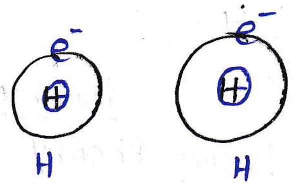
Chemical Bond

- atom → donot exist → independently (~~exp~~ except Noble gas)
- Group of atom → exist → molecule → The attractive force which holds atom, ions togather In a molecule is called chemical bond.
- attraction ↑ Energy ↓ Stability ↑ Strength of bond.

Cause of chemical bond

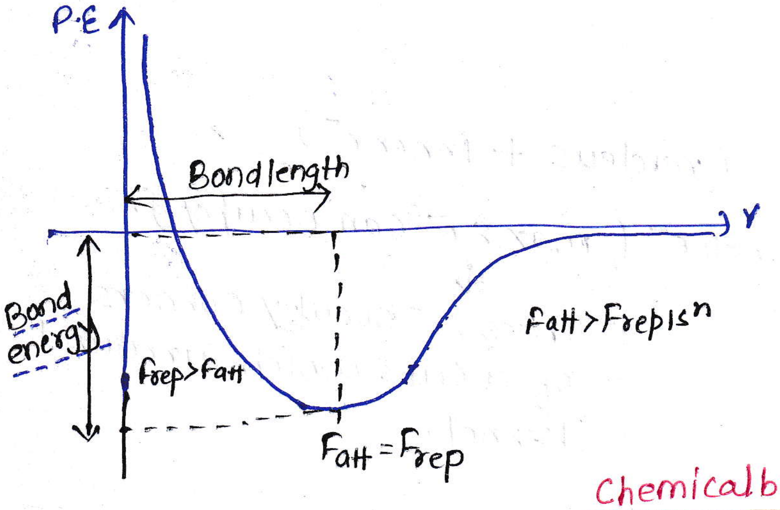
① • Tendency to aquire min energy →



② ~~octet Rule~~

nucleus ⟶ nucleus → attraction
e⁻ ⟵ e⁻

nucleus ---- nucleus → repulsion
e⁻ ---- e⁻



~~octet Rule~~

Chemicalbond

Strongbond (interatomic bond)
- Covalent
- ionic
- metallic
- cordinate

(200-400KJ/mol)

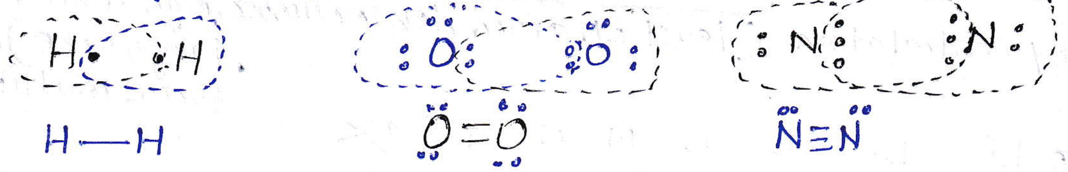
weakbond (intermolecularbond)
- Vanderwaal (2-8 KJ/mol)
- H·Bond (8-40 KJ/mol)

(2-40 KJ/mol)

Covalent bond

- Sharing of electrons to complete its octet. (H → duplet)
- Bond formed b/w nonmetal & non-metal.

eq:-



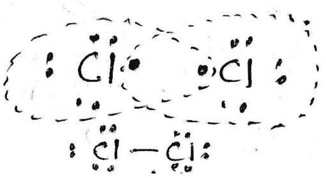
Single cov bond
2e⁻ share

double cov bond
4e⁻ share

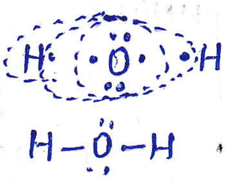
Triple cov bond
6e⁻ share

The dots represent valence e⁻ & these str are k/a Lewis str.

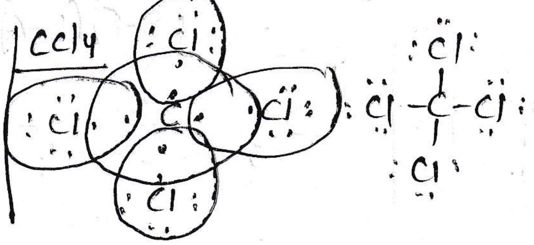
Cl_2



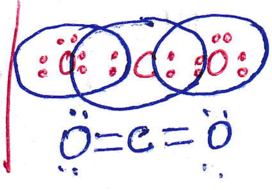
H_2O



CCl_4

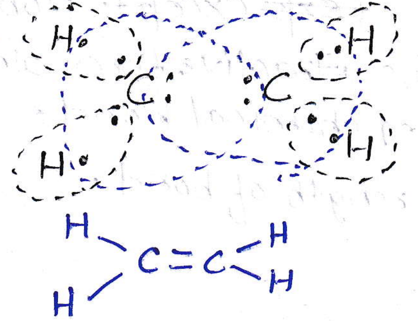


CO_2



~~Chemical Bond~~

C_2H_4



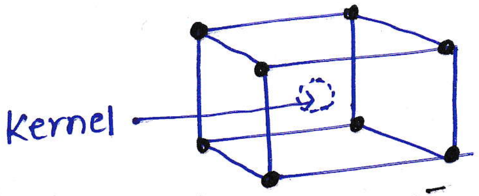
C_2H_2

H − C ≡ C − H

Theories of Covalent bond

1. Lewis theory
2. VBT
3. VSEPR Theory
4. MOT

Lewis theory :- atom → kernel (nucleus + inner e^-)
→ outershell e^- (max 8 e^- can occupy).
↓
These 8e^- occupy corners of a cube which surround kernel.



8 corner → valence e^-

Octet Rule → given by Lewis & kossel

also k/a electronic theory of chemical bond

- Atoms combine to complete its octet in their outermost orbit

↓ Sharing of e^-
eq. Cl_2, N_2, O_2 etc

↓ Complete transfer of e^-
eq NaCl, $CaCl_2$, MgO etc.

Rules to draw Lewis dot str

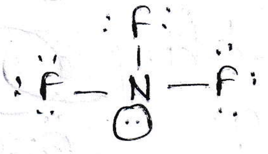
- Identify central atom (least EN atom, less in number, high atomic number, large size)
- forms multiple bond.

- ~~arrange~~ Li Be B C N O F ~~Ne~~

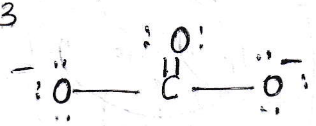
Li	Be	B	C	N	O	F
1	2	3	4	3	2	1

P	S	Cl
(3-5)	(2-6)	(1-7)

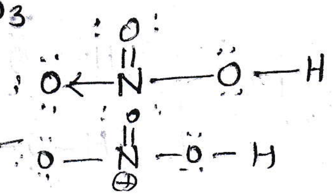
NF_3



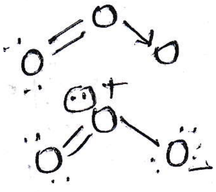
CO_3^{-2}



HNO_3

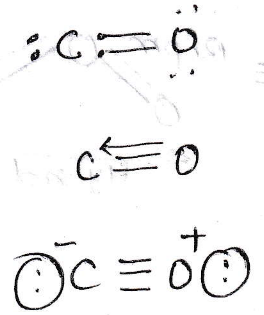


O_3



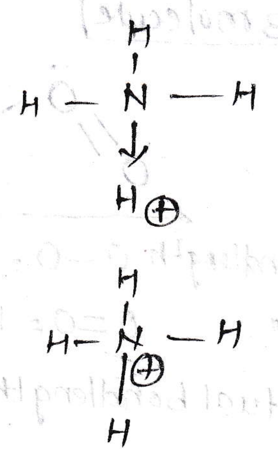
②

CO

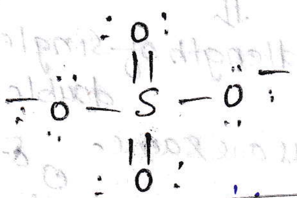


NO_2^-

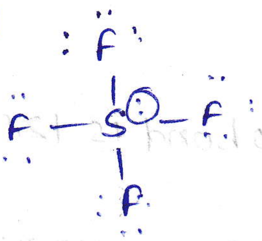
NH_4^+



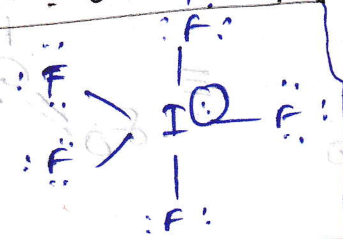
SO_4^{-2}



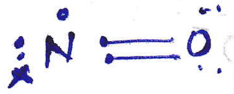
SF_4



IF_5



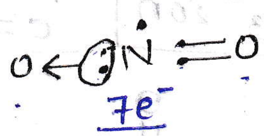
NO



odd e^- molecule

octet Rule fails

NO_2



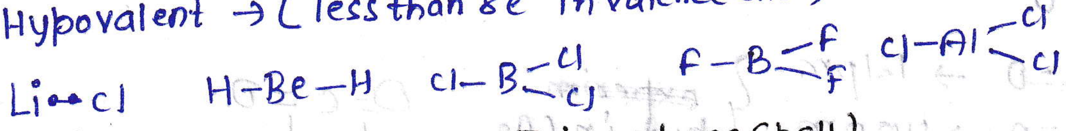
7e^-

odd e^-

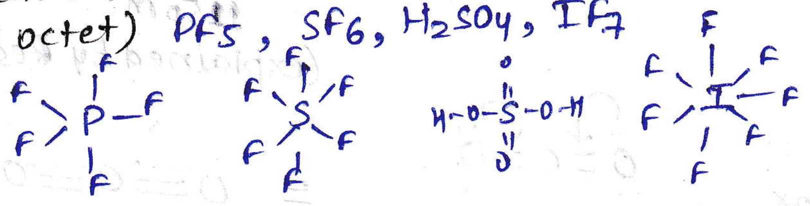
octet rule fails

Drawbacks of Lewis theory

- could not explain str of any compd.
- could ——— B.L, B.O, B.E etc.
- Hypovalent → (less than 8e^- in valence shell)



- Hypervalent → (more than 8e^- in valence shell) (expanded octet) PF_5, SF_6, H_2SO_4, IF_7



- odd electron species

NO & NO_2 & ClO_2

- compounds of noble gases are also formed

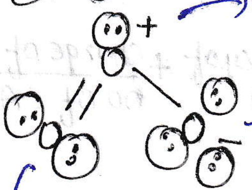
XeF_2, KrF_2, $XeOF_2$, XeO_3, $XeOF_4$, XeF_6

Formal charge

- ~~Formal~~ Charge of an indivisual atom is formal charge.

$$F.C = \text{valence } e^- - (\text{bonds} + \text{dots})$$

① O_3



→ $6-(3+2) = ①$

→ $6-(1+6)$

$6-7$

(−1)

$6-(2+4)$

⓪

CN^-

$\overset{\ominus}{:C \equiv N:}$

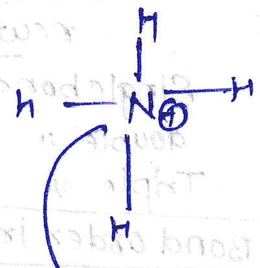
$4-(3+5)$

-1

$5-(3+2)$

0

NH_4^+

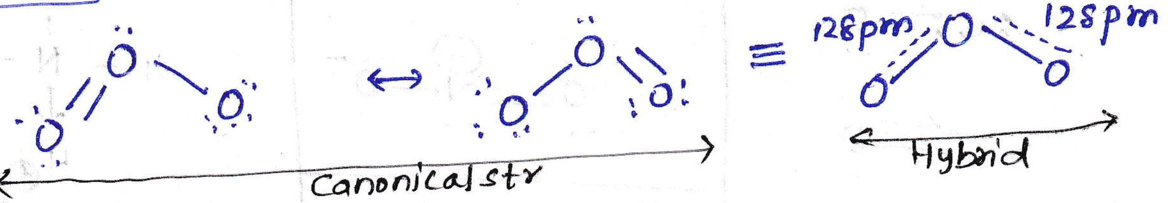


$5-(4+0)$

①

Resonance

① **O$_3$ molecule**



Bondlength O—O = 148 pm

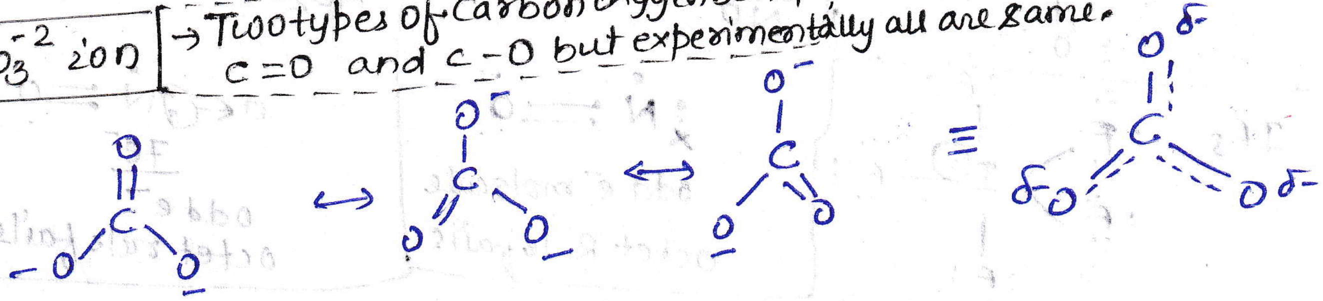
" O=O = 121 pm

actual bondlength of O & O bond is 128 pm (explained by Reso)

⇓

bondlength of single bond ↓
double bond ↑

② **CO_3^{-2} ion** → Two types of Carbon oxygen bond C=O and C–O but experimentally all are same.

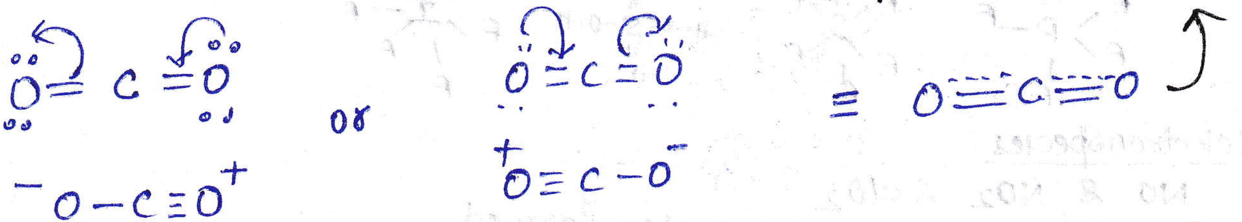


③ **CO$_2$ molecule**

O= C =O

actual C=O → 121pm }
" C≡O → 110pm } ~~experim~~ but in CO$_2$

O=C=O
↓ ↓
125pm
(explained by Resonance)



- Resonance hybrid is real str. & Canonical forms are hypothetical.
- Resonance hybrid has less energy than energy of any single canonical str so, Resonance Stabilizes the molecule.

Bond order

neutral molecule

Single bond ⇒ BO = 1

double " = 2

Triple " = 3

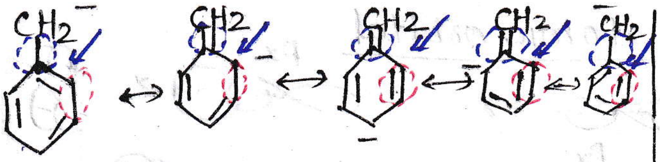
Bond order In Resonance str

$$BO = \frac{\text{Total no of bonds b/w two atoms in all str}}{\text{Total no of RS}}$$

Radical (charged)

PO_4^{3-}, SO_4^{-2}, ClO_4^-

$$BO = \text{Valency of SA} + \frac{\text{Charge of com}}{\text{no of SA}}$$



BO = $\frac{8}{5}$ = 1.6

BO = $\frac{8}{5}$ = 1.6

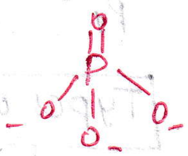
BO = $\frac{6}{5}$ = 1.2

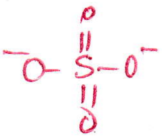
PO_4^{-3}, SO_4^{-2}, ClO_4^-

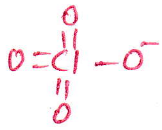
BO = $2 + \frac{(-3)}{4}$ = $\frac{5}{4}$ = 1.25

$2 + \frac{(-2)}{4}$ = 1.5

$2 + \frac{(-1)}{4}$ = 1.75







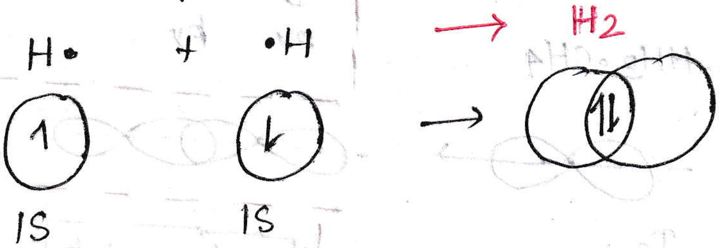
more π bond → more Bond order

Bond order ∝ Bond strength ∝ Bond En ∝ stab ∝ $\frac{1}{\text{Bond length}}$

if $\boxed{\text{Bond order = +ve Integer}}$ → compd is stable
= 0/ -ive → Unstable
= fraction (grater than 1) → compd should isomerism
= +1/2 → Unstable but exist → H_2^+, He_2^+

$\boxed{\text{Valence Bond Theory}}$ → Overlapping Theory
→ Hybridization Theory

- Covalent bond is formed when atomic orbital combine.

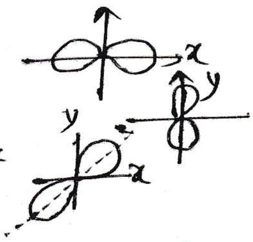


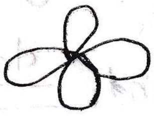
- overlaping orbital → half filled
  → must have opposite spin
- Extent of overlap should be less than 50% (In case of more than 50% repulsion b/w both nucleus occurs)
- Extent of overlap ∝ strength of bond ∝ stability ∝ bond energy ∝ $\frac{1}{\text{Bond length}}$.

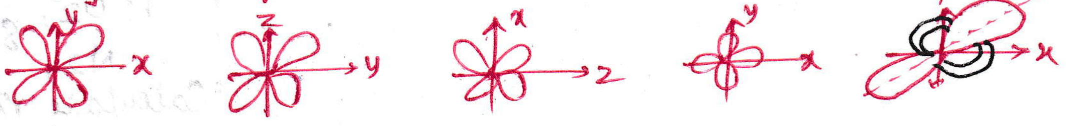
Atomic orbital

Spherical  S orbital (nondirectional)

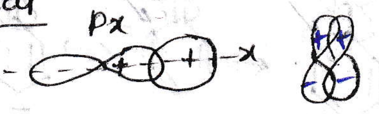
dumbell  P " (directional) → Px, Py, Pz



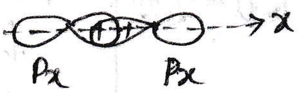
double dumbell  d " (directional) → dxy, dyz, dzx, dx²-y², dz²



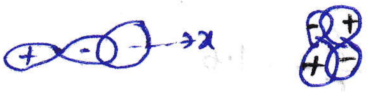
overlap of atomic orbital



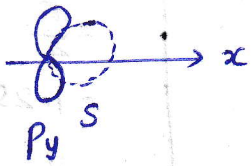
overlap
- +ve overlap

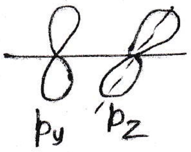


- -ve overlap



- zero overlap





Types of overlap

axial or headon

Sigma bond

parallel or Sideways

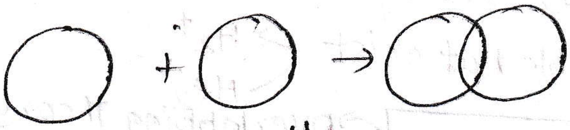
Pi bond

s–s overlap

s–p overlap

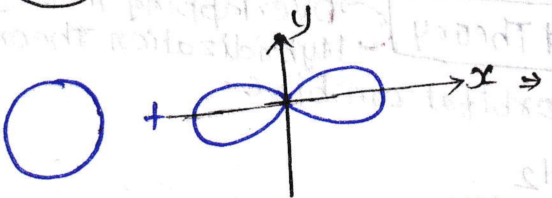
p–p overlap

S-S



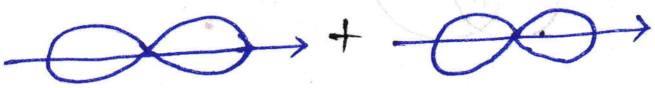
eq H_2

S-P



eq:- HF, HCl, H_2S, NH_3, CH_4

P-P



eq F_2, Cl_2, Br_2, I_2

$P_x + P_x \rightarrow x = INA$

$P_y + P_y \rightarrow y = INA$

$P_z + P_z \rightarrow z = INA$

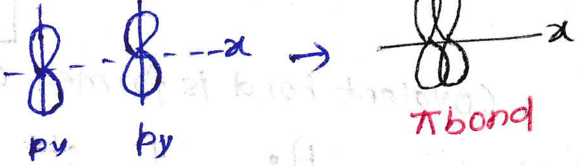
axial/head on overlap

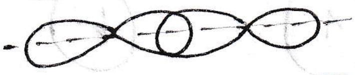
p–p overlap, p–d overlap

d–d overlap

p-p overlap → overlap not on internuclear axis

overlap is above or below internuclear axis.

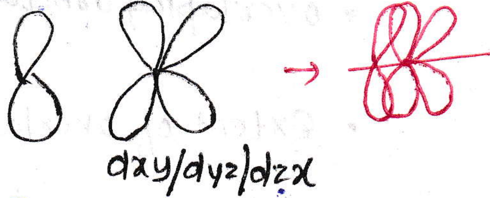


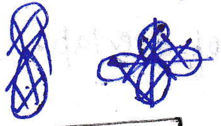


$p_z + p_z \rightarrow$ axis x or y

$p_x + p_y \rightarrow$ axis y or z

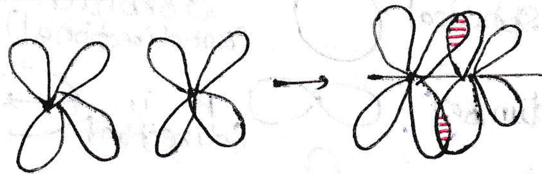
p-d overlap





→ zero overlap

d-d overlap



d-d overl

example of π bond.

eq: O_2, N_2, SO_3, SO_4^{-2}, PO_4^{-3}

Calculate pπ-pπ and pπ-dπ bonds

O_2

$\ddot{O} = \ddot{O}$

2nd Period

no d orbital

So, 1 Pπ–Pπ bond

N_2

$\ddot{N} \equiv \ddot{N}$

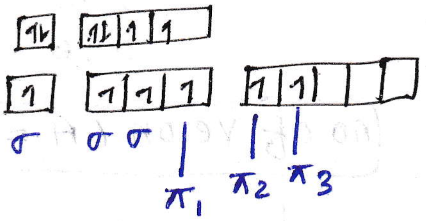
2nd Period

no d orbital

2 Pπ–Pπ bond

SO_3

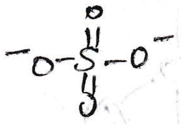
$1s^2 2s^2 2p^6 3s^2 \underline{3p^4}$

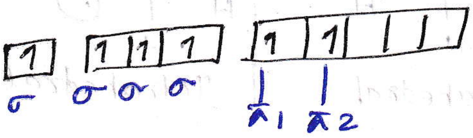


1 pπ–pπ

2 dπ–pπ

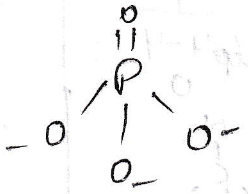
SO_4^{-2}



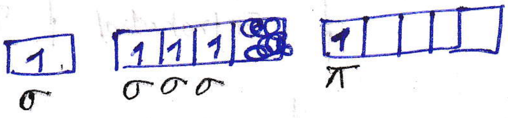


2 dπ–Pπ

PO_4^{-3}



$1s^2 2s^2 2p^6 3s^2 3p^3$



1 dπ–pπ

Hybridization

- for bond formation

① intermixing of orbital → Hybridization → Hybrid orbital.

(orbital of slightly different energy) (→ orbital of Equivalent energy & shape)

② overlapping of orbital

(i) • num of hybrid orbital = no of atomic orbital intermixed.

(ii) • Hybrid orbital ~~are more effective in~~ forming stable bond than atomic orbital

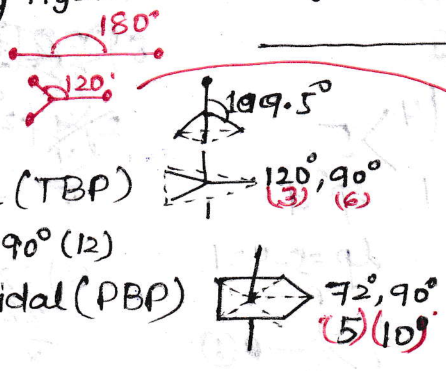
↳ bcoz hybrid orbitals have less Energy than Pure orbital.

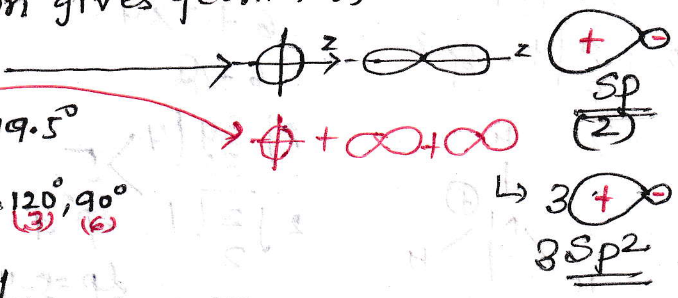
(iii) • It is a theoretical concept

(iv) • electron donot participate in hybridization only orbitals participate.

(V) • Hybrid orbital arrange themselves in such a geometry in which repulsion is min. (Hybridization gives geometry).

HO		Geo
2	sp	Linear
3	sp^2	Trigonal planar
4	sp^3	Tetrahedral
5	sp^3d	Trigonal bipyramidal (TBP)
6	sp^3d^2	Octahedral
7	sp^3d^3	Pentagonal bipyramidal (PBP) (not in NCERT)





Calculation of Hybridization

① Sum of valence e^-

② SVE >2 ≤ 8 $\div 2$

>8 ≤ 56 $\div 8$

>56 $\div 18$

③ $\boxed{\text{no of ve on CA = HO − SA}}$

Steric number rule

$\boxed{\text{Hybrdsn = no of σ bond + no of lone pair}}$

$BeCl_2$

$2+2\times7$

8|16|2 −sp

16

x

lp=2−2 =0

Cl−Be−Cl

Linear

BCl_3

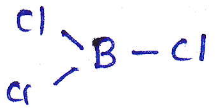
$3+3\times7$

8|24|3 sp^2

24

x

lp=3−3 =0



T.P

CH_4

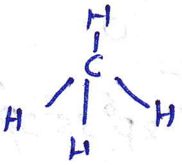
$4+1\times4$

2|8|4 sp^3

8

x

lp 4−4 0



Tetrahedral

NH_3

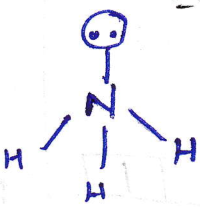
$5+1\times3$

2|8|4 Sp^3

8

x

lp=4−3 =1



Tetrahedral

H_2O

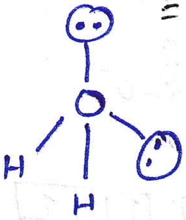
$6+1\times2$

2|8|4 Sp

8

x

lp= 4−2 =2



Tetrahedral

PCl_5

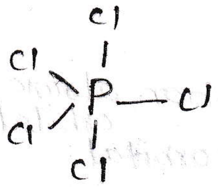
$5+7\times5$

8|40|5 sp^3d

40

x

lp=5−5 =0



TBP

SF_6

$6+7\times6$

8|48|6 sp^3d^2

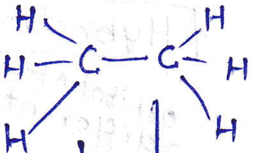
48

X

lp=6−6 =0

Octahedral

C_2H_6

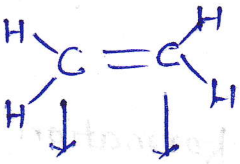


4σ sp^3 4σ sp^3

~~C−C 1.54A°~~

~~C−H 1.09A°~~

C_2H_4



3σ sp^2 3σ sp^2

~~1.34A°~~

~~1.08A°~~

C_2H_2

$H-C\equiv C-H$

2σ sp 2σ sp

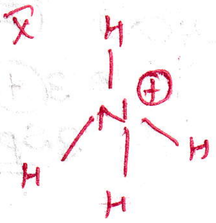
NH_4^+

$5+4-1$

2|8|4 − sp^3

8

x



SF_4

$6+7\times4$

6+28

8|34|4 >5

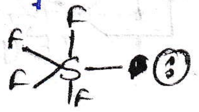
32

2|2|1 sp^3d

2

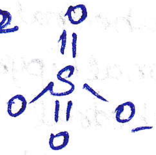
x

lp =5−4=1



SO_4^{-2}

$6+6\times4+2$



8)32(4 sp3

32

x lp=0

Tetrahedral

NO_3^-

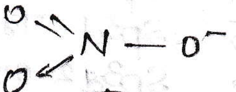
$5+6\times3+1$

5+18+1

8)24(3 −sp^2

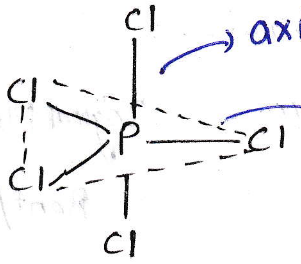
24

x lp=0



Toplanar

PCl_5



axial bonds (more bond length) (weak)

Equitorial bonds (less bond length) (strong)

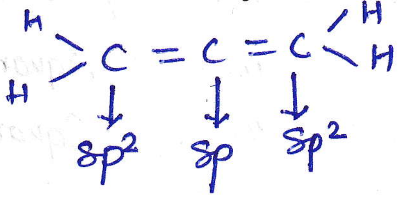
PCl_5 (reactive) $\xrightarrow{\Delta}$ $PCl_3 + Cl_2$

PF_5

all equitorial & axial bonds have same bond length. (bcoz F is highly En)

$sp^3d \rightarrow d_{z^2}$ orbital hybridizes.

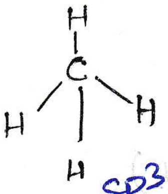
Que Cal hybridization of all carbon in allene (C_3H_4)



VSEPR Theory

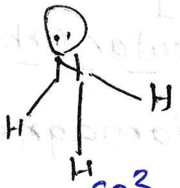
Valence Shell electron pair repulsion Theory

CH_4



sp^3
$109.5°$

NH_3



sp^3
$107°$

H_2O

sp^3
$104.5°$

lp - lp replsⁿ > lp-bp replsⁿ > bp - bp replsⁿ

Geometry → depends on lp & bp both.

Shape → depends on bp only.

Geo - Tetrahedral
Shape - ,,

Tetrahedral
pyramidal

Tetrahedral
Bent/angular

Hybrid orbital		BP	LP	Geo	Shape
• 2	sp	2	0	Linear	Linear $BeCl_2, HgCl_2,$
• 3	sp^2	3	0	T.P	T.P $BF_3,$
		2	1	T.P	bent/angular SO_2/O_3

4	sp^3	4	0	Tetra ——	Tetrahed	CH_4, NH_4^+
		3	1	"	Trigonal pyramidal	NH_3
		2	2	"	Bent/angular	H_2O
5	sp^3d	5	0	T·B·P	T·B·P	PCl_5
		4	1	"	Seesaw	SF_4
		3	2	"	TShape	ClF_3
		2	3	"	Linear	XeF_2
6	sp^3d^2	6	0	octahedral	Octahedral	SF_6
		5	1	"	Square pyramidal	BrF_5
		4	2	"	Square planar	XeF_4
7	sp^3d^3	7	0	P·B·P	P·B·P	IF_7
		6	1	"	Capped octahedral distorted octahedral	XeF_6

$\boxed{\text{MOT}}$

Molecular Orbital Theory

A|c VBT → O_2 → diamagnetic X

O_2 → paramagnetic (experiment)
↑
MOT

- Two atomic orbital first overlap to form 2 MO.

AO + AO → BMO (Bonding molecular orbital) → less Energy
(constructive interferance)
→ ABMO (antibonding molecular orbital) → more En
(destructive interferance)

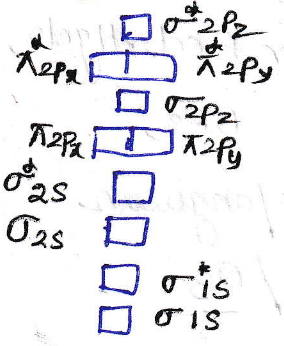
- In MOT, e^- are filled a|c to aufbau, Pauli, Hund's Rule.

aufbau → lower energy orbital is filled first

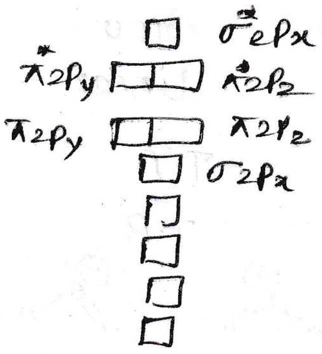
Pauli → In orbital electrons are opposite.

Hund's Rule → first all orbitals of same energy will be singly occupied then pairing starts

≤14e^- – 2121



>14e^- – 1221



O_2 - 16e⁻ 1221

□ ——— LUMO
↑ | ↑ -Para } -A ——→ HOMO
↑↓ | ↑↓ } - B
↑↓
↑↓ — A
↑↓ — B
↑↓ — A
↑↓ — B

N_2 - 14e⁻ 2121

□ } — A
□ | □ ——— LUMO
↑↓ ——— HOMO
↑↓ | ↑↓ } — B
↑↓ ——— A
↑↓ ——— B
↑↓ ——— A
↑↓ —— B

$$BO = \frac{10-4}{2} = \boxed{3}$$

$$\boxed{BO = 2}$$

$$BO = \frac{10-6}{2} = \frac{4}{2} = 2$$

$$\boxed{\text{Bondorder} = \frac{N_b - N_a}{2}}$$

BO ≠ 0 (-ve) species dne (Unstable)
BO = 1 - Singbond
2 - double "
3 - Triple "

- BO ↑ doublebond character ↑ Stab ↑ B.L ↓
- unpaired e⁻ → para
- no upaired e⁻ → dia

10	1
11	1.5
12	2
13	2.5
14 ——	3
15	2.5
16	2
17	1.5
18	1

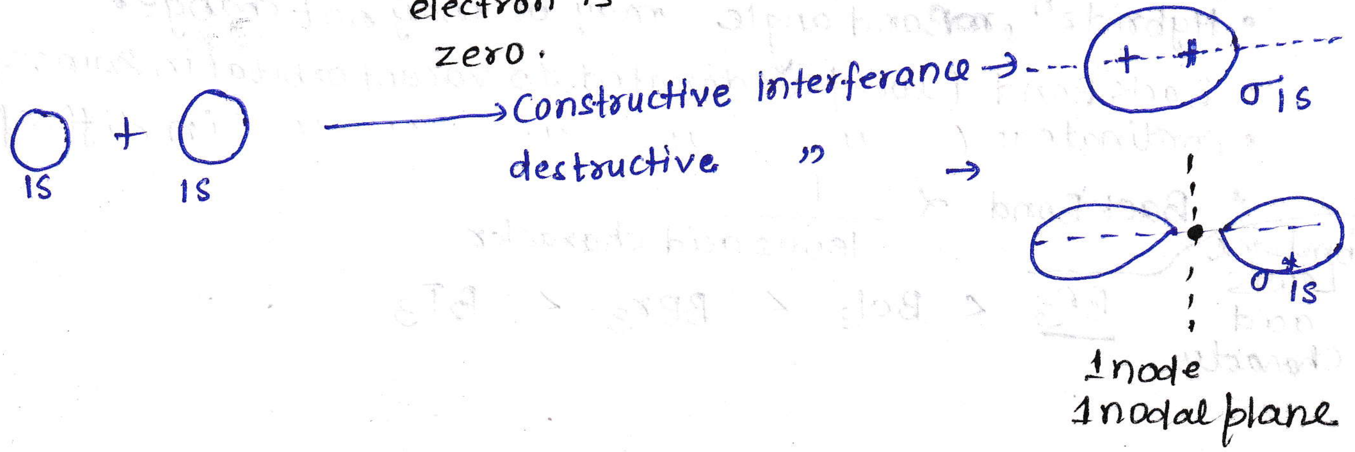
all odd e⁻ → para } except 10 & 16
all even → dia }

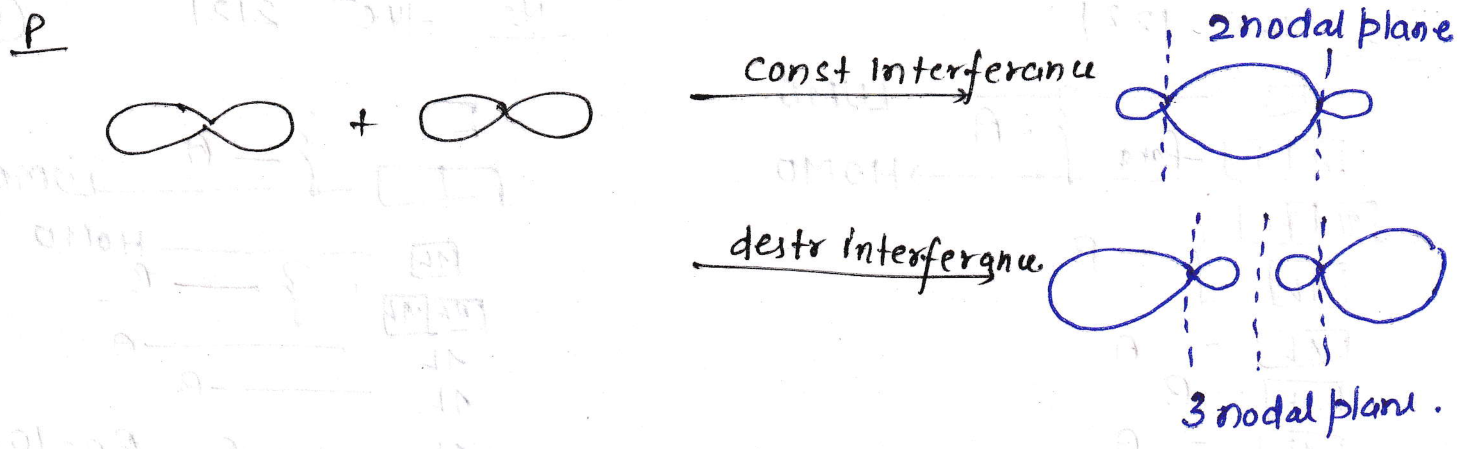
if Bo of 2 molecule is same then
more antibonding e⁻ ⇒ less stable
less " " ⇒ more stable

Nodes & Nodal plane

↓ Point at which Prob of finding electron is zero.

↓ Plane at which probability of finding electron is zero.

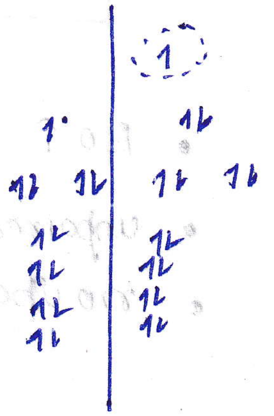




Que write B.O & stability order of N_2, N_2^+, N_2^-
↓ ↓ ↓
3 2.5 2.5 (more ABe → less stable)

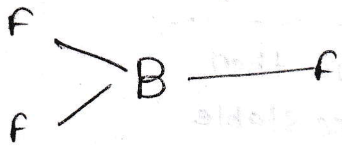
Stability

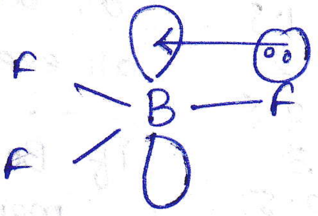
$\boxed{N_2 > N_2^+ > N_2^-}$

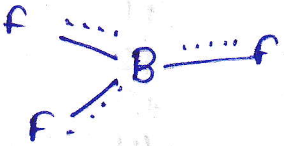


more ABE so N_2^- is less stable.

Back Bond







B–F → 1.50 A°
→ 1.30 A° (experiment)

- It takes place b/w 2 bonded atom
- one atom should have lonepair to donate & other atom should have vacant orbital.
- Bond strength always ↑ & Bond length always ↓
- Hybridzⁿ, Bond angle may or may not change.
- Back Bond (lonepair donated to vacant orbital in same species).
- Cordinate " (" " " " " in diff species).
- Back Bond ∝ $\frac{1}{\text{lewis acid character}}$

Compare Lewis acid Character

$BF_3 < BCl_3 < BBr_3 < BI_3$.

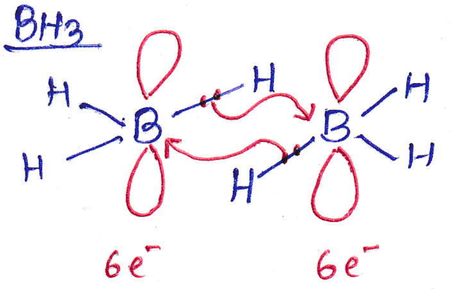
Banana Bond

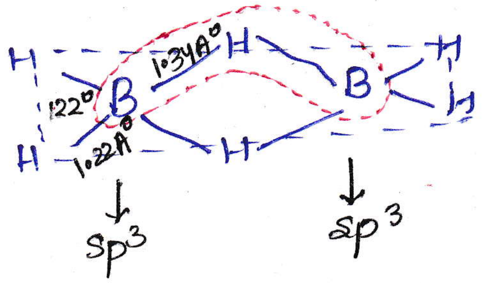
Bonding in e⁻ deficient comp

BH_3, BeH_2, BCl_3, $AlCl_3$

3 center 2e⁻ (e⁻ def)   3 center 4e⁻

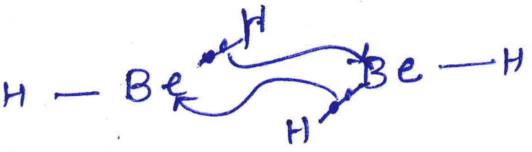
BH_3

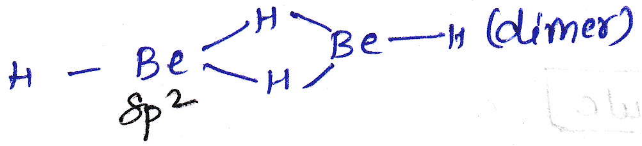


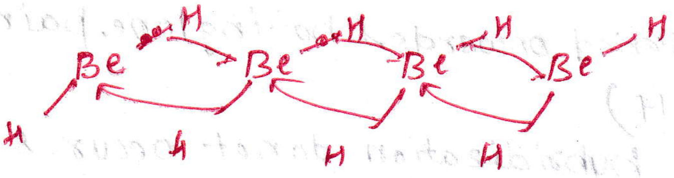


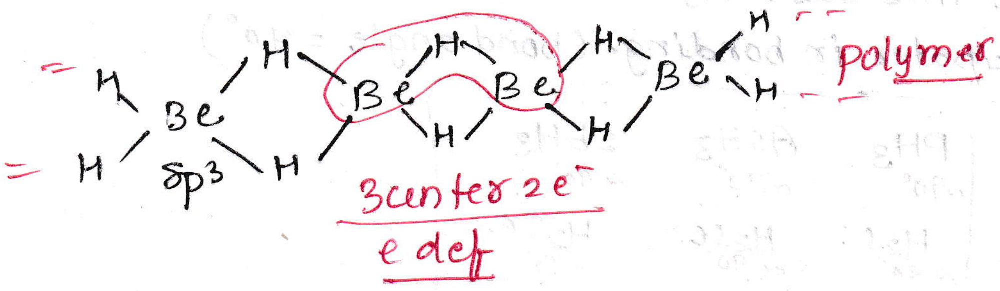
- Boron momentalily completes its Octet.
- Hybrd^{Z} → sp^2 → sp^3
- B_2H_6 → ~~incomplete octet~~ (e⁻ def)
- 4H → same plane
2B → " } → 6 atom in one plane
- 2 bridging hydrogen → out of plane.
- B_2H_6 → non planar

BeH_2 → sp

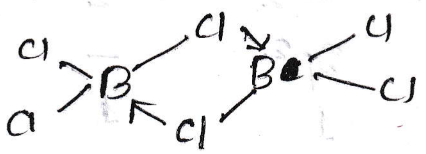








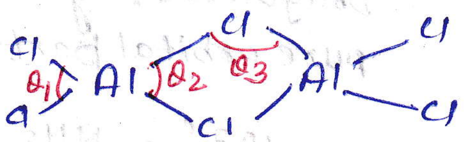
BCl_3



3 center 4e⁻

- Stable
- non planar
- not e⁻ def.

$AlCl_3$



3 center 4e⁻

sp^3

$\theta_1 > \theta_3 > \theta_2$

Comparison of Bond parameter

① BA ∝ % S   sp−50% s sp^2→33% s sp^3→25% s

② BA ∝ $\frac{1}{\text{lp on CA}}$

③ BA ∝ En of CA

④ BA ∝ $\frac{1}{\text{En of SA}}$

Compare Bond angle :-

Q. $BeCl_2$ > BCl_3 > CCl_4 > PCl_5

sp sp^2 sp^3 sp^3d

Q. NH_3 < NH_4^+

sp^3 sp^3

lp=1 lp=0

Q. CH_4 > NH_3 > H_2O

sp^3 sp^3 sp^3

lp 0 1 2

Q. PI_3 > AsI_3 > SbI_3

sp^3 — —

1 1 1

Q. SF_2 < SCl_2 < SBr_2 < SI_2

sp^2 — — —

1 1 1 1

CA — — —

SA

DRAGO Rule

- CA → G15, G16, G17 & 3rd Period onwards & having lone pair
- SA → En ≤ 2.5 (SA = H)

Drago rule says in this case hybridization do not occur & pure orbital participates in bonding. (bond angle = 90°)

107° ← NH_3

104.5° ← H_2O

180° ← Cl-H

PH_3 ~90° AsH_3 ~90° SbH_3 ~90°

H_2S ~90° H_2Se ~90° H_2Te ~90°

Br-H ~90° I-H ~90°

Compare B.Angle
Que

NH_3 NF_3 PF_3 PH_3

sp^3 sp^3 sp^3 Drago Rule (90°)

Lonep — —

catom —

NH_3, NF_3 > PF_3 > PH_3

$BA \propto \frac{1}{\text{En of SA}}$ ⇐ NH_3 > NF_3 > PF_3 > PH_3

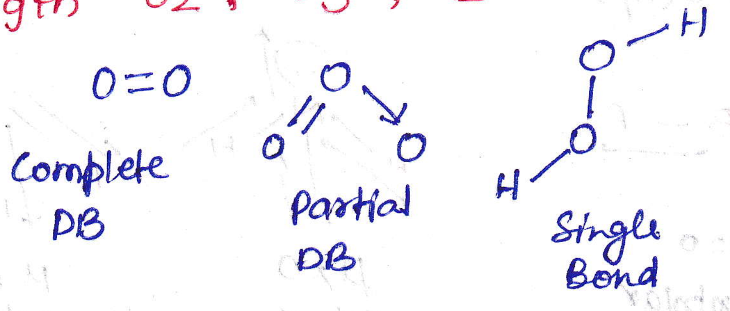
Bond length

① $B.L \propto \frac{1}{\Delta EN}$

② $B.L \propto \frac{1}{BO}$

③ Resonance & Back Bond ↓ Bond length

Que) Compare Bond length $O_2 < O_3 < H_2O_2$



Bond energy

$B.E \propto \Delta EN$

$B.E \propto B.O$

$B.E \propto \frac{1}{\text{size of atom}}$

Que compare Bond energy $HF > HCl > HBr > HI$

$C-C > \underbrace{\ddot{N}-\ddot{N} > :\ddot{O}-\ddot{O}: > :\ddot{F}-\ddot{F}:}_{lp\text{-}lp\ repls^n}$

Que __________

$Si-Si < P-P < S-S < Cl-Cl$

Que __________ $C-C > Si-Si$ (size)

Que __________

$N-N < P-P$
$O-O < S-S$ {lp-lp replsn}
$F-F < Cl-Cl$

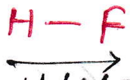
Que __________ F_2 Cl_2 Br_2 I_2

$Cl_2 > Br_2 > F_2 > I_2$

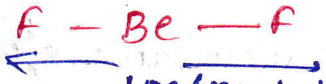
Dipolemoment → Tells about polarity of a molecule.

- Draw arrow (less En to more En)
  (Atom to lone pair)
- equal & opposite vector cancel each other.

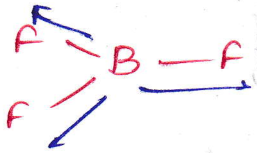
μ=0(np)



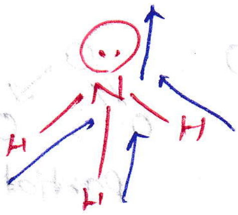
μ≠0 (polar)



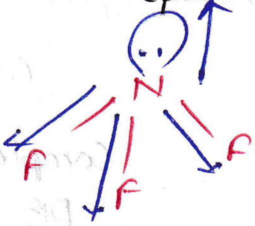
μ=0 (nonpolar)



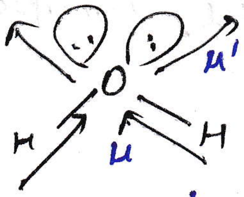
μ=0
nonpolar



μ≠0
Polar

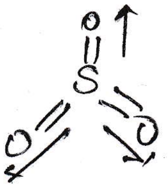


μ≠0
polar



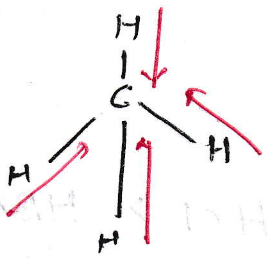
μ+μ'
μ≠0
polar

SO3



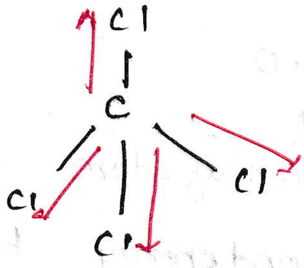
μ=0
nonpolar

CH4



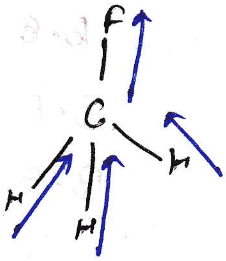
μ=0
np

CCl4



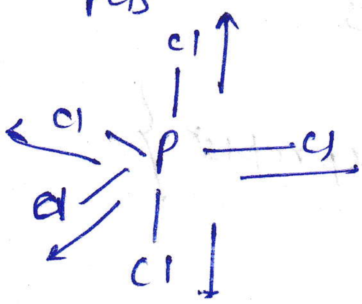
μ=0
np

CH3F



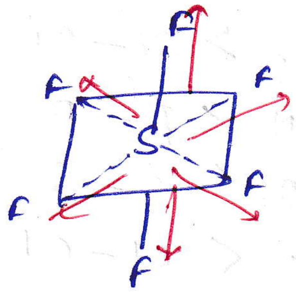
μ≠0
polar

PCl5

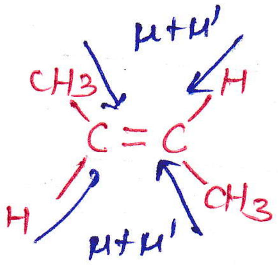


u=0
np

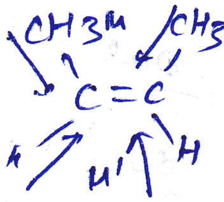
SF6



μ=0
np



μ=0
np



μ≠0
polar

Socandarybond → (2-40 kJ/mol)

① vanderwall force of attraction (2-8 KJ/mol)

② Hydrogen Bond (8-40 KJ/mole)

Vanderwall

vanderwall ∝ At wt/mol wt

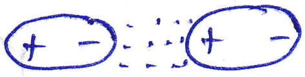
Vanderwall ∝ B.P.

Que F_2, Cl_2 → gas, Br_2 → liq, I_2 → ~~gas~~ solid. Explain

$F_2 < Cl_2 < Br_2 < I_2$ (mwt) (VFOA)

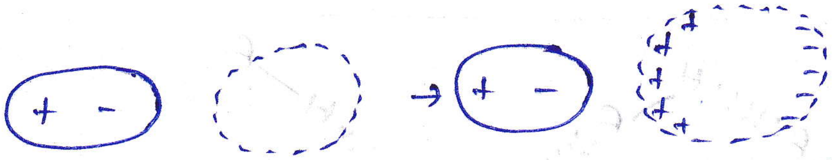
① Ion - dipole $Na^+ \vdots \delta^- \vdots H_2O$

② dipole-dipole

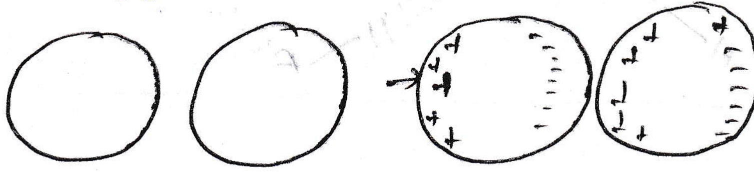


③ Ion - induced dipole

④ dipole induced dipole



⑤ Instanstaneous induced dipole.
(London dispersion force)



Que HCl has more B.P than H_2 why ??

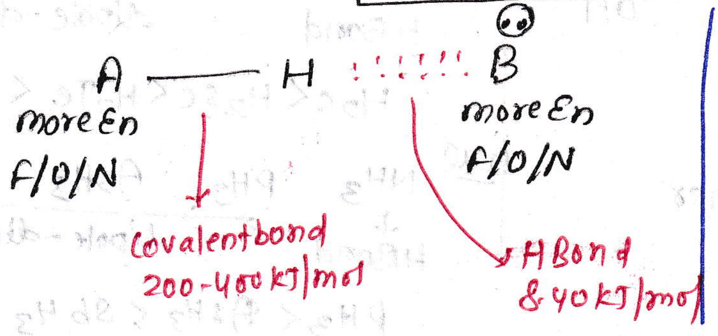
HCl ↓ dipole-dipole

H_2 ↓ L.D.F

Que compare BP H_2 Cl_2 N_2 Br_2 C_2 F_2

$H_2 < C_2 < N_2 < F_2 < Cl_2 < Br_2$

Hydrogen Bond



Strength of H Bond ∝ En of A

" " " ∝ $\frac{1}{\text{En of B}}$

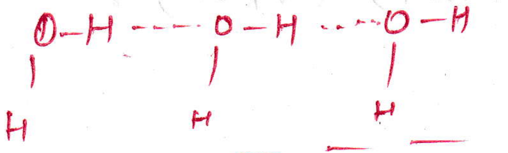
Que Compare H·Bond Strength

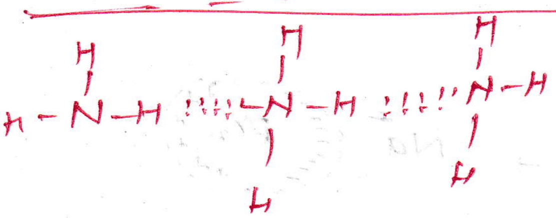
a) O—H ------ F
b) O—H ----- O
c) F—H ---- F
d) F—H ---- N

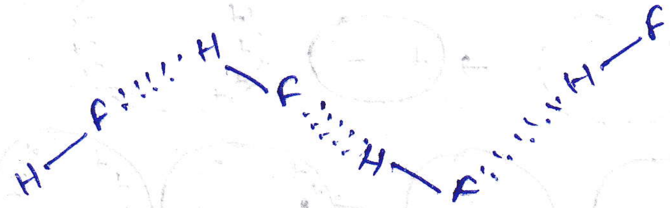
(d) ✓

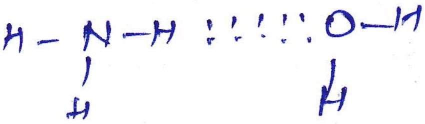
HBond

Intermolecular

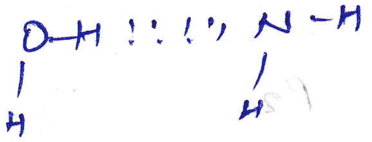




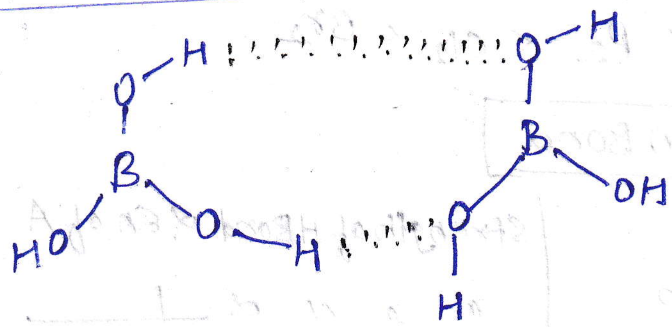




or

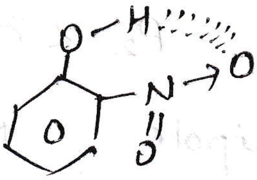


(more strong)

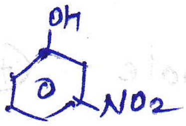


H_3BO_3 → exists as dimer

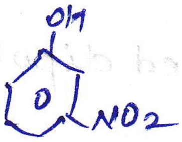
Intramolecular



6 member

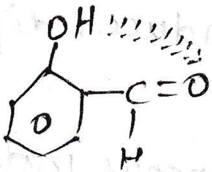


×

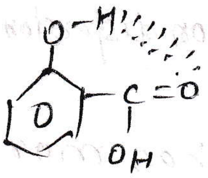


×

} inter molecular HB·



Salicaldehyde



Salicyclic acid

Compare B.P

Que HF HCl HBr HI

HF → HBond; HCl, HBr, HI → dipole-dipole

$HCl < HBr < HI < HF$

Que H_2O H_2S H_2Se H_2Te

H_2O → HBond; H_2S, H_2Se, H_2Te → dipole-dipole

$H_2S < H_2Se < H_2Te < H_2O$

Que NH_3 PH_3 AsH_3 SbH_3

NH_3 ↓ HBond; PH_3, AsH_3, SbH_3 → dipole-dipole

$PH_3 < AsH_3 < SbH_3 < NH_3$

Inert pair effect

- only applicable in G-13, G-14, G-15.
- as we move down the group, zeff increases (poor shielding of d & f electro) & ns^2 e^- bcome inert
- ~~zeff ↑ so, ns^2 electrons are not excited for reaction (attraction of nucleus) & become inert.~~

G13	G14	G15
$\boxed{+1}$ $\boxed{+3}$	$\boxed{+2}$ $\boxed{+4}$	$\boxed{+3}$ $\boxed{+5}$
$ns^2 np^1$	$ns^2 np^2$	$ns^2 np^3$
B → +3	C — +4	N — +5
Al → +3	Si — +4	P — +5
Ga → $\boxed{+3}$, +1	Ge — +4, +2	As — $\boxed{+5}$, +3
In → $\boxed{+3}$, +1	Sn — +4, +2	Sb — $\boxed{+5}$, +3
Tl → +3, $\boxed{+1}$	Pb — +4, $\boxed{+2}$	Bi — +5, $\boxed{+3}$

- as we move down the group stab of lower O.S ↑.