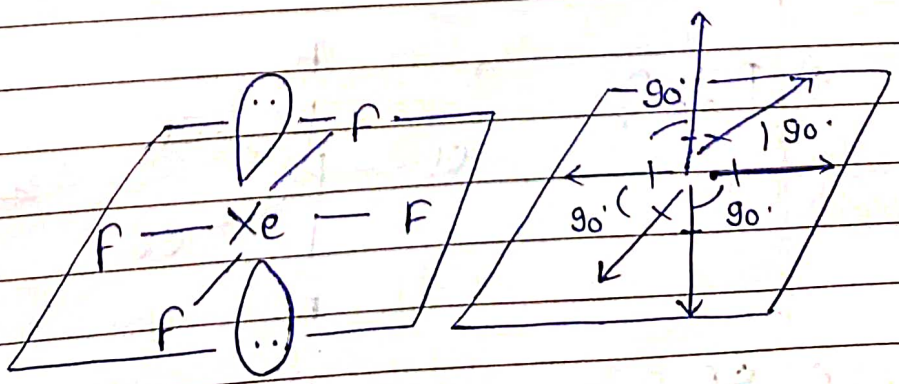
$\Rightarrow$ Non Polar



Eg : XeF_4

$\mu = 0$

$\Rightarrow$ Non Polar.



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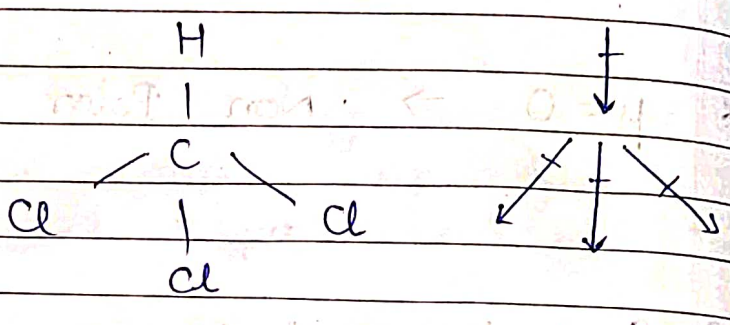
- If molecule is NOT symmetrical, then ($\mu \neq 0 \Rightarrow$ Polar)

Eg: $CHCl_3$

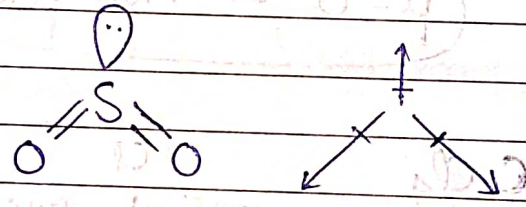


$\mu \neq 0$

$\Rightarrow$ Polar

Q) Tell Polar or Non-Polar.

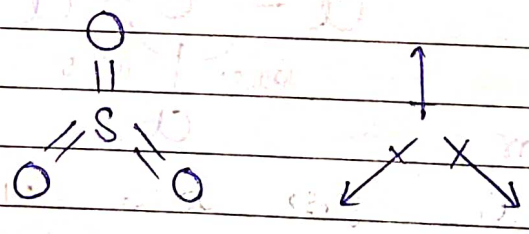
1) SO_2



$\mu \neq 0$

Polar

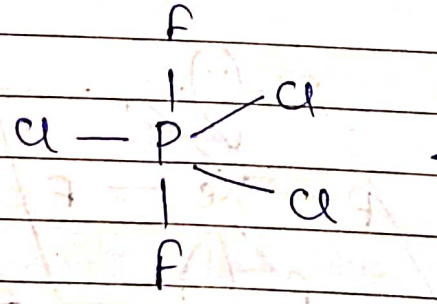
2) SO_3



$\mu = 0$

Non Polar

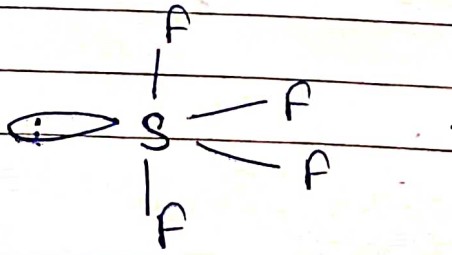
4) PCl_3F_2



$\mu = 0$

Non Polar

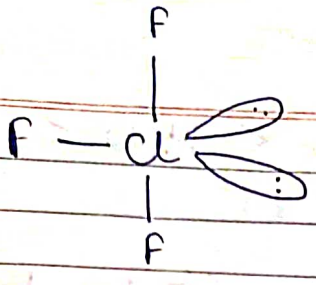
5) SF_4



$\mu \neq 0$

Polar

6) ClF_3

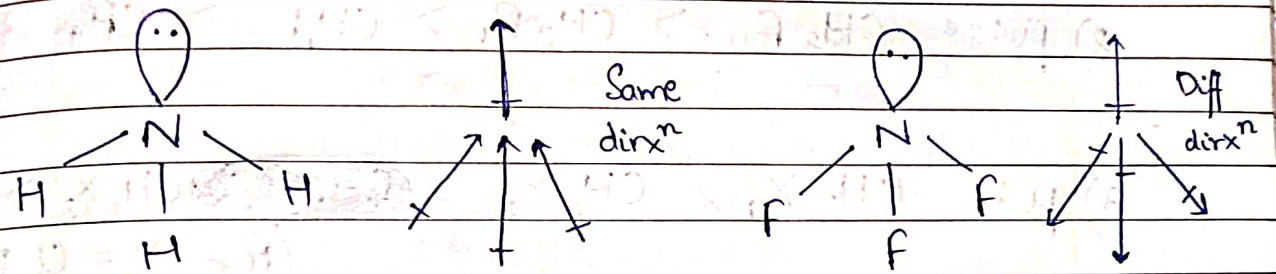


$\mu \neq 0$

Polar

7) NH_3 & NF_3 — (also compare their μ).

A)



Polar $\quad \mu \neq 0$ $\quad$ Polar $\quad \mu \neq 0$.

Dipole moment of N—F is somewhat cancelled by N ⊙

$\Rightarrow \quad \mu_{NH_3} > \mu_{NF_3}$

— In comparison of dipole moment among polar molecules, charge is dominant over bond length. factor. partial (Apply when side atoms same & all μ same dirⁿ) (δ)

Q) Compare μ.

1) $H-F > H-Cl > H-Br > H-I$

2) $H_2O > H_2S > H_2Se > H_2Te$

3) $CH_4 = SiH_4 = GeH_4 = SnH_4 = 0$

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4) $CH_4 < NH_3 < H_2O < HF$

Special Cases (Data based)

1) μ: $CH_3-Cl > CH_3-F > CH_3-Br > CH_3-I$

2) μ: $CH_2F_{②} > CH_3F_{①} > CH_1F_{③} > CF_{④}$
(F: 2 > 1 > 3 > 4)

3) μ: $CH_3X_{①} > CH_2X_{②} > CH_1X_{③} > CX_{④}$
(X: 1 > 2 > 3 > 4) (for X = Cl, Br, I)

ii) Calc. % ionic character (in Polar Covalent bond)

$$(\%\text{ ionic character}) = \frac{|\delta|}{|e|} \times 100\%$$

Q) Calc. the % ionic character of a bond having bond length 0.92 Å and 1.91 D as its observed dipole moment.

A) $|\delta| = \left(\frac{\mu}{d}\right) \Rightarrow (\%\text{ ionic char.}) = \frac{|\delta|}{|e|} \cdot 100\%$

$$= \left(\frac{\mu}{de}\right) \cdot 100\% = \frac{(1.91\ D) \cdot 100\%}{(0.92 \cdot 10^{-8}\ cm)(4.8 \times 10^{-10}\ esu)}$$

$\Rightarrow$ (% ionic char.) $\approx$ 40 %

GOOD WRITE

Q) Experimental value of dipole moment of AB bond is 1.2 D. The length of AB bond is 1 Å. Find % ionic char.

A) $|\delta| = \left(\frac{\mu}{d}\right) \Rightarrow (\%\text{ ionic char.}) = \frac{|\delta|}{|e|} \cdot 100\%$

$= \left(\frac{\mu}{d|e|}\right) \cdot 100\% = \frac{(1.2\,D) \cdot 100\%}{(10^{-8}\,cm)(4.8 \cdot 10^{-10}\,esu)}$

$\Rightarrow$ $\boxed{(\%\text{ ionic char.}) \approx 25\%}$

Molecular Orbital Theory (MOT)

VBT could NOT explain: Paramagnetic nature of O_2, stability of molecules like H_2^+, He_2^+, ..., fractional bond order, ...

Hence, Molecular Orbital Theory was intro.

Postulates –

1) All at. orbitals of same energy of diff. atoms combine to form equal no. of orbitals known as molecular orbitals.

2) Molecular orbital is a region in space surrounding 2 nuclei where probab. of finding e^- is max.

3) Orig. at. orbitals lose their identity.

4) Molecular Orbitals → Bonding Molecular Orbitals (BMO)
→ Anti Bonding Molecular Orbitals (ABMO)

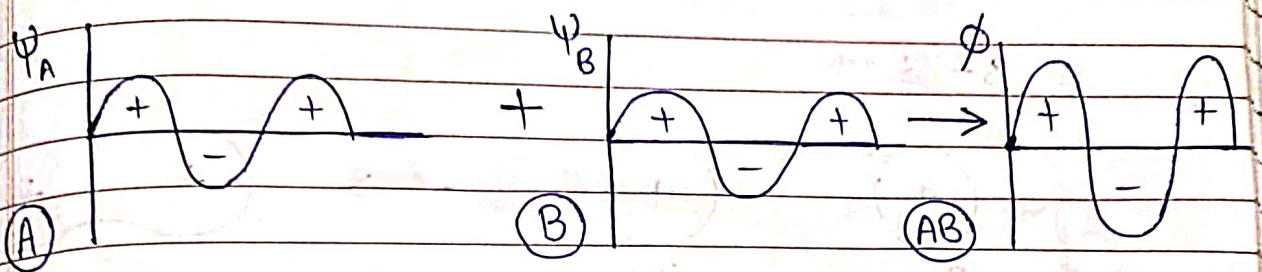
5) Molecular Orbitals representation: σ, σ^*, π, π^*, ...

6) In filling of $\bar{e}$ in M.O., Aufbau's Principle, Pauli's Exclusion Principle, Hund's Rule follow.

At. Orbitals	Molecular Orbitals
$\bar{e}$ under influence of only 1 nucleus.	$\bar{e}$ under influence of multiple nuclei.
Exist bcos of inherent prop^t of atom.	Formed by combination of 2 at. orbitals.
Less Stable. Simple Shape.	More Stable. Complex Shape

Bonding M.O. (σ, π, ...)	Anti Bonding M.O (σ^*, π^*, ...)
(+)(+) OR (−)(−) Same phase	(+)(−) OR (−)(+) Opp. phase
Constructive overlapp.	Destructive overlapp.
$\bar{e}$ in BMO lead to attraction. So $\bar{e}$ density ↑ ⇒ Stability ↑	$\bar{e}$ in ABMO lead to lead to repulsion. So $\bar{e}$ density ↓ ⇒ Stability ↓

i) Linear Combination of At. Orbitals :-

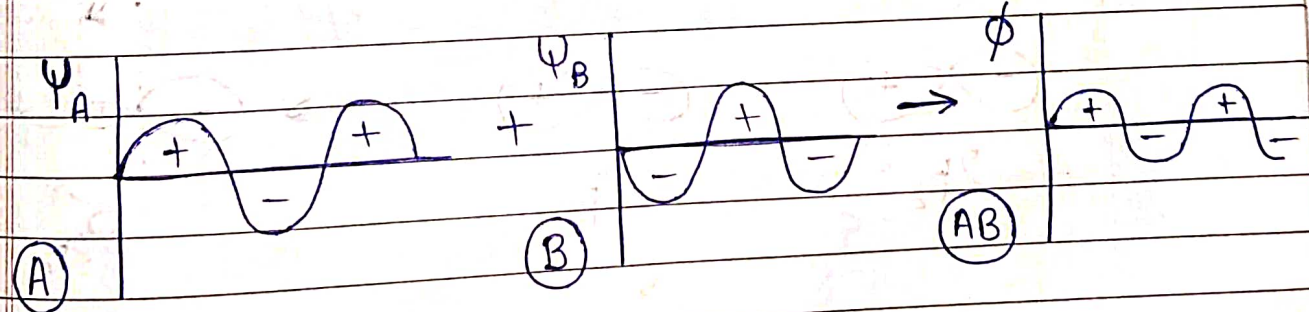


ϕ (Wave fx^n of M.O.) = $\psi_A + \psi_B$

Probab. Density : ψ_A^2 ψ_B^2 $(\psi_A + \psi_B)^2$

Now, $\phi^2 = (\psi_A + \psi_B)^2 > \psi_A^2 + \psi_B^2$

$\Rightarrow$ (Probab. Density after Bonding) > (Probab. Density before Bonding)



ϕ (Wave fx^n of M.O.) = $\psi_A - \psi_B$

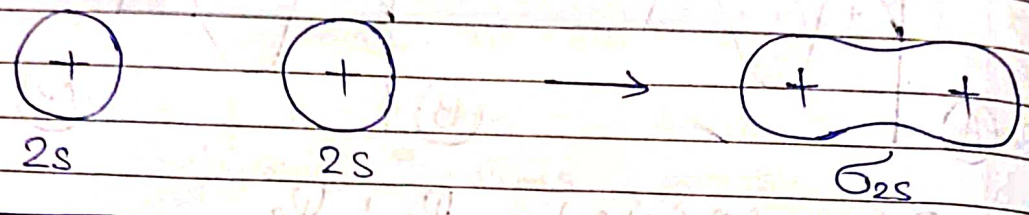
Probab. Density : ψ_A^2 ψ_B^2 $(\psi_A - \psi_B)^2$

$\phi^2 = (\psi_A - \psi_B)^2 < \psi_A^2 + \psi_B^2 \Rightarrow$ (Probab. Density after Bonding) < (Probab. Density before Bonding)

11/9/22

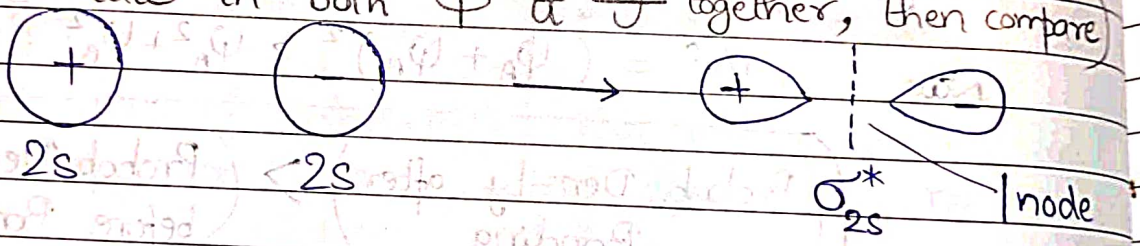
ii) Add^n of Atomic Orbitals –

1) s – s

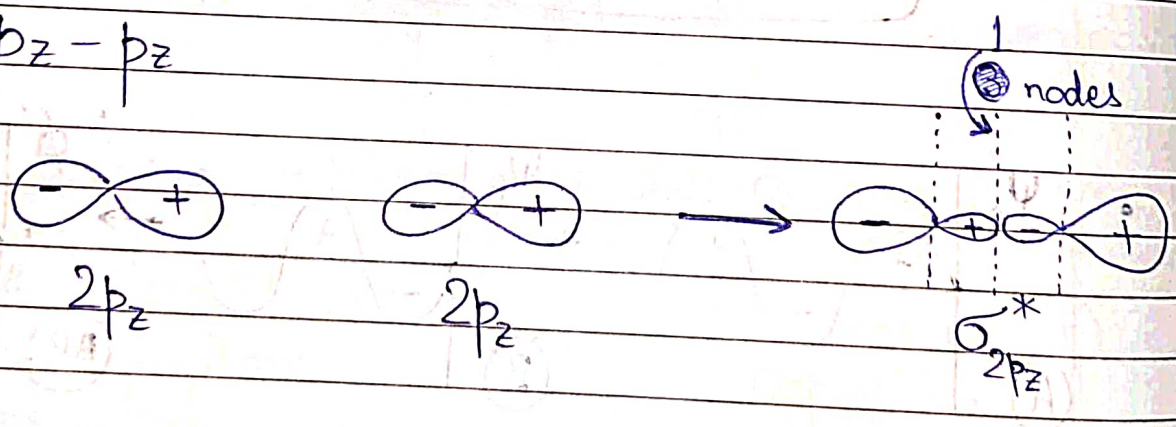


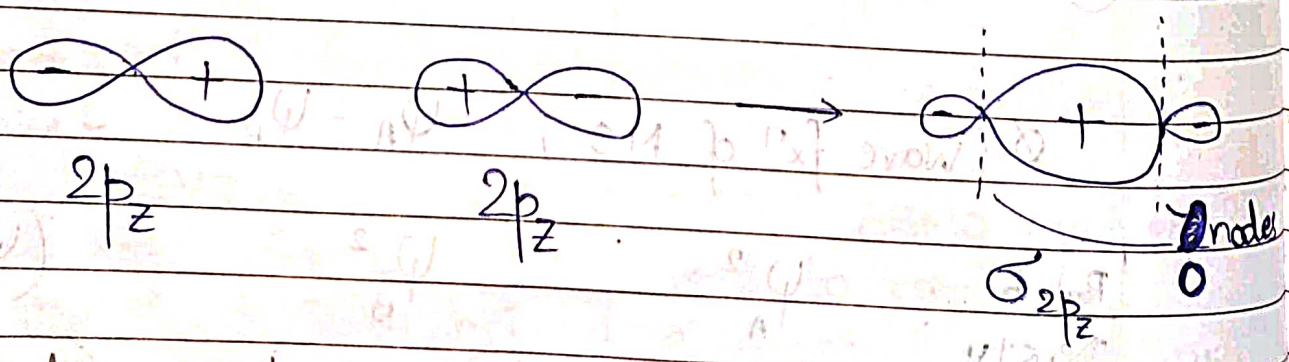
★ Gerade Orbitals : MOs which are symmetric wrt. its centre

(To check, rotate in both ↻ & ↺ together, then compare)



2) $p_z - p_z$





Nodes calcd. at centre.

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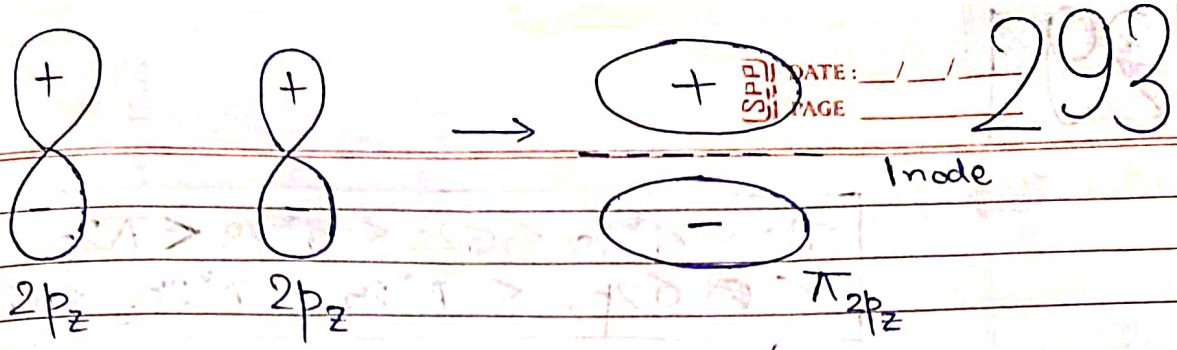
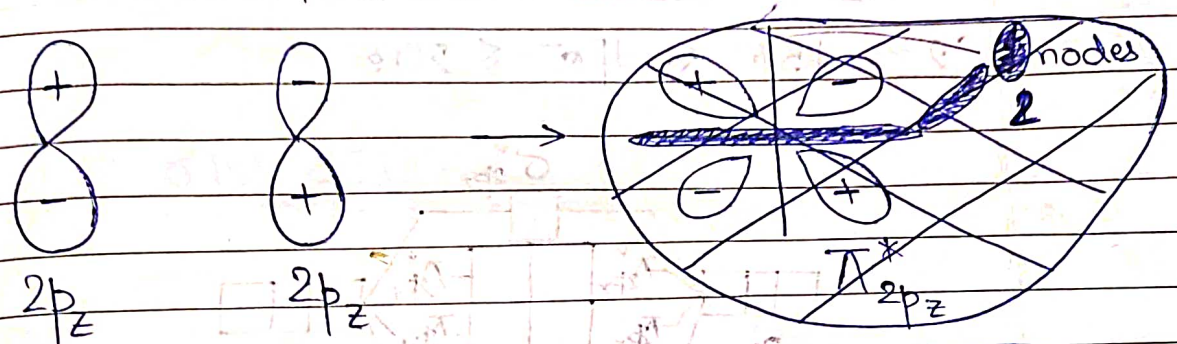
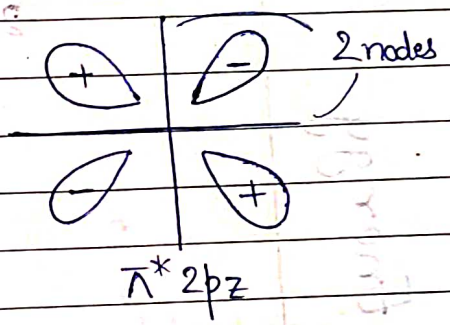


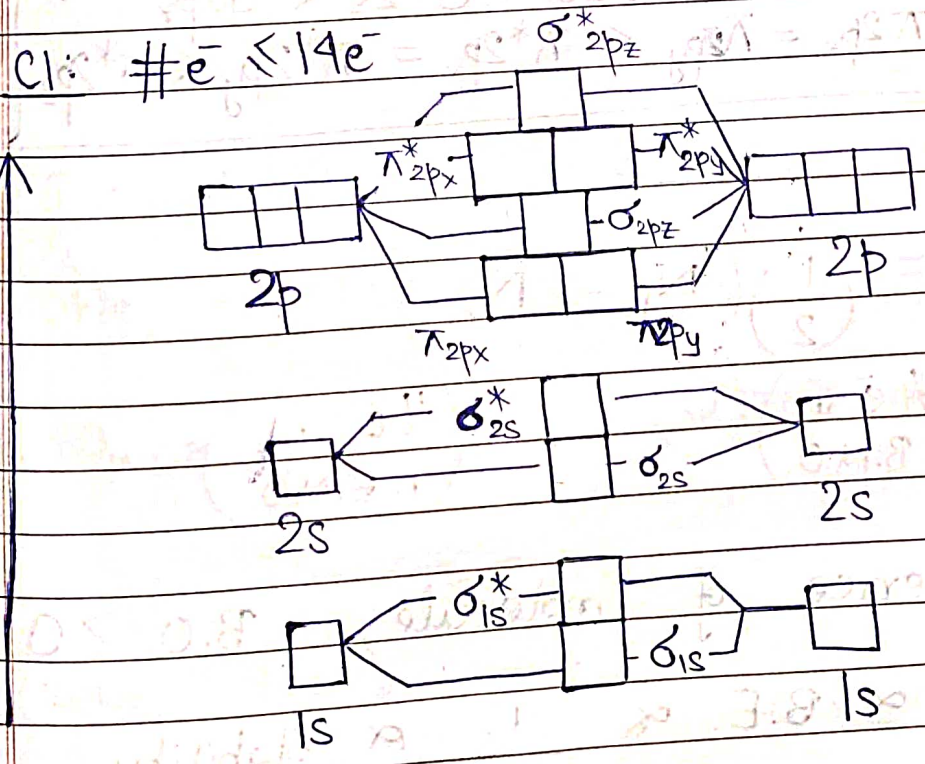




☆ - Gerade : σ , π*
Ungerade : σ* , π

iii) Electronic Config. & Behavior of Molecules – (only for diatomic molecules)

Cl: #e⁻ = 14e⁻



In this case, 2s of one atom mix with 2pz of other atom also.

⇒ Energy of σ2pz , σ*2pz ↑

⇒ Energy of σ2s , σ*2s ↓

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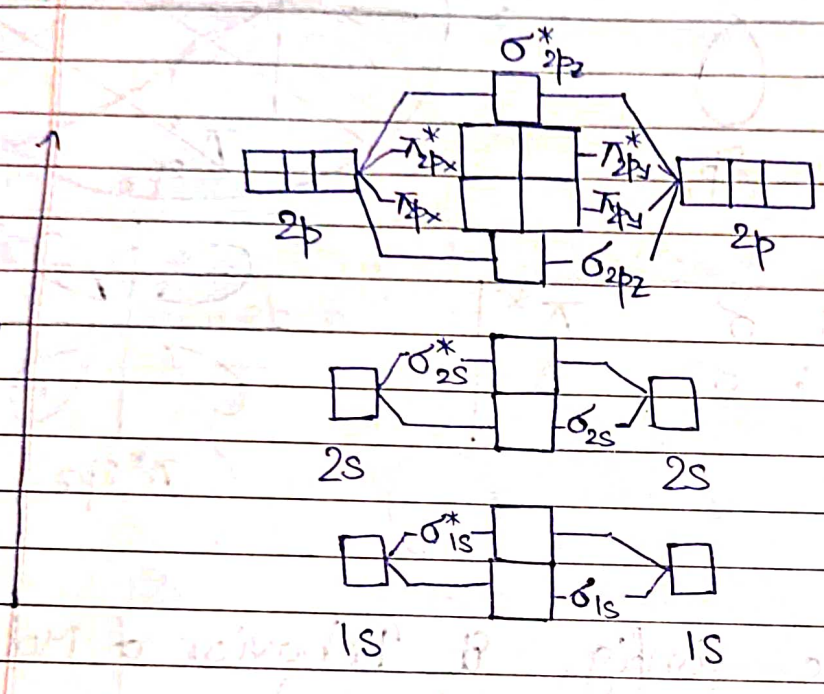
$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \pi 2p_x = \pi 2p_y < \sigma 2p_z < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$

C2: $15e^- \leq \#e^- \leq 20e^-$



'2' of one atom does NOT mix with 'p' of the other atom.

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

★

$$B.O. = \frac{1}{2}(N_b - N_a)$$

(N_b: $\#\bar{e}$ in B.M.O.; N_a: $\#\bar{e}$ in A.B.M.O.)

for existence of molecule, B.O. > 0.
(If same, then check ABNO $\bar{e}$)

$$B.O. \propto B.E. \propto \frac{1}{B.L.} \propto \text{Stability}$$

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Q) Write E.C. for H_2, H_2^+, H_2^-. Compare stability & magnetic behavior.

A) $H_2 = \sigma 1s^2$ $\quad H_2^+ = \sigma 1s^1$

$H_2^- = \sigma 1s^2 \sigma^* 1s^1$

$BO_{H_2} = \left(\frac{1}{2}\right)(2-0) = 1$ $\quad BO_{H_2^+} = \left(\frac{1}{2}\right)(1-0) = \frac{1}{2}$

$BO_{H_2^-} = \left(\frac{1}{2}\right)(2-1) = \frac{1}{2}$

Stability: $H_2 > \underbrace{H_2^+ > H_2^-}$ (more antibonding e^- than H_2^+)

Diamag $\therefore$ H_2

Paramag: H_2^+, H_2^-

Q) Does He_2 exist?

A) $He_2 = \sigma 1s^2 \sigma^* 1s^2$

$BO_{He_2} = \left(\frac{1}{2}\right)(2-2) = (0) \Rightarrow$ Does NOT exist.

296 (H.O.M.O. = Highest Occupied M.O.
L.U.M.O. = Lowest Unoccupied M.O.)

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Q) Write EC. for following —

1) Li_2 = $\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2$

2) Be_2 = $\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2$

★ 3) B_2 = $\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \pi 2p_x^1\ \pi 2p_y^1$

This has 1 π bond. ← (BMO & ABMO cancel)

★ 4) C_2 = $\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \pi 2p_x^2\ \pi 2p_y^2$

This has 2 π bonds. ← (BMO & ABMO cancel)

5) N_2 = $\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \pi 2p_x^2\ \pi 2p_y^2\ \sigma 2p_z^2$

★ 6) O_2 = $\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2\ \pi 2p_y^2\ \pi^* 2p_x^1\ \pi^* 2p_y^1$

O_2 is paramagnetic ← (Still it is colorless) (Energy: L.U.M.O > H.O.M.O)

Short Trick

Total # e^-	B.O.
12	2
13	2.5
14	3
15	2.5
16	2

Imp. Pts. –

1) Total # e^- = even ⇒ B.O. = int.

2) Total # e^- = odd ⇒ B.O. ≠ int.
⇒ Always Paramag.

3) e^- add^n → in BMO ⇒ BO ↑ ⇒ BL ↓
→ in ABMO ⇒ BO ↓ ⇒ BL ↑

4) e^- remove → from BMO ⇒ BO ↓ ⇒ BL ↑
→ from ABMO ⇒ BO ↑ ⇒ BL ↓

Q) Arrange in order of stability.

1) $N_2 > N_2^+ > N_2^-$
BO = 3 (BO = 2) more ABMO e^-

2) O_2, $O_2^{\ominus}$, $O_2^{2\ominus}$, $O_2^{\oplus}$, $O_2^{2\oplus}$

A) Stability : $O_2^{2\oplus} > O_2^{\oplus} > O_2 > O_2^{\ominus} > O_2^{2\ominus}$

B.O. : 3 2.5 2 1.5 1

★Q) Compare E_1, E_2

$N_2 \xrightarrow{E_1} N_2^+$

$NO \xrightarrow{E_2} NO^+$

A) $E_1 > E_2$
More diff. to remove BMO e^- than ABMO e^-.

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☆ Q) Write order of energy levels in CO

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

Energy of $\sigma^* 2s$ inc very much.

☆ Q) Calc. bond order in CO^+

A) $CO^+ = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2 \sigma^* 2s^1$

$B.O. = \left(\frac{1}{2}\right)[10 - 3] \Rightarrow$ **BO = 3.5**

☆ Color of Halogen gas (even though diamag.)

X_2	F_2	Cl_2	Br_2	I_2
Color	Pale Yellow	Light Green	Brown	Violet

(Energy of H.O.M.O. & L.U.M.O. similar)

Imp Pts. —

1) In $O_2^{2\oplus}$ (and like), even though # $e^- \leq 14$ use EC of # $e^- \geq 15$ as # e^- in $O_2 \geq 15$.

2) In $N_2^{\ominus}$ (and like), even though # $e \geq 15$ use EC of # $e \leq 14$ as # e^- in $N_2 \leq 14$

3) Boil. Pt.: $H_2O > HF > NH_3$ as H_2O has 2 hydrogen bonds.