PERIODIC TABLE

5/4/17

* MOSELEY'S LAW ⇒

The chemical and physical properties of elements are periodic function of their atomic nos.

- $\sqrt{\nu} = a(Z-b)$ $\sqrt{\nu} \propto Z$
- ν of X-Ray emitted by those heavy metals was a physical property of those metals.

* ELECTRONIC CONFIGURATION ⇒

Generally outer shell $e^{\ominus}$ config. of elements of a particular group is same, except group 5, 6, 8, 9, 10, 18.

- Group 10
  Ni = $3d^8\ 4s^2$
  Pd = $4d^{10}\ 5s^0$
  Pt = $5d^9\ 6s^1$

- I A (Alkali Metals) — ns^1
  II A (Alkaline Earth Metals) — ns^2
  III A (Boron Family) — $ns^2\ np^1$
  IV A (Carbon Family) — $ns^2\ np^2$
  V A (Pnicogens) — $ns^2\ np^3$
  VI A (Chalcogens) — $ns^2\ np^4$
  VII A (Halogens) — $ns^2\ np^5$

- He = 2 $1s^2$
  Ne = 10 $2s^2\ 2p^6$
  Ar = 18 $3s^2\ 3p^6$
  Kr = 36 $4s^2\ 4p^6$
  Xe = 54 $5s^2\ 5p^6$
  Rn = 86 $6s^2\ 6p^6$
  Uuo = 118 $7s^2\ 7p^6$

- 3d series = $3d^4$, $3d^9$ → X
  4d series = $4d^3$, $4d^6$, $4d^9$ → X
  5d series = $5d^8$ → X

Only d^5 and d^{10} are repeated.

- ~~3d ${}_{21}$Sc Ti V Cr Mn Fe Co Ni Cu Zn~~
  ~~${}_{18}$[Ar] $3d^1 4s^2$ $3d^2 4s^2$ $3d^3 4s^2$~~
  ~~4d Y Zr Nb Mo Tc Ru Rh Pd Ag Cd~~
  ~~5d La Hf Ta W Re Os Ir Pt Au Hg~~

	3	4	5	6	7	8	9	10	11	12
3d	${}_{21}$Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
${}_{18}$[Ar]	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$
4d	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
${}_{36}$[Kr]	$4d^1 5s^2$	$4d^2 5s^2$	$4d^4 5s^1$	$4d^5 5s^1$	$4d^5 5s^2$	$4d^7 5s^1$	$4d^8 5s^1$	$4d^{10} 5s^0$	$4d^{10} 5s^1$	$4d^{10} 5s^2$
5d	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
${}_{54}$[Xe]	$5d^1 6s^2$	$5d^2 6s^2$	$5d^3 6s^2$	$5d^4 6s^2$	$5d^5 6s^2$	$5d^6 6s^2$	$5d^7 6s^2$	$5d^9 6s^1$	$5d^{10} 6s^1$	$5d^{10} 6s^2$

- Lanthanoids (58 - 71) ⇒ Rare Earth Metals = La + Lanthanoids

सिर	पर	नदियाँ	प्रेम	की	समाई
Ce	Pr	Nd	Pm		Sm
यूरी	गद्गद्	तब	दिल		हुआ
Eu	Gd	Tb	Dy		Ho
अरे	तुम	यल्लु			
Er	Tm	Yb Lu			

<u>Lanthanoids</u> : अब तक 56 भरो ([Xe] $6s^2$), फिर सारे 4f में डालो; Ce, Gd, Lu में $5d^1$, बाकियों में $5d^0$

$_{57}La = {}_{54}[Xe]\ 4f^0\ 5d^1\ 6s^2$ (n+l rule exception : orbital contracⁿ)

$_{58}Ce = [Xe]\ 4f^1\ \boxed{5d^1}\ 6s^2$ (n+l rule exception) d→1

$_{59}Pr = [Xe]\ 4f^3\ 5d^0\ 6s^2$

$_{60}Nd = [Xe]\ 4f^4\ 5d^0\ 6s^2$

$_{61}Pm = [Xe]\ 4f^5\ 5d^0\ 6s^2$

$_{62}Sm = [Xe]\ 4f^6\ 5d^0\ 6s^2$

$_{63}Eu = [Xe]\ 4f^7\ 5d^0\ 6s^2$

$_{64}Gd = [Xe]\ 4f^7\ \boxed{5d^1}\ 6s^2$ (n+l rule exception : ½ filled) d→1

$_{65}Tb = [Xe]\ 4f^9\ 5d^0\ 6s^2$

$_{66}Dy = [Xe]\ 4f^{10}\ 5d^0\ 6s^2$

$_{67}Ho = [Xe]\ 4f^{11}\ 5d^0\ 6s^2$

$_{68}Er = [Xe]\ 4f^{12}\ 5d^0\ 6s^2$

$_{69}Tm = [Xe]\ 4f^{13}\ 5d^0\ 6s^2$

$_{70}Yb = [Xe]\ 4f^{14}\ 5d^0\ 6s^2$

$_{71}Lu = [Xe]\ 4f^{14}\ \boxed{5d^1}\ 6s^2$ ~~(n+l rule exception: full filled) d→1~~

- $_{89}Ac = {}_{86}[Rn]\ 5f^0\ 6d^1\ 7s^2$ (n+l rule exception)
orbital contraction

$_{90}\underline{\underline{Th}} = {}_{86}[Rn]\ \boxed{5f^0}\ \boxed{6d^2}\ 7s^2$ (n+l rule exception)

$_{91}Pa = [Rn]\ 5f^2\ 6d^1\ 7s^2$ (n+l rule exception)

$_{92}U = [Rn]\ 5f^3\ 6d^1\ 7s^2$ (n+l rule exception)

$_{93}Np = [Rn]\ 5f^4\ 6d^1\ 7s^2$ (n+l rule exception)

$_{94}Pu = [Rn]\ 5f^6\ 6d^0\ 7s^2$

$_{95}Am = [Rn]\ 5f^7\ 6d^0\ 7s^2$

$_{96}Cm = [Rn]\ 5f^7\ 6d^1\ 7s^2$ (n+l rule exception ⇒ ½ filled)

$_{97}Bk = [Rn]\ 5f^9\ 6d^0\ 7s^2$

$_{98}Cf = [Rn]\ 5f^{10}\ 6d^0\ 7s^2$

$_{99}Es = [Rn]\ 5f^{11}\ 6d^0\ 7s^2$

$_{100}Fm = [Rn]\ 5f^{12}\ 6d^0\ 7s^2$

$_{101}Md = [Rn]\ 5f^{13}\ 6d^0\ 7s^2$

$_{102}No = [Rn]\ 5f^{14}\ 6d^0\ 7s^2$

$_{103}Lr = [Rn]\ 5f^{14}\ 6d^1\ 7s^2$

- **Actinoids - (90 - 103)**

d में $e^{\ominus}$ है

तुम्हें पढ़ाऊँ Newspaper | पुराना

Th Pa U ↗ Np | Pu

आम | कम | बिके, कैफे में पेश

Am | Cm | BK Cf Es

फरमाते मेडोना | लाश |

Fm Md No | Lr |

Q. 1 which is not an alkaline earth metal :

[✓ a)] Be b) Ra c) Ba d) Ca

BeO → amphoteric, not alkaline

Q. 2 Total no. of d $e^{\ominus}$ in an element having Z = 78 :

a) 19 b) 28 c) 9 [✓ d)] 29

78 → Pt → $5d^{9}\ 6s^{1}$ पूरा Group exceptional है।

$\Rightarrow 3d + 4d + 5d = 10 + 10 + 9 = 29$

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* **MAGIC Nos.** ⇒

- IA ⇒ $\underbrace{{}_{1}H \quad {}_{3}Li}_{2} \underbrace{\quad {}_{11}Na}_{8} \underbrace{\quad {}_{19}K}_{8} \underbrace{\quad {}_{37}Rb}_{18} \underbrace{\quad {}_{55}Cs}_{18} \underbrace{\quad {}_{87}Fr}_{32}$

IA → 2, 8, 8, 18, 18, 32.

- II A ⇒ Be Mg Ca Sr Ba Ra

  8 8 18 18 32

II A → 8, 8, 18, 18, 32

- III B ⇒ Sc Y La Ac

  18 18 32

III B → 18, 18, 32

- 18th ⇒ $_2He$ $_{10}Ne$ $_{18}Ar$ $_{36}Kr$ $_{54}Xe$ $_{86}Rn$ $_{118}Uuo$

  8 8 18 18 32 32

18th → 8, 8, 18, 18, 32, 32

- 13th - 17th ⇒ 8, 18, 18, 32, 32

- d-block (except III B) ⇒ 18, 32, 32

Q. 3 At. nos. of liquid metal and liquid non metal are –

a) 37, 31 b) 87, 31 c) 35, 87 [✓ d) 80, 35]

Ans. Liquid Elements = $\underbrace{Cs, Fr, Ga, Hg, Uub}_{M}$, $\underbrace{Br}_{NM}$ = 6

$_9F$] 8

Cl – 17] 18

Br – 35

Liquid Elements @ Room Temp. = $\underset{M}{Hg}$, $\underset{NM}{Br}$ = 2

- TOTAL GASES = H_2, O_2, N_2, F_2, Cl_2 + 6 inert gases
- TOTAL ELEMENTS = 114
- All d and f block elements are metals.
- p block contains metal, NM, metalloids.
- METALLOID → Si, Ge, As, Sb, Te, At
- B → [✓ NM] / Metalloid   Se → NM / [✓ Metalloid]

  Po → [✓ Metal] / Metalloid

Q.4 Which of the following is metalloid-

a) B   [✓ b) Ge]   c) F   d) Na

[✓ a)] B   b) Ga   c) F   d) Na

PERIOD NO.	OUTER SHELL NO	PERIOD SUBSHELL	NO. OF ELEMENTS	PERIOD NAME
1	1	1s	2	Shortest
2	2	2s 2p	8	Short
3	3	3s 3p	8	Short
4	4	4s 3d 4p	18	Long
5	5	5s 4d 5p	18	Long
6	6	6s 4f 5d 6p	32	Longest
7	7	7s 5f 6d 7p	32 (28) 114	Incomplete
n	n	ns → (n-2)f → (n-1)d → np		

- Period No. = Outermost shell no.

- No. of elements in a period = Max. no. of $e^{\ominus}$ in period subshell.

n = no. of period ↳ (even) $\frac{(n+2)^2}{2}$ or $\frac{(n+1)^2}{2}$ (odd)

- No. of period subshell (n) = $\sqrt{\frac{\text{no. of elements}}{2}}$

- For eg. Period no. = 10

10s 6h 7g 8f 9d 10p = 6.

No. of element = 2 + 22 + 18 + 14 + 10 + 6 = 72 elements

No. of elements = $\frac{(10+2)^2}{2} = \frac{144}{2}$ = 72 elements.

No. of period subshells = $\sqrt{\frac{72}{2}}$ = 6.

Q.5 Assertion : d block elements start frm. 4th period

Reason : $e^{\ominus}$ filling in 3d subshell starts after $e^{\ominus}$ filling in 4s subshell.

Ans (A)

Q.6 Assertion : There are only 8 elements in 3rd period but 4th period contains 18 elements.

Reason : Each period starts from ns and ~~a~~ ends up at np except 1st period.

Ans Reason doesn't say 'ns and np', it says 'starts @ ns, ends @ np' ⇒ others can come. (A)

Q.7 Assertion: There are 14 lanthanides and 14 actinoids in modern periodic table.

Reason: f orbital can hold max. 14 $e^{\ominus}$.

Ans ~~(A)~~ (C)

Q.8 If each orbital can hold max. 3 $e^{\ominus}$, total no. of elements in 8th period would be –

Ans $\frac{(8+2)^2}{2} \times \frac{3}{2} = \frac{\overset{25}{\cancel{100}} \times 3}{\cancel{4}} = \cancel{50}\ 75$

Q.9 If Aufbau rule would not have been followed, then which of the following element will not have changed its position acc. block classification: a) K ✗ b) Ge ✓ c) Sr ✗ d) Se ✓

Ans Sr ⇒ 38 = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ \underline{\underline{4d^2}}$

s → d.

Ge ⇒ 6 C
Si]8
Ge]18 → 32

⇒ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \cancel{4s}\ 3d^{10}\ 4s^2\ 4p^2$

$\underline{p \to p}$ ✓

Se ⇒ 8 O
S]8
Se]18 → 34

⇒ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^4$

$\underline{p \to p}$ ✓

- Total s block elements = 14 (6 + 6 + H + He)
- Total f block elements = 28 (Lu, Lr में last in d, but at. no. ↑↑ ⇒ Z_{eff} ↑ ⇒ energy level diff ↓↓ ⇒ where last $e^{\ominus}$ went → ?)
- Block classification has exceptions: Th, Lu, Lr, etc.
  But still. f block = 28.

- Total p block elements = $6 \times 6 - 4 = 32$ (114)

Q. 10 Pair of elements which are exception of block classification: on the basis of position in PT :

a) La, Ac   b) Zn, Cd   ✓~~c)~~ H, He   d) Ce, La

Q.11 Min. atomic no. which can change the present model of PT (follow n+l rule) :

a) 119   ✓~~b)~~ 121   c) 132   d) 144

Ans $118 + 2 = 120 \Rightarrow 121 \rightarrow$ g block.

* IUPAC NAMING :- $Z \geq 100$

0 - nil
1 - uni
2 - bi
3 - tri
4 - quad
5 - pent
6 - hex
7 - sept
8 - oct
9 - ~~non~~ enn

- Z = 108 = uni-nil-oct-ium = Uno
- Z = 143 = un-quad-tri-ium = Uqt
- Next alkaline earth metal ⇒ 120 = Un-bi-nil-ium = Ubn
- Last d block element ⇒ ~~90 + 10 = 100 + 14 = 114~~

18 [Zn = 30
  Cd
18 [Hg
32 [__ = 112   Uub

- Next metal of IB group ⇒ 18 [Cu = 29
  Ag
  32 [Au
  32 [_ = 111 = Uuu Known
  50 [_ 161 = Uhu

Next magic no. = 50

- 2] 6 p
  8] 10 d
  18] 14 f
  32] 18 g
  50
  72] 22 h

* **GROUP & PERIOD IDENTIFICATION** ⇒

- When at no. is given –

→ $58 \leq Z \leq 71$ ⇒ Lanthanoid ⇒ Group = III B
Period = 6th

→ $90 \leq Z \leq 103$ ⇒ Actinoid ⇒ Group = III B
Period = 7th

→ Largest group of PT = 32 (4 + La + Ac..)

Q.12 Assertion: f block elements belong to III B
Reason: General O.S. of f block elements is +3
Ans (A)

→

He	Ne	Ar	Kr	Xe	Rn	Uuo
2	10	18	36	54	86	118

- Check inert gas that has just higher at. no. than given at. no.
- Period. No. = Period No. of that inert gas
- Group No. = $18 - [Z_{inert} - Z_{given}]$

Q.13 Identify group and period -

a) $Z = 46$ Ay 54 ⇒ group $= 18 - (54-46) = 18 - 8 = \underline{10}$ $(\overline{VIII})$
period = 5th

b) $Z = 89$ ⇒ III ~~A~~B 7th period ⇒ Ac

c) $Z = 82$ → $18 - (86-82) = 18 - 4 = 14^{th}$ group = $\underline{IV}$ A; 6th period

d) $Z = 57$ → $54 + 3$ = $\underline{III}$ B; 7th period.

- When $e^{\ominus}$ config. is given

→ Period No. = Outermost Shell No.

→ Block Identification -

- If $np\ e^{\ominus}$ is present, p block.
  Group No. = $12 + np\ e^{\ominus}$
- If $np\ e^{\ominus}$ is absent, s/d/f block.

a) $(n-2)f^{0}$ $(n-1)d^{0}$ ns^{1-2} ⇒ s block ⇒ group no. = ns $e^{\ominus}$

b) $(n-2)f^{1-14}$ $(n-1)d^{0-1}$ ns^{2} ⇒ f block ⇒ group no. = IIIB

c) Any other config. or $(n-1)d^{1-10}$ ns^{0-2} ⇒ d block
Group No. = $(n-1)d$ $e^{\ominus}$ + ns $e^{\ominus}$

Q.14 Identify group, period and block.

a) [Xe] $4f^{14}$ $5d^{10}$ $6s^{2}$ $6p^{3}$

Ans n=6 Period No. = 6 block = p. Group = 15th. = VA

b) [Xe] $4f^{14}$ $5d^{10}$ $6s^{2}$ $6p^{6}$ $7s^{2}$

Ans n=7 Period No. = 7 block = s Group = IIA

c) [Xe] $4f^{14}$ $5d^{2}$ $6s^{2}$

Ans n=6 Period No. = 6 block = d Group = 2+2 = 4th = IVB.

d) $[n-2]f^{7}$ $[n-1]d^{1}$ $[n]s^{2}$

Ans block = f Group = IIIB (always)

* e) [Kr] $4d^{10}$ $5s^{0}$ (Pd)

Ans block = d Group = 10th = $\overset{\text{VIII}}{\cancel{\text{IIA}}}$ Period = 5th.
Acc. to (n+l) rule = [Kr] $4d^{8}$ $5s^{2}$.
Also ⇒ 36+10 = 46 = At no. ⇒ Group = ~~18 = (46-36) = 8 10~~
18 − (54−46) = 10th
Period = 5th.

f) $[Rn]\ 6d^2\ 7s^2$

Ans $n = 7$ Period = 7 $Z = 86 + 2 + 2 = 90 \Rightarrow$ Actinoid (Th)
Group = III B f block

g) $[Ne]\ 3s^2\ 3p^5\ 4s^1$

Ans $Z = 10 + 2 + 5 + 1 = 18 \Rightarrow Ar$

Q.15 No. of $e^\ominus$ in pre penultimate shell of f block elements

a) 1-14
[✓ b)] 19-32
c) 1-18
d) 8-9

Ans pre penultimate = $n-2 \Rightarrow (n-2)f^{1-14} \Rightarrow (n-2)s^2 + (n-2)p^6 + (n-2)f^{1-14} + (n-2)d^{10}$
$= 19 - 32.$

Q.16 Max. no. of $e^\ominus$ in outermost shell of s, p, d, f block elements –

a) 2, 6, 10, 14
b) 2, 8, 18, 32
c) 2, 8, 10, 2
[✓ d)] 2, 8, 2, 2

Ans s block $\Rightarrow ns^{1-2} = 2$
p block $\Rightarrow ns^2\ np^{1-6} = 8$
d block $\Rightarrow (n-1)d^{1-10}\ ns^{01-2} \Rightarrow 2$
f block $\Rightarrow (n-2)f^{1-14}\ (n-1)d^{0-1}\ ns^2 \Rightarrow 2$

* BOHR CLASSIFICATION ⇒

INERT GASES	NORMAL / REPRESENTATIVE	TRANSITION	INNER-TRANSITION
n^{th} shell complete ⇓ $e^{\ominus} = 8$ Total = 6	n^{th} shell incomplete Except - inert gases "s and p blocks" ns^{1-2} np^{0-5}	n^{th}, $(n-1)^{th}$ both incomplete either in atomic or ionic form "d block metals" except Zn, Cd, Hg, Uub ↓ non typical transition elements	n^{th}, $(n-1)^{th}$, $(n-2)^{th}$ shell incomplete. "f block elements"

Q.17 Which of the following sets of at. no. represents representative elements ?

a) 13, 33, (64) La, 83
b) 7, ㉕, 31, 84
3d Sc = 21
c) 9, 32, ㊹ Xe, 82
✓ ~~d)~~ 5, 33, 52, 83

* TYPICAL ELEMENTS ⇒

Elements of 3rd period (except inert gases) are typical elements. e.g. Na, Mg, Al, Si, P, S, Cl.

Q.18 2nd period elements show some different properties than their group due to :

a) small size
b) high IP or EN
d) absence of vacant d orbital
✓ ~~c)~~ all

* **DIAGONAL RELATIONSHIP** :-

(similarities in properties)

$$\begin{tikzcd}
Li \arrow[dr] & Be \arrow[dr] & B \arrow[dr] & \\
& Mg & Al & Si
\end{tikzcd}$$

Reason: Almost same ionic potential. (ϕ)

$\phi = \frac{\text{charge of cation}}{\text{size of cation}}$ eg. $\underset{\hookrightarrow}{\phi} = \frac{Be^{+2} \simeq Al^{+3}}{2 \cdot 2}$

Q.19 Li and Mg show diagonal relationship due to-

✗ a) almost same ionic potential

b) almost same atomic radius

[✓ c)] almost same ionic radius

d) None

$\frac{Li^{+}}{0.76 \mathring{A}}$ $\frac{Mg^{+2}}{0.72 \mathring{A}}$

If ionic radius is not in option, Ans = ionic potential
(general trend, but fails in Li-Mg)

* **BRIDGE ELEMENT** –
Acc. to Mendeleev's PT, 3rd period elements like Na, Mg, Al, etc. are bridge elements.

- Li, Be, B are considered as bridge elements acc. to modern PT.

* **TRANSURANIC ELEMENTS** – $Z > 92$ $(_{92}U)$

$\underbrace{_{90}Th\ \ _{91}Pa\ \ _{92}U}_{\text{Natural Actinoid}}\ \left[\underbrace{Np\ \ Pu \cdots\cdots Lr}_{\text{Actinoids} = 11}\ \ \underbrace{Unq \cdots\cdots Uub}_{\text{d-block} = 9}\right]\ \underbrace{114\ \ 116}_{p = 2}$

- All transuranic elements are radio and man made.
- All actinoids are radioactive. All actinoids aren't manmade.
- I man made element = Tc
- Man made radio lanthanoid = Pm
- Po At Rn Fr Ra ⇒ Radioactive
  84 85 86
- Np and Pu are also present in U ore U_3O_8 (Pitch Blend).
- Total natural elements are 94.

* **PERIODICITY** ⇒
Repetition of properties after regular interval.

- **Reason** : Similar outer shell $e^{\ominus}$ config.
- Z_{eff}, A.R., IP, EN, EA, etc. are periodic properties.

* **Z_{eff}** :- $\boxed{Z_{eff} = Z - \sigma}$

- **SLATER'S RULE** ⇒

→ **Z_{eff} Calculation for ns or np $e^{\ominus}$**

- for n^{th} shell $e^{\ominus}$ $\sigma = 0.35$
- for $(n-1)^{th}$ shell $e^{\ominus}$ $\sigma = 0.85$
- for $(n-2)$, $(n-3)$ shell $e^{\ominus}$ $\sigma = 1$

→ • Z_{eff} calculation for nd or nf $e^{\ominus}$

- for nd or nf $e^{\ominus}$ $\sigma = 0.35$
- for each $e^{\ominus}$ present @ left side of nd or nf $\sigma = 1$

→ σ for 2 $e^{\ominus}$ species like He, Li^+, $\sigma = 0.30$

Q.20 Calculate Z_{eff} :-

a) For Zn

Ans. $Z = 30$ $\quad \underbrace{1s^2}_{n-3}\ \underbrace{2s^2\ 2p^6}_{n-2}\ \underbrace{3s^2\ 3p^6\ 3d^{10}}_{n-1}\ \underbrace{4s^{2*}}_{n}$ ✓

$\sigma = 2(1) + 8(1) + 18(0.85) + 1(0.35)$
$= 2 + 8 + \cdots\cdots = 25.65$

$Z_{eff} = 30 - 25.65 = \underline{4.35}$

b) For 3d $e^{\ominus}$ of Zn

Ans $Z = 30$ $\quad \underline{1s^2}\ \underline{2s^2\ 2p^6}\ \underline{3s^2\ 3p^6\ \underset{nd}{\overset{*}{3d^{10}}}}\ \underline{4s^2}$

$\sigma = (2+2+6+2+6)1 + 9(0.35)$
$= 18 + 3.5 = 21.5 - .35 = 21.15$

$Z_{eff} = 30 - \overset{21.15}{} = \underline{8.85}$

c) For K

Ans $Z = 19$ $\quad \underbrace{1s^2}_{n-3}\ \underbrace{2s^2\ 2p^6}_{n-2}\ \underbrace{3s^2\ 3p^6}_{n-1}\ \underbrace{4s^{1}}_{n}$ *

$\sigma = 2(1) + 8(1) + 8(0.85) = 10 + 6.8 = 16.8$
$\Rightarrow Z_{eff} = Z - \sigma = 19 - 16.8 = \underline{2.2}$

d) For 3d $e^{\ominus}$ of Mn

Ans $Z = 25$ $\quad \underbrace{1s^2}_{n-3}\ \underbrace{2s^2\ 2p^6}_{n-2}\ \underbrace{3s^2\ 3p^6\ \overset{*}{3d^5}}_{n-1}\ \underbrace{4s^2}_{n}$

$3d \downarrow nd.$

$\sigma = 1\,(2+2+6+2+6) + 4\,(0.35) = 18 + 1.4 = 19.4$

$Z_{eff} = 25 - 19.4 = \underline{5.6}$

e) For N^{3-}

Ans $Z = 7$ $\quad \underbrace{1s^2}_{n-1}\ \underbrace{2s^2\ 2p^6}_{n}$

$\sigma = 0.85(2) + 0.35(7)$
$= 1.7 + 2.45 = 4.15$

$Z_{eff} = 7 - 4.15 = \underline{2.85}$

f) For He

Ans $Z_{eff} = 2 - 0.3 = \underline{1.7}$

- No. of $e^{\ominus}$ ↑ → σ ↑
  No. of $e^{\ominus}$ ↑ ↓
  σ ↑

- <u></u>Z_{eff} for normal elements acc. to Slater's Rule —

— Z_{eff} increases by 0.65 on moving left to right.

→ Z_{eff} increases by 0.90 on moving from 2nd to 3rd period

– Z_{eff} remains constant beyond 3rd period

– Z_{eff} increases by 0.15 on moving left to right in d block (generally)

Q.21 If Z_{eff} of Ca is x, then Z_{eff} of B is –

Ans $\;{}^{20}Ca \qquad {}^{5}B$

~~$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$~~

$x - 0.9 \qquad x - 0.9 + 0.65 \Rightarrow \underline{x - 0.25}$

2 $\quad Be \longrightarrow B$

3 $\quad Mg = x$

4 $\quad Ca = x$

Q.22 In which of the following move Z_{eff} increases by 0.65 ⇒

a) $C \to O$ $\qquad$ c) $Na \to K$

b) $Ti \to V$ $\qquad$ [✓ d)] $Cu \to Zn$ check $e^{\ominus}$ config

Last $e^{\ominus}$ enters in $ns \Rightarrow 1 - 0.35 = 0.65$

• Z_{eff} for isoelectronic species and ions of 1 element ⇒

a) $O^{2-} \quad F^{-} \quad Ne \quad Na^{+} \quad Mg^{2+}$

$\xrightarrow{\hspace{2em}} Z\uparrow$; no. of $e^{\ominus}$ = same ⇒ $Z_{eff} \uparrow$

$O^{2-} < F^{-} < Ne < Na^{+} < Mg^{2+}$

b) $O^{2-} \quad O^{1-} \quad O \quad O^{+}$

$\xrightarrow{\hspace{2em}} Z$ = same ; no. of $e^{\ominus} \downarrow \Rightarrow \sigma \downarrow \Rightarrow Z_{eff} \uparrow$

$O^{2-} < O^{-} < O < O^{+}$

- $Z_{eff} \propto \frac{+ve\ charge}{-ve\ charge}$ $Z_{eff} \propto \frac{Z}{No.\ of\ e^{\ominus}}$

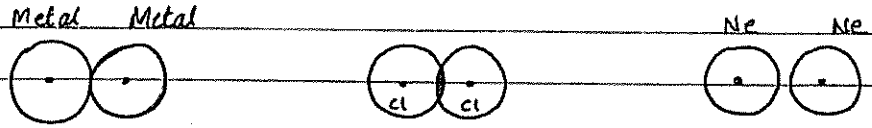
- Shielding Effect : $ns > np > nd > nf$
  (Due to diffused shape) poor negligible

- Z_{eff} increases on moving down a group in d block.
  (only for application use)

- Z_{eff} increases on moving from Ce to Lu (Lanthanoids) due to poor shielding effect of $4f\ e^{\ominus}$.

* ATOMIC RADIUS ⇒

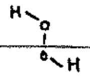
Half of internuclear distance of 2 same bonded atoms.



Metallic Bond (r met. std. radius for metals) | Covalent (r cov. std. radius for NM) | Vander Waal Bond (r vdw std. radius for inert gases)

- Both covalent and VDW radii are possible for NMs.

- $r_{vw} > r_{metallic} > r_{cov.}$

Q.23 Incorrect match for SBCR (Single Bond Covalent Radius) —
a) for Oxygen — H_2O_2

b) for Carbon — C_2H_6 $\geqslant C-C \leqslant$ d) None
[✓ c)] for Nitrogen — N_2H_2 $H-N=N-H$
N → $>N-N<$ Hydrazine

- If 2 different atoms are bonded with each other, then we use Schomaker – Stevenson equation :

$$d_{A-B} = r_A + r_B - 0.09\,(\Delta EN) \quad \text{Å}$$

- COMPARISON OF ATOMIC RADIUS :-

→ IN A PERIOD : $A.R. \propto \frac{1}{Z_{eff}}$

– $Li > Be > B > C > N > O > F \ll \underline{Ne}_{\,VWR}$

$\xrightarrow{\hspace{2cm}} Z_{eff} \uparrow$

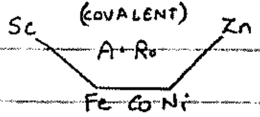
– Max. atomic radius in a period – inert gases
– Max. covalent radius in a period – IA
– Min. atomic radius in a period – Halogen

– Lanthanide Contraction –
Atomic radius and ionic radius gradually decreases on moving from Ce to Lu due to poor shielding effect of 4f $e^\ominus$. ~~AR of Yb and~~

Q.24 Assertion : Atomic Radius of Eu and Yb are exceptions of Lanthanide Contraction
Reason: Eu and Yb involve only 2 $e^\ominus$ in metallic bonding rather than 3 $e^\ominus$.

Ans $Ce >>>> < \underset{4f^7\,6s^2}{\underline{Eu}} >>> < \underset{4f^{14}\,6s^2}{\underline{Yb}} > Lu$

Eu has max. atomic radius among Lanthanides. (A)



– **Covalent radius for 3d series :**

Irregular and partial changes

$Sc \geqq Ti \geqq V \geqq Cr \geqq Mn \geq Fe \simeq Co \simeq Ni \leqq Cu < Zn$

$Z_{eff} \uparrow (0.15) \Rightarrow A.R. \downarrow$ $\quad \underbrace{3d^6 \quad 3d^7 \quad 3d^8}_{Z_{eff} \simeq \text{same}; \text{ so } A.R. \simeq \text{same.}}$, $\underbrace{3d^{10} \quad 3d^{10}4s^2}_{Z_{eff} \downarrow (\text{as } \sigma \uparrow) \text{ so } AR \uparrow}$

σ depends on pairing of inter electronic repulsive electrons.

Q.25 Assertion: Metallic radius of Mn is > that of Cr

Reason : Metallic bond strength of Mn is < that of Cr

Ans Metallic radius for 3d series : $Sc \geqq Ti \geqq V \geqq Cr \bigcirc\!\!\!\!< Mn \geqq Fe \simeq Co \simeq Ni \leqq Cu < Zn$

$3d^5 4s^1$ → 6e^- participate
for breaking d^5 stability, II IP is required.

$3d^5 4s^2$ only 2e^- participate in metallic bonding
Here III IP is v. high So, not possible.
weak ⇒ A.R.↑

– Ionic radius for 3d series : $\boxed{Sc^{2+}} > Ti^{2+} > > > > > \boxed{Ni^{2+}} \leqq Cu^{2+} < Zn^{2+}$

Sc^{2+} ↓ Does not exist

Ni^{2+} ↳ smallest bivalent cation for 3d series.

→ IN A GROUP : A·R· ∝ No. of shell

– $F < Cl < Br < I$

– $Be < Mg < Ca < Sr < Ba$

– $N < P < As < \underbrace{Sb < Bi}_{32}$ But still size ↑ as lanthanide contr. weakens.

– Lanthanide Contraction in d block :

$$\text{IVB} \longrightarrow \text{IIB}$$

18 [3d Ti
↓ → No. of shell ↑ ⇒ dominant ⇒ size ↑
→ Z_{eff} ↑
4d Zr]

32 [4d Zr
↓ → no. of shell ↑
→ Z_{eff} ↑↑
] = balance each other; size ≃ same
5d Hf]

↳ Lanthanides ⊕ ⇒ $4f^{14}$ ⇒ σ ↓↓

Transition Contraction (CONTROVERSY) $\Rightarrow$

$\hookrightarrow$ Covalent (both) $Si \simeq Ge$

Si $\rightarrow$ Covalent; Ge $\rightarrow$ metallic $Si < Ge$ Si is more NMic

— • Size : $3d < \underset{\text{Lanth. Contr.}}{4d \simeq} \underset{\text{Actinoid Contr.}}{5d \simeq} 6d$

EXCEPT :- III B, II B

$$\begin{array}{ccccccc} 3d & < & 4d & < & 5d & \simeq & 6d \\ Sc & < & Y & < & La & \simeq & Ac \end{array}$$

III B $\Rightarrow$ $\underbrace{\underbrace{Sc < Y}_{18} < La}_{18} \simeq Ac$ (32)

No. of shell ↑ Z_{eff} ↑↑

If $\Delta Z = 32$, size remains almost same.

— Down a group, size increases. In last 2 elements, size remains almost same (exception N family)

Q. 26 — Actinoid Contraction is dominating than Lanthanide Contraction

— 5f orbitals are more diffused than 4f orbitals.

Ans (A)

→ FOR ISOELECTRONIC SPECIES & IONS OF AN ELEMENT —

$$\text{IONIC RADIUS} \propto \frac{1}{Z_{eff}} \propto \frac{\ominus\ \text{charge}}{\oplus\ \text{charge}}$$

— $S^{2-} > Cl^{-} > Ar > K^{+} > Ca^{2+}$ ($18\ e^{\ominus}$)

— $I^{-} > I > I^{+}$

— $\underset{-1}{NaH} > \underset{0}{H_2} > \underset{+1}{HCl}$ (For r_H)

→ TRANSITION CONTRACTION —

All $e^{\ominus}$ were in s and p. So, σ ↑ $\Rightarrow Z_{eff}$ ↓ $_{13}Al$

↕ $\Rightarrow Z_{eff}$ ↑

$10\ d\ e^{\ominus}$ (σ ↓) Z_{eff} ↑ introduced (21 ⟶ 30) $_{31}Ga$

→ No. of shell ↑
→ Z_{eff} ↑
] Balance each other

$Al \simeq Ga$

Q.27 Compare radii :

2nd - 3rd group, period, adjacent elements

a) Be > B
^ ^
Mg > Al

2 < 2 < 3 < 3
⇒ B < Be < ~~Mg~~ < Mg
Al

b) N > O
^ ^
P > S

2 2 3 3
O < N < S < P

c)

$$\begin{tikzcd}
Li & Be \arrow[l] \\
Na & Mg \arrow[l] \\
K \arrow[d] & Ca \arrow[d] \\
Rb \arrow[d] & Sr \arrow[d] \\
Cs & Ba \arrow[uul]
\end{tikzcd}$$

$$\begin{tikzcd}
Li \arrow[dr] & Be \\
Na \arrow[dr] & Mg \\
K & Ca
\end{tikzcd}$$

Same order for ionic radius
EXCEPT : $Li^{+} \geq Mg^{2+}$

$Li > Be > B$ 5,7,17   8
4,26   145

3. S-block size order

$$\begin{tikzcd}
\mathrm{Li} \arrow[dr] & \mathrm{Be} \arrow[l] \\
\mathrm{Na} \arrow[dr] & \mathrm{Mg} \arrow[l] \\
\mathrm{K} \arrow[d] & \mathrm{Ca} \arrow[d] \\
\mathrm{Rb} \arrow[d] & \mathrm{Sr} \arrow[d] \\
\mathrm{Cs} & \mathrm{Ba} \arrow[uul]
\end{tikzcd}$$

$Cs > Rb > K > Ba > Sr > Ca > Na > Mg > Li > Be$

28/04/17

Same order of for Ionic Radius except $Li^{+} \geq Mg^{2+}$

4. K^{+} Sr^{+2} $K^{+} > Sr^{+2}$

5. $F^{-} < Cl^{-} < Br^{-} < H^{-}$ $I^{-} > H^{-}$
↳ Smallest Anion of Periodic Table.

6. F^{-}, Na^{+}, Ne $Ne > F^{-} > Na^{+}$
VWR.

7. Mg, Mg^{2+}, Al, Al^{+3} When 2 ~~neut~~ neutral & 2 ions, 1st compare 2 neutral → 2 ion → 1 neutral, 1 ion.

$\underbrace{Mg > Al}_{3\,shell} > \underbrace{Mg^{+2} > Al^{+3}}_{2\,shell}$

8. O, O^{-2}, F, F^{-}

$O^{-2} > F^{-} > O > F$

Adjacent elements : ~~Cation~~ Anion > Neutral > Cations

x y z → L.C.

9. $Li < Na < K < Rb < Cs \approx Fr$ > > z

$\underbrace{Na < K}$ max. radius diff.

10. $B < Al \approx Ga < In \cancel{\approx} Tl$

$B < Al \approx Ga < In \leq Tl$

11. $C < Si < Ge < Sn \leq Pb$

12. $Cr < Mo \approx W$

13. $V < Nb \approx Ta$

14. $Cu < Ag \approx Au$

15. $Ti^{+4} < Zr^{+4} \approx Hf^{+4}$

16. $Sc < Y < La \approx Ac$

17. $Zn < Cd < Hg$ Exception

↳ liq. ⇒ metallic bonding is weak ⇒ radius ↑

↳ no. of paired e^- ↑↑ ⇒ Repulsion ↑↑ ⇒ metallic bond weak.

18. $KMnO_4$ MnO_2 Mn Mn Radius

$Mn^{+7} < Mn^{+4} < Mn$

19. $Cl^{35} = Cl^{37}$ $Cl^{37} \approx Cl^{35}$

20. $H^- > Li^+ > Be^{+2} > B^{+3}$

21. N, O, P, S $N > O$

$P > S > N > O$ $\hat{P} > \hat{S}$

C   Si   Mg   F

C   F

Mg   Si $Mg > Si > C > F$

22. B, Al, ~~G~~C, Si   B C

$Al > Si > B > C$ Al Si

23. $La^{+3} > Ce^{+3} > Gd^{+3} > Lu^{+3}$

24. $[Ne]\,3s^2 3p^1$ $[He]\,2s^2 2p^5$ $[He]\,2s^2$ $[Ne]\,3s^1$

Al   F   Be   Na

Be   F

Na Mg   Al

$Na > Al > Be > F$ Be >

~~Ques Which of~~

25. Be^{+2} Br^- Te^{-2} K^+ Mg^{+2} Cl^- Na^+ Se^{-2}

Li Be   O F

Na Mg   S Cl

K   Se Br

Te

isoelectronic

$Be^{+2} < Mg^{+2} < Na^+ < K^+ < Cl^- <$ ~~[illegible]~~ $Br^- < Se^{-2} < Te^{-2}$

same grp

Ques Which radius order is correct?

I > Br > C

1. $Na^+ > Mg^{+2} > Al^{+3} > Li^+$ B C N O
2. $Li > I > Cl < Br$ ✓   Al   S
3. ~~[illegible]~~ $O > C < S < Se$
4. $Al > S > O > N$

Li → Weak metallic radius
I → Cov. radius

↳ Transition Elements show similarity in properties in both horizontal & vertical direction due to comparable size.
Zeff almost same

IONISATION POTENTIAL

↳ Minimum required energy to remove most loosely bonded ~~electron of~~ outermost e^- of an isolated gaseous atom.

↳ Ionisation Energy is an endothermic Term ~~of~~ for neutral atom.

Net Attraction Force ↑ IE ↑

Ques Which of the following process ~~rep~~ represent 1st IE?

1. $Na(s) \xrightarrow{E_1} Na^+(g)$ $E_1 = SE + IE_1$ Endo.
2. $\frac{1}{2}F_2(g) \xrightarrow{E_2} F^+(g)$ $E_2 = \frac{1}{2}BE + IE_1$ (B.D.E) Endo.
3. $Mg(g) \xrightarrow{E_3} Mg^{+2}(g)$ $E_3 = IE_1 + IE_2$ Endo.

Te^{-2} ✓4. $Xe(g) \longrightarrow Xe^+(g)$ $E_4 = IE_1$ Endo.

Ques ↳ $Al(g) \xrightarrow{E_1} Al^+(g) \xrightarrow{E_2} Al^{+2}(g) \xrightarrow{E_3} Al^{+3}(g)$

E_1 ↓ IE_1 of Al

E_2 ↓ IE_2 of Al
IE_1 of Al^+

E_3 ↓ IE_3 of Al
IE_2 of Al^+
IE_1 of Al^{+2}

⟶ +ve charge ↑ Zeff ↑ IE ↑

* $\boxed{IE_1 < IE_2 < IE_3}$

↳ ~~IP has no relation with VWR~~

↳ IP has no relation with VWR

- Comparison of IE :

A. For Isoelectronic species & ions of an element →

$$\boxed{IE \propto Z_{eff.} \propto \frac{+ve\ charge}{-ve\ charge}} \Rightarrow \text{Only charge}$$

i) $O^{-2} < F^- < Ne < Na^+ < Mg^{+2}$

ii) $O^{-2} < O^- < O < O^+$

B. In a group. → $\boxed{IE \propto \frac{1}{Size}}$

i) $Be > Mg > Ca > Sr > Ba$

ii) $He > Ne > Ar > Kr > Xe$

↳ On moving down a group, if size is same or almost same due to L.C. or T.C., then IP increases ↑ because Zeff. ↑

Gen. Size Order in d-Block → 3d < 4d ≈ 5d

~~3d~~

Gen. IP Order in d-Block → 3d > 4d < 5d

~~3d > 5d > 4d~~

⇓ Except 4, 5, 6, 10 (5d > 3d > 4d)

⇓

3d < 4d < 5d

~~Ti < Zr < Hf~~
~~V < Nb < W~~
~~Cr < Tc <~~

Ti < Zr < Hf
V < Nb < Ta
Cr < Mo < W
Ni < Pd < Pt

IP ⇒ eV/atom
IE ⇒ kJ/mol

$\boxed{\uparrow\downarrow}$

c. <u>In a Period</u> → i. Check elec. config. & outermost shell.

only when $\Delta Z = 1$

ii. $\boxed{IE \Rightarrow np^3 > np^4}$
↳ Applicable upto 4th Period.

iii. $\boxed{IE \Rightarrow ns^2 > np^1}$
↳ Penetration Effect
Closeness to nucleus: s > p > d > f

Except ⇒ $\boxed{Ca > Ga}$ IP
$4s^2$ $4s^2 4p^1$
$\Delta Z = 11$

*

iv. If charge & outermost shell are same, then Inert gas config. has max IP.

v. $\boxed{IE \propto Z_{eff}}$

1. $Li < Be > B < C < N > O < F < \overset{max.}{Ne}$
$2s^1$ $2s^2$ $2p^1$ $2p^2$ $2p^3$ $2p^4$ $2p^5$ $2p^6$

$Li < B < Be < C < O < N < F < \underline{Ne}$

2. Na Mg Al Si P S Cl Ar IP_2
p^6 s^1 s^2 p^1 p^2 p^3 p^4 p^5

$Mg < Si < Al < P < Cl < S < Ar < Na$ IP_2

↳ Max IP_I in a period ⇒ Inert Gases. (Max. radius)
↳ Min. IP_I in a period ⇒ Alkali Metals
↳ Max. IP_{II} in a period ⇒ Alkali Metals
↳ Min IP_{II} in a period ⇒ Alkaline Earth Metals

$1s^1$ $1s^2$ $1s^2 2s^1$ $1s^2 2s^2$

3. Li Be B C IE_3
~~$2s^1$~~ ~~$2s^2$~~ ~~$2s^2 2p^1$~~ ~~$2p^2$~~

$Be > Li > C > B$ $\rightarrow Z_{eff} \uparrow$

↳ IP values of lanthanoids generally ↑es from Ce to Lu because Zeff ↑.

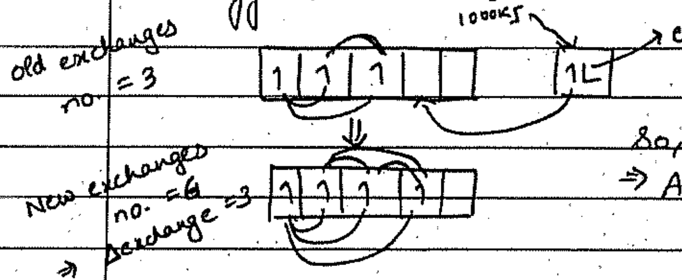
Ce < < < < < < < < Lu.

↳ IP changes in a d-series are irregular due to :

a. Irregularity in size & Zeff.

b. Exceptions of elec. configuration

c. After removal of 1e⁻, remaining ns e⁻ is shifted into (n-1) d sub-shell which change the value of exchange energy. As a result, IP values are also changed.



Let per exchange = 30 KJ

So, 30 × 3 = 90 KJ

⇒ Actual energy = 910 KJ

↳ IP Values ↑es on moving from left to right in 3d series except interval no. 2, 6, 7.

$$Sc \underbrace{<}_{1} Ti \underbrace{>}_{2} V \underbrace{<}_{3} Cr \underbrace{<}_{4} Mn \underbrace{<}_{5} Fe \underbrace{>}_{6} Co \underbrace{>}_{7} Ni \underbrace{<}_{8} Cu \underbrace{<}_{9} Zn$$

↳ Max. IP in a Series : Last element

Min. IP in a Series : First element.

1. O, F, Cl, S

np^4 O S — F Cl np^5

F > O > Cl > S

3, 3, 2, 2

2. Be, B, Mg Al

ns^2 Be Mg — B Al np^1

Be > B > Mg > Al

3 K, K^+, Cu, Cu^+

K — Cu

$4s^1 \xrightarrow{\quad} 4s^1 3d^{10}$

$Z_{eff}\uparrow$

$\Downarrow$

K < Cu

$K^+ > K$ $Cu^+ > Cu$

~~$K^+ > Cu^+ > K > Cu$~~

$K^+ > Cu^+ > Cu > K$

K^+ — Cu^+

$3s^2 3p^6$ — $3s^2 3p^6$ ~~$4s^0$~~ $3d^{10}$

Inert — Pseudo - Inert

$K^+ > Cu^+$

$\Downarrow$ $18e^-$

Less stable than inert as $3d^{10}$ is closer to nuc. so e^- removal is easier

4. Cu, Cu^+, Zn, Zn^+

~~Cu~~ Zn > Cu

$Zn^+ > Zn$

$Cu^+ > Cu$

$Cu^+ > Zn^+ > Zn > Cu$

Cu^+ — Zn^+

$3d^{10}$ — $4s^1$

$Cu^+ > Zn^+$

Ni — Cu

5. Pd — Ag

$4d^{10}5s^0$ — $4d^{10}5s^1$

~~Ag > Pd~~ Pd > Ag

IP ~~[illegible]~~ Yb^{+3}
U^{+3} Cf^{+3} La^{+} Zn
s-block.

6. N, Ne^+, Na, O, O^+

~~np^3 np^5 np~~ $N > O > Na$ $Ne^+ < O^+$

$2p^3$ $2p^5$ $3s^1$ $2p^4$ $2p^3$ $2p^3$ $2p^4$ $3s^1$ $2s^2\,2p^5$ $2p^3$

$Z_{eff} \propto \frac{Z}{e}\uparrow$ ~~[illegible]~~

~~[illegible]~~

$Ne^+ > \underline{O^+ > N} > O > Na$
iso-elec.

7. Li Na K Rb Cs Fr

~~Li < Na < K < Rb < Cs~~

$Li > Na > K > Rb > Fr > Cs$

* Min. IP in Periodic Table ⇒ Cs

* Max. IP in Periodic Table ⇒ He

8. H^- He Li^+ Be^{+2}

$Be^{+2} > Li^+ > He > H^-$ Isoelec.

9. B Al Ga In Tl

~~B > Ga > Al > In > Tl~~ ~~B > Ga > Al > Tl > In~~

~~B < Al~~ $B > Al \leq Ga > In < Tl$

~~B < In~~ $\underline{B > Tl > Ga \geq Al > In}$

10. $C > Si > Ge > Sn < Pb$

11. $\underline{N > P > As > Sb > Bi}$ LC Not applicable as moving further after B and C family into p block, $pe^{\ominus}\uparrow \Rightarrow \sigma$ strong.

12. $Cu > Ag < Au$

~~$2s^1 < 2p^3$~~

$1s^2$ $2s^1 < 2p^2 > 2p$

~~C > Be > B C~~

Li >

13. 6th Cr > Mo ~~[illegible]~~ > W   4th, 5th, 6th, 10th groups में लगातार ↑ing IP.

14. 10th Ni > Pd > Pt $4s^2 3d^8$ 10

15. Sc > Y > La < Ac

16. Li Be B C IE_2 Li > ~~B~~ > Be > C > B

17. Na < Mg > Al < Si IE_1

18. $^{35}Cl = {}^{37}Cl$

19. Zn > Ga
Cd > In
Hg > Tl
} ΔZ = 1

20. $N^{-3} < N$
$Cu^{+} < Cu^{+2}$
$Mn^{+2} < Mn^{+3}$
$Ne < Ne^{+}$
ions ~~elements~~ of same element ⇓ charge

21. np^3 · np^4
N > O
P > S
As > Se
~~Sb > Te~~
Sb < Te
} $np^3 > np^4$ → upto 4th Pd.

22. $[He]2s^2 2p^4$ (1) $[Ne]3s^2 3p^5$ (2) $[Xe]6s^2$ (3) $[He]2s^2 2p^3$ (4)

4 > 1 > 2 > 3

Application of IP:

1. **No. of Valence Electrons**

Ques Match →

1	ns^1	P	26, 32, 40, 48, $\boxed{260}$	Sudden Jump.
2	ns^2	Q	22, 30, 36, 250	
3	ns^2np^1	R	24, 28, 200, 240	
4	ns^2np^2	S	19, 190, 210, 230	

1 → S 2 → R 3 → Q 4 → P

No. of valence $e^{\ominus}$ + 1 = No. of sudden jump

2. **Stable Oxidation State**

a. ~~Diff~~ If diff. b/w 2 successive IP values is less than 11 eV, then higher Oxidaⁿ State is more stable.

b. If diff. b/w 2 successive IP values is more than 16 eV, then lower O.S. is more stable.

$$M(g) \xrightarrow[7.6eV]{} M^+(g) \xrightarrow[15eV]{} M^{+2}(g) \xrightarrow[85eV]{} M^{+3}(g)$$

$\Delta IP_1 \Rightarrow 7.4eV \Rightarrow M^+ < M^{+2}$

$\Delta IP_2 \Rightarrow 70eV \Rightarrow M^{+2} > M^{+3}$

Diff. b/w successive IP ↓ ⇒ Easier for rxⁿ mixture to supply energy to create H.O.S.

Stability of OS depends on:

① element itself

② element it forms bond with in the reaction mixture.

3. $\boxed{\begin{array}{l} \text{METALLIC CHARACTER} \\ \text{ELECTROPOSITIVE CHARACTER} \\ \text{REACTIVITY OF METALS} \end{array} \propto \dfrac{1}{\text{I.P.}}}$

→ Non Metallic Character ↑

↓

Metallic Character ↑

- $Li < Na < K < Rb < Cs$ (Electropositive)
  $\xrightarrow[\text{IP} \downarrow]{}$

- $N < P < As < Sb < Bi$ (Metallic character)

- $\underset{\text{STEAM}}{Be} < \underset{\text{HOT}}{Mg} < \underset{\text{COLD}}{\underline{Ca < Sr < Ba}}$ (Reactivity with H_2O)

* ELECTRON AFFINITY / ELECTRON GAIN ENTHALPY

- Amount of released energy when an $e^{\ominus}$ is added into outermost shell of a gaseous isolated atom. ══ EA
  OR
- Total enthalpy change in this process. ══ $e^{\ominus}$ gain enthalpy.
- Net attraction on incoming $e^{\ominus}$ ↑ ⇒ EA ↑
- $Cl\,(g) + e^{\ominus} \longrightarrow Cl^-\,(g) + \underset{}{\boxed{348\ KJ/mol}}^{EA}$
- $Cl\,(g) + e^{\ominus} \longrightarrow Cl^-\,(g) \qquad \Delta H_{eg} = -348\ KJ/mol$
- $\left.\begin{array}{l} Ne + e^{\ominus} \longrightarrow Ne^- \quad \Delta H = +116\ KJ/mol\ ;\ EA = 0 \\ He + e^{\ominus} \longrightarrow He^- \quad \Delta H = +48\ KJ/mol\ ;\ EA = 0 \end{array}\right]$ Definition

- So, representation by ΔH_{eg} is better than by EA.

- Generally, addition of 1st $e^{\ominus}$ in a neutral atom is exo.

- Addition of 2nd $e^{\ominus}$ in a neutral atom is always endo. due to anion - $e^{\ominus}$ repulsion. So, II EA of any element is 0.

- $O(g) + e^{\ominus} \longrightarrow O^{-}(g) \quad \Delta H_{eg} = -141$ KJ/mol

$$O^{-}(g) + e^{\ominus} \longrightarrow O^{2-}(g) \quad \Delta H_{eg} = +744 \text{ KJ/mol}$$

$$O(g) + 2e^{\ominus} \longrightarrow O^{2-}(g) \quad \Delta H_{eg} = \oplus$$

- Formation of a polynegative anion is always endo.

Q. A: Formation of O^{2-} is endo but mostly MO contain O^{2-} anion
R: II ΔH_{eg} of O is compensated by Lattice Energy of MO.

Ans. (A)

- COMPARISON OF EA ⇒

→ For isoelectronic species and ions of an element,

$$\boxed{EA \propto Z_{eff} \propto \frac{\oplus}{\ominus}}$$

— $O^{2-} < F^{-} < Ne < Na^{+} < Mg^{2+}$

— $I^{-} < I < I^{+}$

→ **In a group:** $\boxed{EA \propto \frac{1}{size}}$

− $Cl > Br > I$

→ EXCEPTION

* * * EA of 2nd period p block element < EA of 3rd period p block element

− New incoming $e^{\ominus}$ enters into smaller 2p subshell that has high $e^{\ominus}$ density, so more repulsion ⇒ less EA.	New incoming $e^{\ominus}$ enters into larger 3p subshell that has lesser $e^{\ominus}$ density, so less repulsion ⇒ more EA.
$O = 2s^2 \; 2p^4 \leftarrow e^{\ominus}$	$S = 3s^2 \; 3p^4 \leftarrow e^{\ominus}$
 $e^{\ominus}$ density ↑	 $e^{\ominus}$ density ↓

→ $B < Al \quad C < Si \quad N < P \quad O < S \quad F < Cl$

→ $F < Cl > Br > I \Rightarrow Cl > F > Br > I$ (values)

− $O < S > Se > Te > Po \Rightarrow S > Se > Te > Po > O$

→ **In a period:**

① Check $e^{\ominus}$ config. and outermost shell.
② Addition of $e^{\ominus}$ in inert gases, alkaline earth metals and N are endo.

- $Ne + e^{\ominus} \rightarrow Ne^{-}$ $\Delta H = +116$ KJ/mol
$2s^2\ 2p^6$ $3s^1$

- $Be + e^{\ominus} \rightarrow Be^{-}$ $\Delta H = +67$ KJ/mol
$2s^2$ $2p^1$

- $N + e^{\ominus} \rightarrow N^{-}$ $\Delta H = +7$[illegible] KJ/mol.
$2p^3$ $2p^4$

- $Ne < Be < N$ $EA \simeq 0$

→ $\boxed{EA = ns^1 > np^1}$ (ns is closer to nucleus, so attraction ↑ so EA ↑.)

→ $\boxed{EA = np^2 > np^3}$ (gaining half filled stability)

→ $\boxed{EA \propto Z_{eff}}$

-

Li	Be	B	C	N	O	F	Ne	
s^1	s^2	p^1	p^2	p^3	p^4	p^5	p^6	$(n=2)$

$\underline{Ne \leq Be \leq} N < B < Li < C < O < F$
EN OO

-

Na	Mg	Al	Si	>	P	S	Cl	Ar
s^1	s^2	p^1	p^2		p^3	p^4	p^5	p^6

$Ar \leq Mg \leq Al < Na < P < Si < S < Cl$

- ~~O > F~~
  ~~S > Cl~~   ~~Cl [illegible] O~~

- $O \ \cancel{>}< F$ $\cancel{F}O < S < F < \cancel{S}Cl$
  $\wedge \qquad\quad \wedge$
  $S \ \cancel{>}< Cl$ $\underset{\text{min.}}{2} \quad 3 \quad 2 \quad \underset{\text{max.}}{3}$ (IP increasing)

* <u>RELATION B/W IP & EA</u> →

- $$\overset{\curvearrowright}{X_{(g)} + e^{\ominus}} \underset{\text{IP}}{\overset{\text{EA}}{\rightleftharpoons}} X^{-}_{(g)}$$

⇒ $$\boxed{\text{EA of } X_{(g)} = \text{IP of } X^{-}_{(g)}}$$

- $$X_{(g)} \underset{\text{EA}}{\overset{\text{IP}}{\rightleftharpoons}} X^{+}_{(g)} + e^{\ominus}$$

⇒ $$\boxed{\text{IP of } X_{(g)} = \text{EA of } X^{+}_{(g)}}$$

Q. Compare IP :-

1. F, F^-, Cl, Cl^-.   IP $F > Cl$ (size ↑)

EA of F < EA of Cl ⇒ IP of F^- < IP of Cl^-

IP of Cl > IP of Cl^- ⇒ Ans $F^- < Cl^- < Cl < F$.

⇒ IP order of monovalent anions is always same as EA order of neutral atom.

2. Li^-, C^-, Si^-, S.

EA ⇒ $\underset{2s^1}{Li} < \underset{2p^2}{C} < Si < S$ ⇒ IP = $Li^- < C^- < Si^- < S^-$

3. O, S, O^-, S^- ⇒ EA ⇒ $O < S$ ⇒ IP = $O^- < S^-$

IP ⇒ $O > S$ ⇒ IP ⇒ $O^- < S^- < S < O$

4. N^-, F^-, S^-, B^- ⇒ EA ⇒ ~~$B < N < F > S$~~
~~$S < N < B < F$~~
~~$N < S < B < F$~~ $N < B < S < F$
⇒ ~~IP ⇒ $N^- < S^- < B^- < F^-$~~. IP ⇒ $N^- < B^- < S^- < F^-$

B O F
$2p^1$ S Cl

Q. Compare EA -

1. C, Si, N, P ⇒ $C > N$ ⇒ $N < P < C < Si$
$\hat{Si} > \hat{P}$ 2 3 2 3

2. N^+, P^+, S^+, O^+ ⇒ IP of X = EA of X^+
$2p^2$ $3p^2$ $3p^3$ $2p^3$

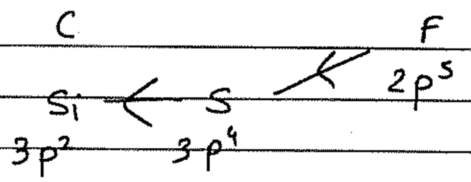
~~IP ⇒ $N < O$ ⇒ $S > O > P > N$ IP~~
~~$\hat{P} < \hat{S}$ ⇒ $S^+ > O^+ > P^+ > N^+$ EA~~

IP ⇒ $S < P < O < N$
3 3 2 2

EA ⇒ $S^+ < P^+ < O^+ < N^+$

3. $[Ne]\,3s^2\,3p^2$ — Si $[He]\,2s^2\,2p^5$ — F $[He]\,2s^2\,2p^2$ — C $[Ne]\,3s^2$ — Mg

⇒ EA Mg < C < Si < F   C < Si



C < F

Z_{eff} ↑ ⇒ EA ↑

4. B, Al, C, Si

Q. Which of the following is least stable –

a) O^- c) C^-
b) B^- ✓ d) Be^-

Ans a), b), c) are exo ΔH_{eg} ⇒ energy ↓ ⇒ stability ↑
d) ⇒ endo ⇒ energy ↑ ⇒ stability ↓.

Q. II ΔH_{eg} of O and S are respectively – (II ΔH_{eg} always endo)

a) +590, +780 X b) −590, −780
X b) −780, +590 ✓ d) +780, +590

Q. IP of an element is X and EA is Y. Then –

a) X > Y b) X < Y
c) X = Y d) Dunno

IP of X > IP of X^- IP of X > EA of X.

IP of Cs > EA of Cl

Q. Identify endo and exo –

X a) $N^- \longrightarrow N$ N c) $S \longrightarrow S^{-2}$

X b) $O^+ \longrightarrow O^-$ X d) $Na^+_{(g)} \xrightarrow[N]{X} Na_{(s)}$

√ e) $\frac{1}{2} N_2 (g) \rightarrow N^- (g)$ $\underset{(LE)}{N}$ f) $NaCl (s) \rightarrow Na^+(g) + Cl^-(g)$

X g) $F_{(g)} \longrightarrow F^-_{(aq)}$ X h) $P \longrightarrow P^-$

√ i) $Xe + He^+ \rightarrow Xe^+ + He$ ⇒ endo

IE of Xe endo   IE of He = EA of He^+ ⇒ exo

j) X $F + I^- \longrightarrow F^- + I$ endo·

exo

$\underset{\text{exo}}{\text{EA of F}}$ >> $\underset{\text{endo}}{\text{IE of } I^-}$ = EA of I

* ELECTRONEGATIVITY ⇒

- EN is a relative tendency of a bonded atom to attract shared $e^\ominus$ pair towards itself.

- EN is unitless and it doesn't depend upon $e^\ominus$ config.

- COMPARISON OF EN –

→ In a period : EN ∝ Z_{eff}

→ In a group : EN ∝ $\frac{1}{size}$

→ EN ∝ $\frac{\oplus \text{ O.S.}}{\ominus \text{ O.S.}}$

- $\overset{+3}{SbF_3} < \overset{+5}{SbF_5}$ (EN of Sb)

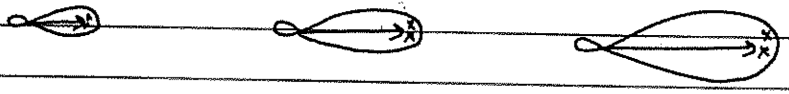
- $-\overset{-3}{CH_3} < -\overset{+3}{CF_3}$

  (2.5) (3.47)

→ EN ∝ s character

- $sp > sp^2 > sp^3$ EN

  ⟶ s character ↓ ; p character ↑



size ↑ ⇒ $e^\ominus$ cloud distance fm. nucleus ↑ ⇒ attraction ↓

- $\equiv C- > =\overset{|}{C}- > -\overset{|}{\underset{|}{C}}-$

  3.25 2.75 2.5

- SOME IMPORTANT EN VALUES –

H = 2.1

MAXIMUM

Li	Be	B	C	N	O	F
1	1.5	2	2.5	3	3.5	4

Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3

Br
2.8

I
2.5

Cs
0.7
MINIMUM

* On moving down a group in d-block, mostly properties depend upon Z_{eff} rather than size, as there are minimal changes in size but Z_{eff} increases regularly.

→ • $Al < Ga$ $In < Tl$ $Sn < Pb$ ($Z_{eff} \uparrow$)

→ $Cu < Ag < Au$ $Zn < Cd < Hg$

• EN SCALES ⇒

1. PAULING SCALE – Based on Bond Energy or Resonance Energy.

$$X_A - X_B = 0.208 \sqrt{\Delta_{AB}}$$

$$\Delta_{AB} = 23.06 \, (X_A - X_B)^2$$

Δ_{AB} = Resonance Energy (in Kcal/mol)
X = EN.
Δ_{AB} = Energy of reso hybrid − energy of most stable reso structure
= Energy of reso hybrid − $\sqrt{E_{A_2} \times E_{B_2}}$

2. MULLIKAN SCALE – $E.N. = \dfrac{IP + EA}{2}$ (eV/atom)

• RELATION B/W X_P and X_M ⇒ $X_P = \dfrac{X_M}{2.8}$

$X_P = \dfrac{IP + EA}{5.6}$ eV/atom $X_P = \dfrac{IP + EA}{540}$ KJ/mol

Q. Correct relationship for compound AB ($\overset{\delta-}{A} - \overset{\delta+}{B}$) :
a) IP of A + IP of B < EA of A + EA of B
b) $IP_A + EA_A < IP_B + EA_B$
✓ c) $IP_A - IP_B > EA_B - EA_A$
d) None

3. ALFRED ROSCHOW SCALE – Based on electrostatic attraction b/w nucleus and new incoming $e^{\ominus}$.

$$X_{AR} = \frac{0.359\ Z_{eff}}{r^2} + 0.744$$ [for atoms too, i.e, acc., $EN_{18} > EN_{17}$ $(EN_{Ne} > EN_F)$]

- EN of inert gases is considered 0 as they don't form compounds due to stable $e^{\ominus}$ config.

- APPLICATIONS –

1. Non Metallic Character $\propto$ EN

2. Bond Polarity $\propto$ ΔEN

3. Ionic character $\propto$ ΔEN

[$\Delta EN > 2.1 \Rightarrow$ % i.c. $> 50\% \Rightarrow$ ionic]

Hanny-Smith eqⁿ :- % ionic character $= 16(\Delta EN) + 3.5(\Delta EN)^2$

– Bond Nature acc. to 'Gallis' $\Rightarrow$ $\Delta EN > 1.7$ = ionic

$\Delta EN < 1.7$ = covalent

except : HF, LiCl, BeF_2, etc.

Q. Compare given properties :-

1. B, O, F, S, P, N (NMC) $B < P < S < N < O < F$

2. $HF > HCl > HBr > HI$ (Bond polarity)

3. $H_2O > H_2S > H_2Se > H_2Te$ (% i.c.)

4. $NH_3 \not\gtrless PH_3 \not\gtrless AsH_3$ (Bond polarity)
0·9 0 ≃ 0·2 or 0·3. (ΔEN)
~~$NH_3 > AsH_3 > PH_3$ Ans~~

5. $NaCl < MgS < AlP$ (covalent character)
0·9 3 1·2 2·5 1·5 ~~2·5~~ 2·1
2·1 1·3 0·6

6. % i.c. of HF ⇒ $\Delta EN = 1·9.$ ⇒ $16(1·9) + 3·5(3·89)$
≃ $16(2) + 3·5(4) = 32 + 14 = 46\%$

* ACIDIC – BASIC CHARACTER ⇒

- LEWIS ACID – LEWIS BASE –

→ All anions can act as Lewis Base. (lp donate)

→ H_2O, NH_3, PH_3, ROR, RNH_2, pyridene, etc. also act as Lewis Base.

→ All $e^\ominus$ deficient species can act as Lewis Acids.
e.g. BF_3, B_2H_6, $BeCl_2$, $AlCl_3$, $ZnCl_2$, $FeCl_3$, $SnCl_2$, etc.
To check this, $e^\ominus$ in outermost shell + no. of bonds < 8.

→ Mostly monoatomic cations act as Lewis Acids.
EXCEPT : Na^+, K^+, Rb^+, Cs^+. (largest cations in PT, charge ↓ and size ↑ ⇒ ⊕ density ↓ ⇒ attraction ↓)

→ Some complete octet species also act as Lewis Acids.
e.g. SiF_4, $SnCl_4$, SbF_5, $TeCl_5$, etc. (central atom is $+\delta$, vacant orbitals ✓)

$A \rightarrow B = \overset{+}{A} - \overset{-}{B}$

$H_2O \rightarrow H^+ = H_2\overset{+}{O} - \overset{-}{H}^+ = H_2\overset{+}{O} - H = H_3O^+$

→ species in which central atom is bonded with more E·N· atom by multiple bond can act as lewis acids.
e.g. CO_2, SO_2, HCN, etc.

- $\ddot{N}H_3$ (L.B.) + BF_3 (L.A.) ⟶ $[H_3N \rightarrow BF_3]$ ADDUCT (Production of addition rxn)

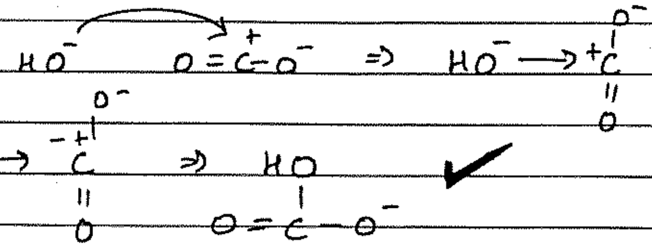
- H_2O (LB) + H^+ (LA) ⟶ $H_2O \rightarrow H^+$ (H_3O^+) PROTONATION (Always coordinate bond)

- $2F^-$ (LB) + SiF_4 (LA) ⟶ SiF_6^{2-}

- SF_6 + H_2O (LB) ⟶ No reaction (S is sterically protected fm. O's lp by 6 F atoms)

- HO^- (LB) + $O=\overset{\delta+}{C}=O$ (LA) ⟶ No reaction (No vacant orbital) X

Electromeric effect :



$HO^- \quad O=\overset{+}{C}-O^- \Rightarrow HO^- \rightarrow {}^{+}C(O^-)(=O) \Rightarrow HO^- \rightarrow C(O^-)(=O) \Rightarrow HO-C(=O)-O^-$ ✓

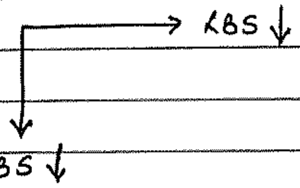
• LEWIS BASIC STRENGTH –

→ In a group : $LBS \propto \frac{1}{size}$

→ In a period : $LBS \propto \frac{1}{E.N.}$

→• For compounds of an element : $\angle BS \propto \frac{\ominus\ O.S.}{\oplus\ O.S.}$

→



- LBS or proton affinity $F^- > Cl^- > Br^- > I^-$ (size ↑)

- $CH_3^- > NH_2^- > OH^- > F^-$ (EN ↑)

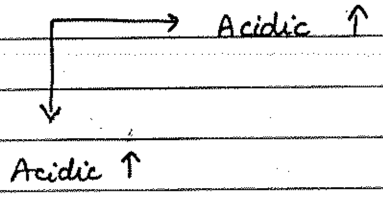
- $\overset{-3}{N}H_3$ $\overset{+3}{N}F_3$ $\overset{0}{N}Cl_3$ ⇒ $NH_3 > NCl_3 > NF_3$

• ACIDIC NATURE OF HYDRIDES OF GROUPS 15, 16, 17. —
NMH

→ In a group: Acidic Nature ∝ Size

→ In a period: Acidic Nature ∝ EN

→



- $HF < HCl < HBr < HI$ (Acid)

$\downarrow \quad \downarrow \quad \downarrow \quad \downarrow \quad -H^+$

$F^- < Cl^- < Br^- < I^-$ (C.B.) ~~stability~~ ~~(forward)~~
~~(size)~~

- $NH_3 < H_2O < HF$

$\downarrow \quad \downarrow \quad \downarrow$

$NH_2^- < OH^- < F^-$ (EN)

- ACIDIC / BASIC NATURE OF OXIDES, HYDROXIDES, OXYACIDS ∝ M HYDRIDE

MO, NMO, MOH, NM OH, MH

$\boxed{X-OH} \Rightarrow X = M ; NM.$

→ $CaO + H-OH \longrightarrow Ca(OH)_2$ Slaking of lime

$MO + H_2O \longrightarrow MOH$

(Basic)

→ $CO_2 + H_2O \longrightarrow H_2CO_3$

$NMO + H_2O \longrightarrow NMOH$

(Acidic)

→ $CaH_2 + 2\,H-OH \longrightarrow Ca(OH)_2 + 2\,H_2$ (MOP of H_2)

$MH + H_2O \longrightarrow MOH + H_2$

(Basic)

→ $\overset{\delta+}{X} - \overset{\delta-}{O} - \overset{\delta+}{H}$ all in aqeous medium ⇒ water = polar.

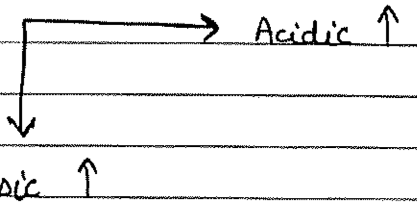
$\hookrightarrow XO^- + H^+ \Rightarrow$ ACIDIC $\Rightarrow \underset{(3.5-EN_x)}{\Delta EN\,(X-O)} < \underset{(1.4)}{\Delta EN\,(O-H)} \Rightarrow X = EN \uparrow$

$\hookrightarrow X^+ + OH^- \Rightarrow$ BASIC $\Rightarrow \underset{(3.5-EN_x)}{\Delta EN\,(X-O)} > \underset{(1.4)}{\Delta EN\,(O-H)} \Rightarrow X = EN \downarrow$

→ Acidic Nature ∝ EN ∝ ⊕ O.S.

→ Basic Nature $\propto \dfrac{1}{EN} \propto \dfrac{1}{\oplus\ O.S.}$

→



Q. Compare ~~acidic~~ nature -

a) $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$ (LBS)

b) $HO^- > HS^- > HSe^- > HTe^-$ (proton affinity)

c) $NH_3 > NH_2-NH_2 > NH_2-OH$ (LBS)

d) $H_2O < H_2S < H_2Se < H_2Te$ (Acidic)

e) $HOCl > HBrO > HOI$ (Acidic)

f) $LiH < NaH < KH < RbH < CsH$ (Basic)

g) $LiOH < Be(OH)_2 < H_3BO_3 < H_2CO_3$ (Acidic)

h) $SiO_2 < P_4O_{10} < SO_3 < Cl_2O_7$ (Acidic)

i) $N_2O_3 > P_2O_3 > As_2O_3 > Sb_2O_3 > Bi_2O_3$ (Acidic)

j) $TiO > VO > CrO > MnO > FeO$ (Basic)

k) $Pr(OH)_3 > Pm(OH)_3 > Eu(OH)_3 > Lu(OH)_3$ (Basic)

l) $Cs_2O > K_2O > ZnO > CO_2$ (Basic)

m) $HClO_4 > HBrO_4 > HIO_4$ (Acidic)

n) $HOCl < HClO_2 < HClO_3 < HClO_4$ (Acidic)

o) $MnO > MnO_2 > Mn_2O_7$ (Basic)

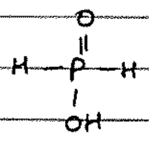
p) $H_2O < H_2O_2$ (Acidic)

q) $H_3PO_4 < H_2SO_4 < HClO_4$ (Acidic)

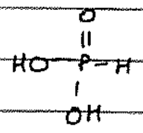
r) $FeO > Fe_2O_3$ (Basic)

s) $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$ (Basic)

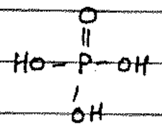
t) $H_3\overset{+1}{P}O_2 < H_3\overset{+3}{P}O_3 < H_3\overset{+5}{P}O_4$ (Acidic) WRONG (acc. to O.S)



$H-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-H$



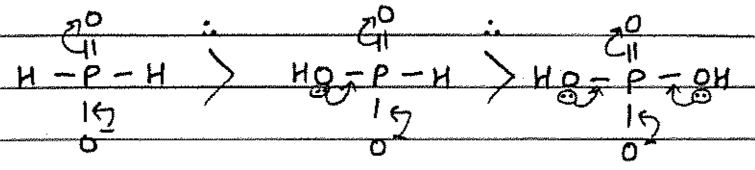
$HO-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-H$



$HO-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-OH$

(Acids)

$H_3PO_2 > H_3PO_3 > H_3PO_4$

- 

$$H-\overset{O}{\overset{\|}{P}}-H > HO-\overset{O}{\overset{\|}{P}}-H > HO-\overset{O}{\overset{\|}{P}}-OH$$

CROSS CONJUGATION

$\ominus$ density on P ↑ ⇒ stability ↓ ⇒ CB ↓ ⇒ Acidic Nature ↓

- ACIDIC / BASIC NATURE OF SALTS –

→ $MnCl_2 + 2\,H-OH \longrightarrow Mn(OH)_2 + 2\,H-Cl$

∴ (Acidic) (W.B) (S.A)

$Mn^{2+} + \cancel{2Cl^-} + 2H_2O \longrightarrow Mn(OH)_2 + 2H^+ + \cancel{2Cl^-}$

CATIONIC HYDROLYSIS ⇒ Acidic Salt ↳ sol^n = acidic.

→ $Na_2CO_3 + 2\,H_2O \longrightarrow 2\,NaOH + H_2CO_3$

∴ (Basic) SB WA

$2\cancel{Na^+} + CO_3^{2-} + 2H_2O \longrightarrow \cancel{2Na^+} + 2\,OH^- + H_2CO_3$

ANIONIC HYDROLYSIS → Basic salt

Q. Which of the following salts has max. pH in aq. sol^n?

a) $MgCl_2$ [✓ c)] $BaCl_2$
b) $AlCl_3$ d) NH_4Cl

- NATURE OF OXIDES –

→ ACIDIC OXIDES : Generally NMO, $\overset{+7}{Mn_2O_7}$, CrO_3

→ BASIC OXIDES : Generally MO,

→ NEUTRAL OXIDES : N_2O, NO, CO, OF_2, H_2O (acc pH)

→ **AMPHOTERIC OXIDES** : सुनो जनाबे आली वे

SnO, SnO_2 ZnO, BeO Al_2O_3 $\overset{+5}{V_2O_5}$ Mainly acidic

सब पंजाबी मन से

$\overset{+3}{Sb_2O_3}$ PbO, PbO_2 $\overset{+4}{MnO_2}$

गाते हैं ऐश करते हैं

Ga_2O_3 $\underset{+3}{As_2O_3}$ $\underset{+3}{Cr_2O_3}$

- Hydroxides of these oxides are always amphoteric in nature. e.g. $Zn(OH)_2$, $Be(OH)_2$, $Al(OH)_3$, $Pb(OH)_2$, $Cr(OH)_3$, etc.

- Bicarbonates also show amphoteric behaviour.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \underset{BASIC}{\rightleftharpoons} H^+ + \underset{AMPHOTERIC}{\boxed{HCO_3}} \overset{ACIDIC}{\rightleftharpoons} \underset{\text{Doesn't exist in free state}}{H^+} + CO_3^{2-}$$

- Species present in aq. sol^n of CO_2 = CO_2, H_2CO_3, HCO_3^-, CO_3^{2-},

- $NaOH$ and $NaHCO_3$ cannot exist together.

$$\underset{S.B.}{NaOH} + \underset{Amphoteric}{NaHCO_3} \longrightarrow \underset{Salt.}{Na_2CO_3} + H_2O$$

$$\underset{Amphoteric}{NaHCO_3} + \underset{S.A.}{HCl} \longrightarrow NaCl + H_2O + CO_2 (\leftarrow H_2CO_3)$$

$V_2O_5 + \overset{HCl}{\cancel{NaHCO_3}} \longrightarrow V(CO_3)_5 +$

Q. Product formed when $\overset{+5}{V_2O_5}$ reacts with acid & base respectively-

a) VO_2^+, $\overset{+7}{VO_4^-}$ ✗ b) ✓ VO_2^+, VO_4^{-3}

c) VO_4^{-3}, VO_2^+ d) ✗ $\overset{+3}{VO^+}$, VO_4^{-3}

Ans. $\overset{+5}{V_2O_5} + \text{acid} \longrightarrow \underset{\text{Cationic part}}{\overset{+5}{\underline{\text{salt}}}} + H_2O$

$\overset{+5}{V_2O_5} + \cancel{oo}\ \text{base} \longrightarrow \underset{\text{Anionic part}}{\overset{+5}{\underline{\text{salt}}}} + H_2O$

- ⊖ S.R.P. metals can displace $H_2(g)$ fm. dilute acids.

- ⊕ SRP metals like Cu, Hg, Ag, Au, Pt (CHAPA) can't displace $H_2(g)$ fm. dilute acids.

- $Zn + \text{dil}\cdot H_2SO_4 \longrightarrow ZnSO_4 + H_2$ (MOP of H_2)

- $Cu + \text{dil}\cdot H_2SO_4 \longrightarrow$ ✗

- Amphoteric metals like Be, Al, Zn, Sn, Pb can react with both acids and bases and form salt + H_2.

$$\begin{array}{ccccccc} & AlCl_3 & & Al & & \overset{+3}{NaAlO_2} \ \text{Sodium Meta Aluminate} & \\ & BeCl_2 & & Be & & Na_2BeO_2 & \\ \underset{(g)}{H_2} + & ZnCl_2 & \xleftarrow{\text{dil. HCl}} & Zn & \xrightarrow{\text{NaOH}} & Na_2ZnO_2 & + H_2(g) \\ & SnCl_2 & & Sn & & Na_2SnO_2 & \\ & PbCl_2 & & Pb & & Na_2PbO_2 & Na_2MO_2 \\ & \text{salts} & & \ominus\ \text{SRP} & & \text{salts} & \end{array}$$

* IA के सारे Hydroxide और $Ba(OH)_2$ को छोड़ पूरी PT के सारी Hydroxide water में <u>insoluble</u> हैं।

- salt + salt
  salt + acid
  salt + base

$\Rightarrow$ अडानबी rxn. = Double displacement

- $AlCl_3 + 3NaOH \xrightarrow[-3NaCl]{} Al(OH)_3\downarrow \xrightarrow{\overset{+}{Na}OH} Na^+[Al(OH)_4]^-$
  (salt) [excess] ampho; L.A. OR $\underline{NaAlO_2 \cdot 2H_2O}$
  Sodium aluminate

- Amphoteric metals NaOH के साथ react कर के जो Product बनाएगा, उसके Oxides, Hydroxides, Salts भी वो ही Products बनाएंगे !!

- $CrCl_3 + 3NaOH \xrightarrow[-3NaCl]{} Cr(OH)_3\downarrow \xrightarrow{Na^+OH^-} Na^+[Cr(OH)_4]^-$
  (salt) (excess)

- $Be(OH)_2 + 2\overset{+}{Na}\overset{-}{OH} \longrightarrow Na_2[Be(OH)_4]$ OR $Na_2BeO_2 \cdot 2H_2O$
  Ampho.(L.A) (excess)

- $ZnCl_2 + 2NaOH \xrightarrow[-2NaCl]{} Zn(OH)_2\downarrow \xrightarrow{Na^+OH^-} Na_2[Zn(OH)_4]$ OR
  salt (excess) $Na_2ZnO_2 \cdot 2H_2O$

- $Al_2O_3 + NaOH \longrightarrow NaAlO_2 \cdot 2H_2O$

- $BeO + NaOH \longrightarrow Na_2BeO_2 \cdot 2H_2O$

- $NH_4HCO_3 + NaCl \longrightarrow NaHCO_3 + NH_4Cl$
  MOP = SOLVAY PROCESS

- TEST OF CO_2 $Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O \xrightarrow{CO_2} Ca(HCO_3)_2$
  (base) (acidic) milky colorless
  slaked lime limestone

- **TEST OF SO_2** $Ca(OH)_2 + SO_2 \rightarrow \underset{\text{milky}}{CaSO_3 + H_2O} \xrightarrow{SO_2} \underset{\text{colorless}}{Ca(HSO_3)_2}$

- $CaCO_3 + 2HCl \rightarrow \underset{\text{less stable}}{H_2CO_3} + CaCl_2 \rightarrow CaCl_2 + H_2O + CO_2$

IIA carbonates are insoluble in water but soluble in dil. HCl.

- $CaSO_3 + 2HCl \rightarrow \underset{\text{less stable}}{H_2SO_3} + CaCl_2 \rightarrow CaCl_2 + H_2O + SO_2$

- CaF_2 + conc. $H_2SO_4 \rightarrow CaSO_4 + 2HF$ (MOP)

- $NaNO_3$ + conc. $H_2SO_4 \rightarrow NaHSO_4 + HNO_3$ (Lab method)

- $NaCl$ + conc. $H_2SO_4 \rightarrow NaHSO_4 + HCl$ (MOP)

- FeS + dil. $H_2SO_4 \rightarrow FeSO_4 + H_2S$ (MOP)

- $\underset{\text{(Lead Acetate)}}{(CH_3COO)_2Pb} + \underset{\text{(TEST)}}{H_2S} \rightarrow \underset{\text{(BLACK PPT.)}}{PbS} + 2CH_3COOH$

- $\underset{\text{(amphoteric)}}{Ca(HCO_3)_2} + \underset{\text{(base)}}{Ca(OH)_2} \rightarrow H_2O + 2CaCO_3\downarrow$ (CLARK METHOD TO REMOVE TEMP. HARDNESS)

- $Ca(OH)_2 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_4OH\ (2NH_3 + 2H_2O)$
  REPRODUCTION OF NH_3 in SOLVAY PROCESS

- Conc. $H_2SO_4 + \underset{\text{(L.B.)}}{2\ddot{N}H_3} \rightarrow 2NH_4^+ + SO_4^{2-} = (NH_4)_2SO_4$

- $FeCl_3 + 3NH_4OH \longrightarrow 3NH_4Cl + \underset{\text{(BROWN)}}{Fe(OH)_3\downarrow}$

- $ZnSO_4 + 2NH_4OH \longrightarrow Zn(OH)_2\downarrow + (NH_4)_2SO_4$

- $(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + \underset{\text{(MOP)}}{2NH_3} + 2H_2O$

- $\underset{\text{(salt)}}{MgCl_2} + Na_2CO_3 \longrightarrow 2NaCl + MgCO_3\downarrow$

  REMOVAL OF PERMANENT HARDNESS

- $CaSO_4 + \underset{\text{Sodium Zeolite}}{Na_2Z} \longrightarrow CaZ\downarrow + Na_2SO_4$

  PERMUTIT METHOD OF REMOVAL OF PERMANENT HARDNESS.

- $2NaOH + SiO_2 \longrightarrow$ ~~$Si(OH)_2\downarrow + Na_2O$~~ $Na_2SiO_2 + H_2O$

  ONLY GLASS SOLUBLE in H_2O = WATER GLASS

- $3NaI + H_3PO_4 \longrightarrow \underset{\text{(MOP)}}{3HI} + Na_3PO_4$

- $FeCl_3 + 3\overset{+}{K}SC\overset{-}{N} \longrightarrow \underset{\text{(RED)}}{Fe(SCN)_3} + 3KCl$ (Test of Fe^{+3})

- $\underset{\text{(BASIC)}}{Fe(OH)_3\downarrow} + \underset{\text{(AMPHO.)}}{Al(OH)_3\downarrow} \xrightarrow{NaOH} \underset{(NaAlO_2\cdot 2H_2O)}{NaAlO_2} + H_2O + Fe(OH)_3\downarrow$ (separation)

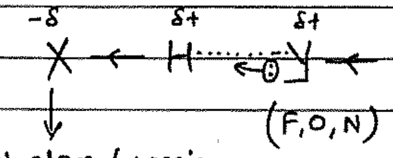
- $BeCl_2 + \underset{\text{(excess)}}{2NaOH} \longrightarrow Be(OH)_2 + 2NaCl$

  $\quad\longrightarrow Na_2[Be(OH)_4] = Na_2BeO_2\cdot 2H_2O$

CHEMICAL BONDING

* HYDROGEN BONDING :-

dipole-dipole attraction
\+ partial donation of lp.



high EN atom / specie
like F, O, N, $-CCl_3$, $-CF_3$, sp C.

- Bond Energy = 8-42 KJ/mol for neutral molecules

- CONDITIONS FOR STRONGER H-BONDING -

a) EN of X should be high
b) If X is same, then EN of Y should be less (so tendency of lp donation ↑ which is dominant over attraction in dipoles.)

- H-BOND STRENGTH ORDER ⇒

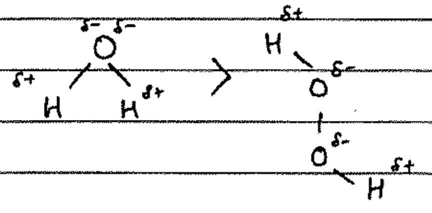
1. $HF > H_2O > NH_3$ (EN of X)

2. $O-H \cdots O > N-H \cdots N > N-H \cdots O$
(EN of X ↑) (EN of Y ↓)

3. $H_2O < D_2O$ (D is more ⊕ than H)

Vibrational Theory: Nucleus plane में Vibrate करता है, ऊपर-नीचे, तो उसका ⊕ charge disperse होता है, which affects H bonding. Mass of nucleus ↑ ⇒ Vibration ↓ ⇒ ⊕ ↑ ⇒ better H bonding : $D_2O > H_2O$
$[T_2O > D_2O > H_2O]$

4.



O पर −δ charge ज्यादा है।

Extent: $H_2O_2 > H_2O$

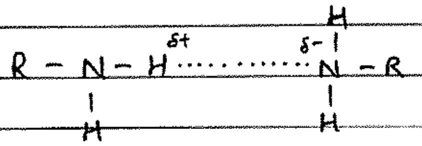
More O centres available for H-bonding potentially

5. CEPTION $\overset{\delta-}{F}-\overset{\delta+}{H}\cdots\cdots\overset{\delta-}{F}- \;>\; \overset{\delta-}{F}-\overset{\delta+}{H}\cdots\cdots\overset{\delta-}{O}-$

- Extent of H-bonding : $HF < H_2O < H_2O_2$

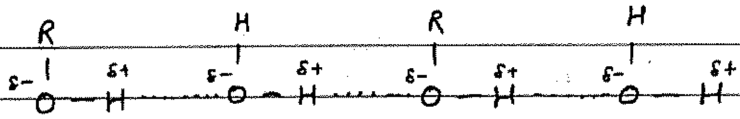
- TYPES OF H-BONDING :

a) Inter Molecular – B/w 2 molecules

– 1.


$R-NH(H)-\overset{\delta+}{H}\cdots\cdots\overset{\delta-}{N}H_2-R$

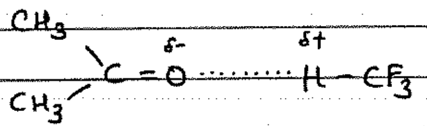
Homo intermolecular

2.


$\overset{\delta-}{O}(R)-\overset{\delta+}{H}\cdots\overset{\delta-}{O}(H)-\overset{\delta+}{H}\cdots\overset{\delta-}{O}(R)-\overset{\delta+}{H}\cdots\overset{\delta-}{O}(H)-\overset{\delta+}{H}$

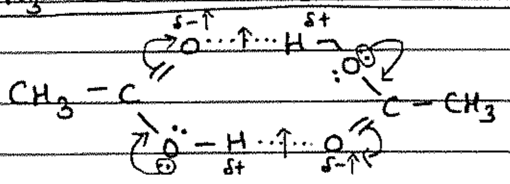
Hetero intermolecular

3. $H-C\equiv\overset{\delta-}{N}\cdots\cdots\overset{\delta+}{H}-\underset{\Delta p}{C}\equiv N$

4.


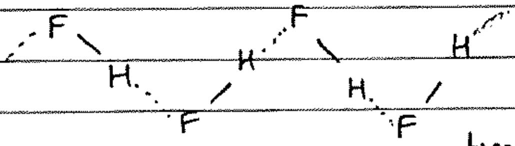
$(CH_3)_2C=\overset{\delta-}{O}\cdots\cdots\overset{\delta+}{H}-CF_3$

5. CH_3-COOH ⇒ exists as dimer in solid, liquid, gas always.



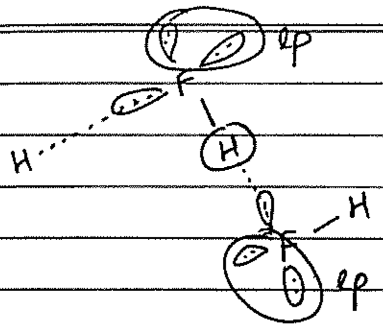
OBSERVED MOLECULAR MASS $= \underline{120}$ (2×60)

6. HF → Zig-Zag structure in solid / liquid state.

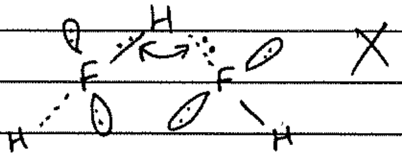


solid → longer chains

liquid → some H-bond break ⇒ short chains → mass ↓ ⇒ VWA ↓ ⇒ dist. ↑



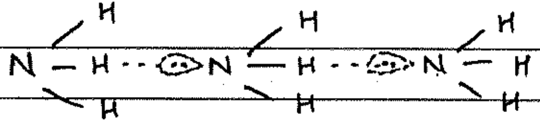
@ max. dist., so ↓↓ repulsion, so this structure. Also, tetrahedral.



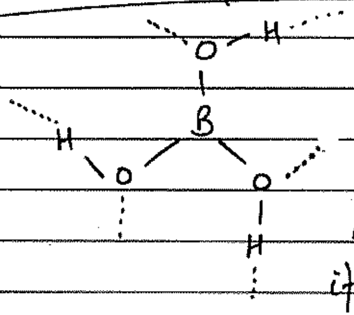
Too much repulsion.

7. NH$_3$ – linear H-bonding

Av. H bonds in N = 2.



8. H$_3$BO$_3$ – 2-D layer like structure; slippery.



→ 1 layer.

⇒ VWA b/w 2 layers ⇒ weak

slippery ⟸

All bonds are in same plane cuz if they would be zig zag locked in 3D, entropy ↓. If ΔS is more, ⊖, spontaneous ↑. So, 2-D.

9. NaOH is deliquescent in nature

$H-O^{\ominus}\overset{x}{\cdots}\overset{\delta+}{H}\overset{y}{-}\overset{\overset{H}{|}}{O} \Rightarrow [H_3O_2^-]$ attraction ↑↑

ion-dipole ≈ covalent bond (in strength)

SYMMETRIC H-BONDING

Bond lengths $x=y$

Resonance.

↳ ion dipole attraction + atoms on both side of H is same

10. $KF + HF \longrightarrow K^+[HF_2^-]$

$\overset{-}{F} \cdots\cdots \overset{\delta+}{H} - \overset{\delta-}{F} \Rightarrow [HF_2]^-$

ion dipole attraction + F and F same ⇒ symmetric H-bonding

11. $\overset{\delta+}{H} - \overset{\delta-}{Cl}$ Ⓧ $\overset{\delta+}{H} - \overset{\delta-}{Cl}$ ⇒ Cl is big ⇒ ⊖ density ↓ ⇒ attraction ↓ ; lp donation tendency ↓

12. $H-Cl + NH_3 \longrightarrow X$ (Acid-Base rxn)

13. $H-Cl + H-F \longrightarrow X$ H–F is stronger than ~~F–H–Cl~~, H bonding, so why would it lower its stability ?!

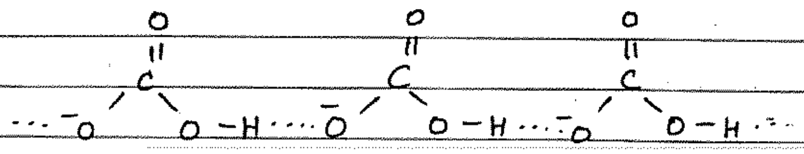
14. $H-Cl + H_2O \longrightarrow X$ (Dissociation)

15. $\overset{-}{Cl} \cdots\cdots \overset{\delta+}{H} - \overset{\delta-}{Cl} \Rightarrow HCl_2^-$

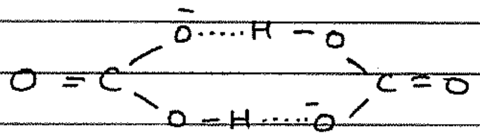
exists only with larger cations like Rb^+, Cs^+.

All cations are surrounded by anions. As big cation is, anions move farther away fm. each other ⇒ anionic repulsion ↓ ⇒ crystal formation and stability is promoted.

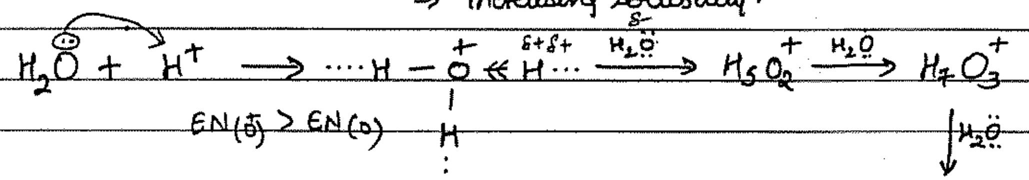
16. <u>$NaHCO_3$ (s)</u> – anions form polymer



17. **$KHCO_3$ (s) – anions form dimer.**



Size of K > size of Na ⇒ K ↑ ⇒ anions are farther away ⇒ dimer formation rather than polymer.
Possibility of anion–anion contact reduces with increase in cation size. $RbHCO_3$ and $CsHCO_3$ have decreasing H bonding ⇒ increasing solubility.

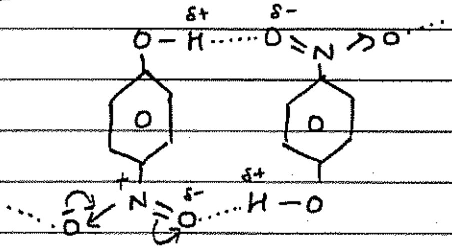
18. 

$$H_2\ddot{O} + H^+ \longrightarrow \cdots H-\overset{+}{O}\underset{\substack{|\\H\\\vdots}}{} \twoheadleftarrow \overset{\delta+\delta+}{H}\cdots \xrightarrow{H_2\overset{\delta-}{\ddot{O}}} H_5O_2^+ \xrightarrow{H_2\ddot{O}} H_7O_3^+ \xrightarrow{H_2\ddot{O}} H_9O_4^+$$

EN($\bar{O}$) > EN(O)

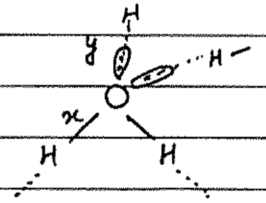
Only H_3O^+ formed by coordinate bond.
Rest species by H-bond.

19. **p-nitrophenol**

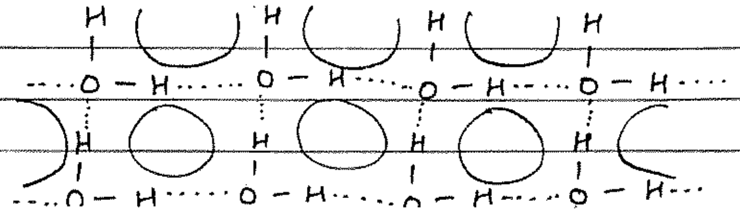


Ek baar में एक Molecule का H और एक O ही H bond बनाएंगा। H भी तो होने चाहिए।

20. **ICE**



sp^3 x < y (Bond length)



open cage like structure ⇒ V ↑↑ ⇒ $\rho_{ice} < \rho_{H_2O(l)}$

Q. Which of the following density orders is incorrect?

a) $H_2O(s) < H_2O(l)$ — Same baat है।

b) $Ga(s) < Ga(l)$ — Ga – Ga covalent bond is stronger. Ga_2 का ⇒ वाली Ga_2 में Metallic bond weak है ⇒

c) $Bi(s) < Bi(l)$ — B.L. ↑↑ ⇒ space ↑ ⇒ V↑ ⇒ $\rho_s < \rho_l$

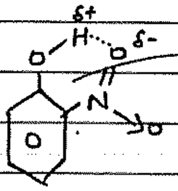
d) $D_2O(s) < D_2O(l)$

~~e)~~ $D_2O(s) < H_2O(l)$ $\rho = \frac{m}{V}$ ⇒ ~~dominated~~ $m_{D_2O} > m_{H_2O}$ ⇒ $\rho_{D_2O} > \rho_{H_2O}$

$V_{D_2O(s)} \ngtr V_{H_2O(l)}$

b) Intra Molecular – within a molecule.

1. O-nitrophenol

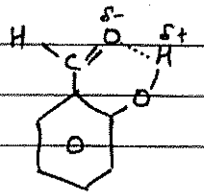


→ 6 Membered ring
⇓
Chelate ring
⇓
Chelation effect
⇓
Increases thermodynamic stability

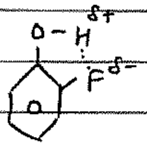
b/w 2 molecules of ONP,
VWA is there. ⇒ weak ⇒ entropy ↑
⇒ ΔS = +ve ⇒ ΔG = −ve = spontaneous
⇒ thermodynamic stability ↑
so intermolecular H bonding X
as it is stronger than VWA
and ΔS = ⊖ there.

m-nitrophenol] Inter molecular
p-nitrophenol

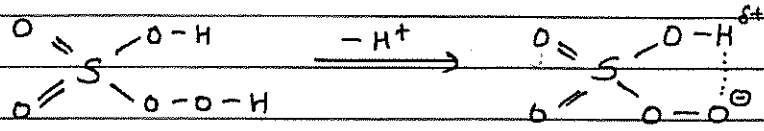
2. Salicylaldehyde



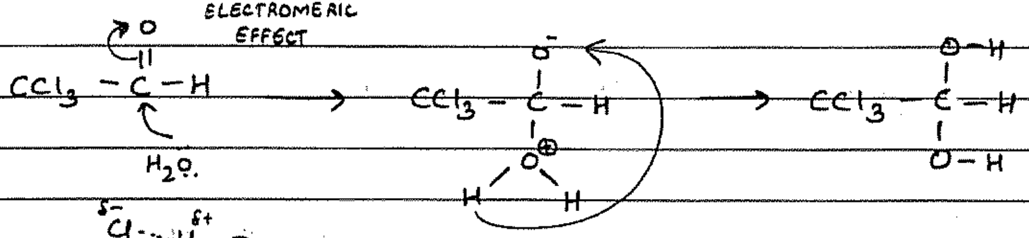
3. O-fluorophenol

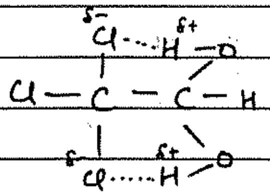


4. Anion of caro's acid (H_2SO_5)



5. Chloral Hydrate $CCl_3CH(OH)_2$ OR $CCl_3 \cdot CHO \cdot 2H_2O$
Chloral





Stable due to intramolecular H-bonding.

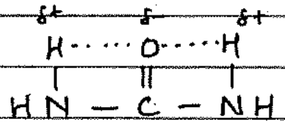
Why H – Cl ⊗ H – Cl and here ✓ ?

① intermolecular < intramolecular (strength)

② Cl = 3 < O = 3·5 ⇒ δ+ of H is more

③ b/w 2 molecules ⇒ KE ↑ ⇒ stability ↓ to form bond. as dist. is variable. ; b/w a molecule ⇒ dist. is not variable.

6 UREA

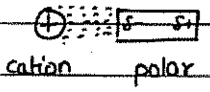


✗ ring formed is 4 membered. It is having ↑↑ angle strain. weaker H bonds can't tolerate that. C-C covalent bonds can do, so cyclopropane and cyclobutane exist.

→ Urea, oxyacids, proteins, DNA, CHOs, etc. have interMolecular H-bonding.

*• WEAK INTER MOLECULAR ATTRACTION FORCES ⇒

• ION - DIPOLE ATTRACTION -



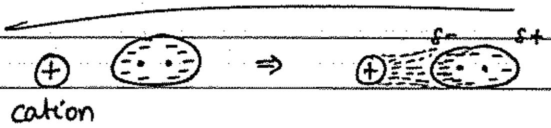
→ $\boxed{\text{interaction energy} \propto \frac{1}{r^2}}$

→ strength depends upon :

① charge density of ion (charge / size)
② polarity of polar molecule

- $Li^+ + H_2O$ — $Cl^- + HCl$
- $NO_3^- + CH_3OH$ — $KCl + H_2O$

• ION - induced DIPOLE ATTRACTION -



→ $\boxed{\text{interaction energy} \propto \frac{1}{r^4}}$

→ weaker, so more distance sensitive.

- $Cl^- + Cl_2$ — $K^+ + \phi$
- $Br^- + CCl_4$

• VW FORCES -

① dipole - dipole (Keesome) [polar + polar]

→ in solid state — interaction energy $\propto \frac{1}{d^3}$

anti parallel — head - tail

→ in liquid / gaseous state — interaction energy $\propto \frac{1}{d^6}$

- $H_2S + H_2S$ — $HCl + HCl$
- $CH_3-C\equiv N + CH_3-\underset{\underset{O}{\|}}{C}-CH_3$ — $CH_3-Cl + CH_3-Cl$

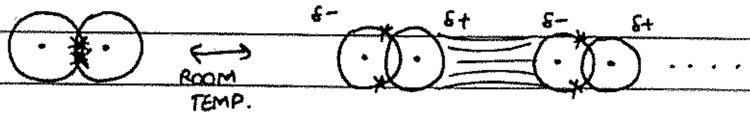
② dipole - induced dipole (Debye) [polar + non polar]

→ $\boxed{\text{interaction energy} \propto \frac{1}{d^6}}$

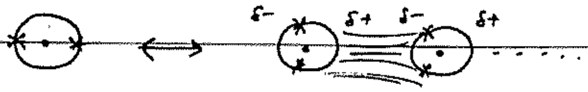
- $Xe + H_2O$ — $Cl_2 + H-Cl$
- $\phi + CH_3-OH$

③ instantaneous dipole - induced dipole (Dispersion force / London force)

→ H_2



→ He



VWF = H_2 > He (regardless of mass, acc. to no. of nucleus in structure ⇒ helps in charge making.)

→ • $\boxed{\text{interaction energy} \propto \frac{1}{d^6}}$

- Xe + Xe - $Br_2 + Br_2$
- $\phi + \phi$ - $CO_2 + CCl_4$

→ $\boxed{\text{VWF} \propto \text{mol. mass}}$ $\boxed{\text{VWF} \propto \text{surface area}}$

$D_2 > H_2$ Xe > He

→ If mass is almost same, $\boxed{\text{Keesom} > \text{Debye} > \text{London}}$

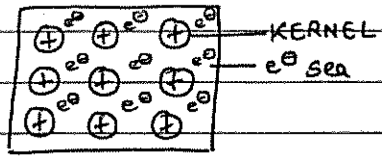
Q. Dispersion force is present b/w -

a) polar + polar c) non polar + non polar
b) polar + non polar ✓d) all

---

* METALLIC BOND →

- $e^{\ominus}$ sea model :



- pauling's theory : Based on resonance
  overlapping of an atomic orbital with >1 orbitals
- band theory : Based on MOT

- **METALLIC BOND STRENGTH :**

→ In a group : $\boxed{MBS \propto \frac{1}{size}}$

— Li > Na > K > Rb > Cs (Sublimation Energy / Heat of atomisation)

→ In a period : $\boxed{MBS \propto \text{no. of } e^{\ominus} \text{ participating in metallic bond.}}$

→ MBS of d-block metals generally increases down a group as $Z_{eff} \uparrow$.

— 3d < 4d < 5d (Heat of atomisation)

- $\boxed{SOFTNESS \propto \frac{1}{MBS}}$

→ Softest s block metal = Cs

→ Hardest s block metal = Be

- Metals are malleable and ductile.
- Metallic lustre is due to oscillation of surface mobile $e^{\ominus}$ by absorption of light energy
- Metals are good conductors of heat and electricity

CONDUCTIVITY ORDER ⇒ Ag > Cu > Au > Al

*• IONIC BOND :-

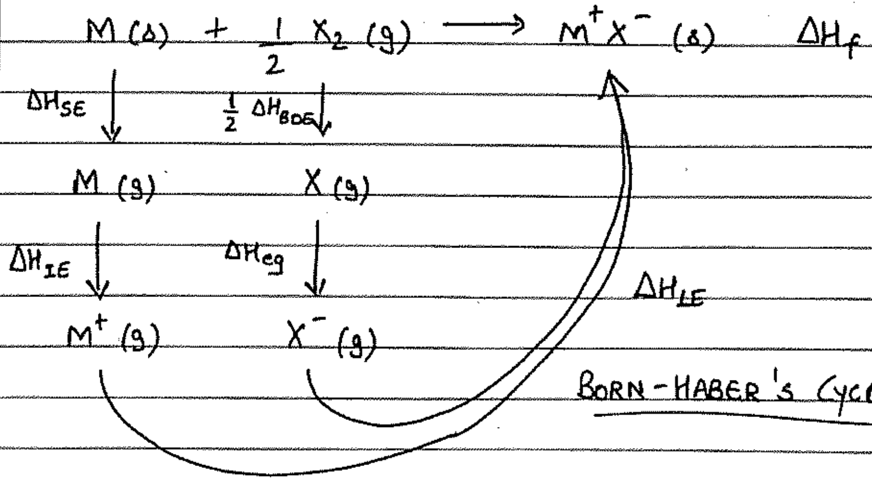
- Cation + Anion = ionic compound
  (Mostly s block metals) (NM)

- Li, Be, Mg forms some covalent compounds.

- Ionic compounds of Li, Be, Mg, Al :
  - LiF, Li_2O, Li Carbides, LiH
  - MgF_2, MgO, Mg_2C_3
  - AlF_3, Al_2O_3, Al_4C_3
  - Be_2C

- Metal salts having polyatomic anions are ionic in nature.

- FAVOURABLE CONDITIONS -



BORN-HABER's CYCLE

Hess's Law

- $\Delta H_f = \Delta H_{SE} + \Delta H_{IE} + \frac{1}{2}\Delta H_{BDE} + \Delta H_{eg} + \Delta H_{LE}$

→ $\underset{\ominus}{\underset{\Downarrow}{\Delta G}} = \underset{\ominus}{\underset{\Downarrow}{\underline{\Delta H}}} - \underset{\oplus}{\underset{\ominus}{\underset{\Downarrow}{T\Delta S}}}$ spontaneous ⇒ $\Delta G = \ominus$

final ⇒ less ; initial ⇒ more.

$$\underset{\Downarrow}{\Delta H_f} = \underset{\downarrow}{\Delta H_{SE}} + \underset{\downarrow}{\Delta H_{IE}} + \frac{1}{2}\underset{\downarrow}{\Delta H_{BDE}} + \underbrace{\overset{\uparrow}{\Delta H_{eg}} + \overset{\uparrow}{\Delta H_{LE}}}_{\text{released}}$$

a) Low SE of metal
b) Low IE of metal or larger cation
c) Low BDE of NM
d) High EA of NM or smaller anion
* e) High LE

→ ΔH_f for alkali metal halides −

− LiF > NaK > KF > RbF > CsF [ΔH_{LE} ; ⊖ value]

− MF > MCl > MBr > MI [ΔH_{LE} ; ⊖ value]

− LiX < NaX < KX < RbX < CsX [X = Cl / Br / I]

- **Lattice Energy** ⇒
Min. required energy to convert 1 mol ionic solid into its gaseous ions.

→ $Na^+Cl^-(s) \longrightarrow Na^+(g) + Cl^-(g)$ $\Delta H_{LE} = +778$ KJ/mol.

→ L.E. is calculated by Born Haber's Cycle

→ Stability of ionic crystals depend on L.E.

- FACTORS AFFECTING L.E. —

→ $\boxed{L.E. \propto Z_+ \cdot Z_-}$ (dominant)

→ $\boxed{L.E. \propto \frac{1}{r_+ + r_-}}$ (intermolecular dist. governs L.E.)

— $KF > KCl > KBr > KI$

— $NaF < MgO < ScN < TiC$

$LE = x \quad \simeq 4x \quad \simeq 9x \quad \simeq 16x$

— $Na_2S < MgCl_2$ $\quad Na^+ > Mg^{2+} \quad S^{2-} > Cl^-$

— $KBr < LiF < MgO$

— ~~$BeCO_3$~~ $BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$

$\xrightarrow{\quad}$ size ↑ ⇒ LE ↓

Q. Incorrect for ionic compounds is —

a) high MP, high BP
b) hard but brittle
c) insulator in solid state but conductor in molten/aq.
d) fast ionic rxn in aq. soln.
✓e) show stereoisomerism

Ans. (c) X, as they have non directional bonds

Q. Which of the following show conductivity –

✓a) AlF_3 (molten) b) $AlCl_3$ (l)
c) HCl (l) ✓d) H_2SO_4 (aq.)
✓e) Na (s) f) $NaNO_3$ (s) [CHILLI SALT PETRE]
✓g) KNO_3 (aq.) [INDIAN SALT PETRE] ✓h) $MgCl_2$ (aq.)
i) CH_3-OH (aq.) ✓j) $CuSO_4 \cdot 5H_2O$ (aq.) [BLUE VITRIOL]
✓k) Graphite (s) ✓l) $AlCl_3$ (aq.)

Ans (h) $MgCl_2$ ⇒ Mg — Cl bond polarity ↑ ⇒ polar solvent dissolves

$$MgCl_2\ (aq) \longrightarrow Mg^{2+}\ (aq) + 2Cl^{1-}\ (aq)$$

small size ⇒ hydration ↑ ⇒ H.E. ↑↑ ⇒ released ⇒ <u>stability</u> ↑

* $MgCl_2$ and $AlCl_3$ become ionic in aq soln. *

* **ISOMORPHISM** ⇒

If 2 ionic compounds have same crystalline structure then they are isomorphous.

- **CONDITIONS** –

1. Both ionic compounds should have same number of ions.
2. Both cations should be isoelectronic or have comparable size and both anions should be isolectronic or have same shape.
hybridisation

||OR||

If ionic compounds have crystalline water, then they should have same general formula

Q. Pair of compounds which are not isomorphous-

$10 e^{\ominus}$

a) $\overset{1}{Na}F$ and MgO No. of ions same.

$10 e^{\ominus}$

b) $\overset{+}{Na}\overset{-}{NO_3}$ and $\overset{+2}{Mg}\overset{-2}{CO_3}$ No. of ions same.

sp^2 ; $8 e^{\ominus}$ (O_3 common)

c) $\overset{+}{K}\overset{-}{MnO_4}$ and $\overset{2+}{Ba}\overset{2-}{SO_4}$ No. of ions same.

comparable size. (Ba < K) $sp^3 \rightarrow SO_4^{2-}$; $d^3s \rightarrow MnO_4^- \rightarrow$ Tetrahedral

d) $\overset{+1}{K}\overset{-1}{I_3}$ and $\overset{+1}{Tl}\overset{-1}{I_3}$ $(K^+) > Ca^{2+}$ ~~[illegible]~~ Ga^+ $\wedge$ In^+ $\overset{55}{Tl^+}$

comparable size

comparable size

✓ ~~e)~~ $\overset{+1}{Na_2}\overset{-2}{SO_3}$ and $\overset{2+}{Mg}\overset{2-}{CO_3}$ No. of ions diff.

Q. Which of the following is not isomorphous with others?

a)	White Vitriol	$ZnSO_4 \cdot 7H_2O$
b)	Epsum Salt	$MgSO_4 \cdot 7H_2O$
c)	Green Vitriol	$FeSO_4 \cdot 7H_2O$
✓ ~~d)~~	Washing Soda	$Na_2CO_3 \cdot 10H_2O$

- **ALUM** :- $M_2SO_4 \cdot M'_2(SO_4)_3 \cdot 24H_2O$

— $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ = POTASH ALUM

— $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$ = CROME ALUM

→ All alums are isomorphous.

→ aq. solⁿ. of alum is acidic in nature.

$K_2SO_4 \xrightarrow{H_2O} \underset{SB}{2KOH} + \underset{SA}{H_2SO_4}$ Neutral

$Al_2(SO_4)_3 \xrightarrow{H_2O} \underset{WB}{Al(OH)_3} + \underset{SA}{H_2SO_4}$ Acidic

→ Species present in aq. solⁿ / solid state of alum are :

$$2[M(H_2O)_6]^{+} + 2[M'(H_2O)_6]^{+3} + 4SO_4^{2-}$$

ion-dipole attraction ⇒ distance ↓ ⇒ M has vacant orbital, $\ddot{\underset{..}{O}}$)

$\Downarrow$

hydrated ion ⇐ 1° layer of incoming H_2O ⇐ coordinate bond

→ Li does not form alum as its max. covalency is 4

→ On heating, alum converts into amorphous solid (DEAD ALUM) due to removal of water molecules.

- PSEUDO ALUM – $\underset{\substack{\uparrow \\ \text{bivalent}}}{M}SO_4 \cdot M'_2(SO_4)_3 \cdot 24H_2O$

* HYDRATION ENERGY ⇒ Amount of energy released during hydration of 1 mol ionic solid.

- Crowding of H_2O (dipole) around ions is working alongside ion-dipole attraction (force) ⇒ energy released.

- Water = polar solvent ⇒ $\varepsilon_r = 81$.
  ϕ = non polar solvent ⇒ $\varepsilon_r = 0$

- Polarity of solvent ↑ ⇒ ε_r ↑ ⇒ solubility of ionic compd. ↑

Q. Solubility of KI is maximum in :-
ionic ⇐ main बात

✓ a) CH_3-OH $(\varepsilon_r = 34)$ c) CH_3-O-CH_3 $(\varepsilon_r = 4.1)$
b) C_2H_5OH $(\varepsilon_r = 27)$ d) $CH_3(CO)CH_3$ $(\varepsilon_r = 21)$

- Solvent = HF H_2SO_4 H_2O_2 H_2O D_2O

$$\varepsilon_r = \underbrace{120 \quad 102}_{\text{ACIDIC}} \quad \underbrace{\quad 98}_{\text{OXIDISING AGENT}} \quad \underbrace{81}_{\text{UNIVERSAL}} \quad 79$$

— D_2O has better intermolecular H bonding than H_2O.
Leaving tendency of molecules (each other) is less.
$\varepsilon_{r(D_2O)} < \varepsilon_{r(H_2O)}$

- $$Na^+Br^- \xrightarrow{H_2SO_4} Na^+ + Br^- \Rightarrow R.A.$$
$$\Big\downarrow \frac{H_2SO_4}{O.A.}$$
$$Br_2 + SO_2 + H_2O$$

- FACTORS AFFECTING H.E. ⇒

→ $\boxed{H.E. \propto Z_+ \cdot Z_-}$ (dominant)

→ $\boxed{H.E. \propto \frac{1}{r_+} + \frac{1}{r_-}}$

Q. Which of the following has highest H.E. ?

a) NH_4^+ b) Li^+ ✓ c) H^+ d) K^+

Q. Which of the following size order is not correct in aq. sol^n?

a) $F^- > Cl^- > Br^- > I^-$
b) $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$
c) $Na^+ < Mg^{2+} < Al^{3+}$
[✓ d)] $Li^+ > Be^{2+} > Mg^{2+}$

Q. Which of the following ions has max. mobility?

[✓ a)] $Rb^+ (aq.)$ b) $Li^+ (aq.)$ c) $Mg^{2+} (aq.)$ d) $Al^{3+} (aq.)$

- H.E. $H^+ > Li^+$ Mobility ⇒ $H^+ > Li^+$ (aq.)
H^+ travels through H_2O and H_3O^+, so its mobility is better

→ Conductivity $\propto$ mobility of ions $\propto \frac{1}{\text{hydrated size}}$

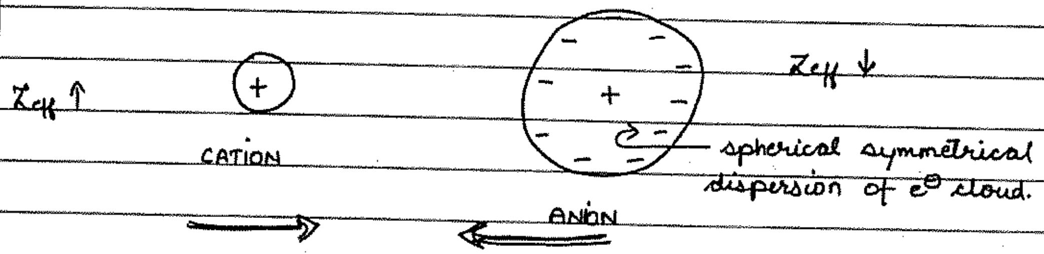
Q. Arrange following in conductivity order - a) NaCl, KCl, RbCl, CsCl.

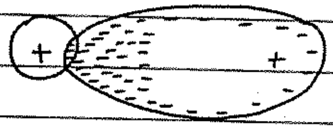
Ans solid state ⇒ NaCl = KCl = RbCl = CsCl (insulator)
molten ⇒ NaCl > KCl > RbCl > CsCl
aq. sol^n ⇒ NaCl < KCl < RbCl < CsCl

b) $BeCl_2$ $BaCl_2$ (molten) ⇒ $\underset{\text{ionic}}{\underline{BaCl_2}} > \underset{\text{covalent}}{\underline{BeCl_2}}$

✱ POLARISATION ⇒

No compound exists as 100% ionic, due to polarisation. Reason: High Z_{eff} of cation





- Polarisation ↑ ⇒ covalent character ↑ ⇒ ionic character ↓
- Polarising Power or ϕ = $\dfrac{\text{charge of cation}}{\text{size of cation}}$
  or IONIC POTENTIAL
- Polarisability of anion ∝ charge of anion
  " ∝ size of anion
- FAJAN'S RULE ⇒

→ $\boxed{\text{Polarisation} \propto Z_{+} \cdot Z_{-}}$

→ $\boxed{\text{Polarisation} \propto \dfrac{\text{size of anion}}{\text{size of cation}}}$

→ If cations have almost same size and same charge, then
POLARISING POWER ⇒ $\underbrace{8\,e^{\ominus}\text{ species} < (18+2)\,e^{\ominus}\text{ sp.} < 18\,e^{\ominus}\text{ sp.}}_{Z_{eff}\uparrow}$

d-block में top to bottom most properties बजाय size के Z_{eff} पर Depend करती हैं क्योंकि Size में Remarkable changes नहीं होते।

- 8 $e^{\ominus}$ species < 18 + 2 $e^{\ominus}$ species < 18 $e^{\ominus}$ species.

s-block	p-block	d-block (last 2 groups)
Na^+, K^+, Ca^{2+}	Pb^{2+}, Sn^{2+}	$Cu^+, Ag^+, Zn^{2+}, Cd^{2+}$

- $Sn = 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^2$

$$Sn^{2+} = \underbrace{4s^2\ 4p^6\ 4d^{10}}_{18} + \underbrace{5s^2}_{2}$$

$$Zn^{2+} = \underbrace{3s^2\ 3p^6\ 3d^{10}}_{18}$$

$$Zn^{2+} = 3s^2\ 3p^6\ \underbrace{3d^{10}}_{9\times0.35} \checkmark \qquad Sn^{2+} = 4s^2\ 4p^6\ \underbrace{4d^{10}}_{10\times0.85}\ 5s^2 \checkmark$$

$\Rightarrow$ σ of p > σ of d $\Rightarrow$ Z_{eff} of d > Z_{eff} of p.

Q. Compare –

a) $LiF < LiCl < LiBr < LiI$ covalent character

b) $BeCl_2 < MgCl_2 < CaCl_2 < SrCl_2 < BaCl_2$ ionic

c) $SF_2 < SF_4 < SF_6$ covalent character

d) $AlF_3 > Al_2O_3 > AlN$ ionic character

e) $KCl > AgCl$ ionic

f) $CaCl_2 > SnCl_2 > CdCl_2$ ionic

g) $ZnCl_2 < CdCl_2 < HgCl_2$ covalent [Z_{eff} of cation ↑ ($\longrightarrow$)]

Non metals का compound ($H_2O, H_2S, H_2Se, \dots HF, HCl, HBr$) ⇒ ΔEN
Metals का compound ⇒ Polarisation.

$\Delta EN = 2$ $\qquad$ $\Delta EN = 1.5$

h) $Al_2O_3 < AlCl_3$ covalent [ΔEN ↑ ⇒ ionic ↑]

charge on anion के Acc. ⇒ $Al_2O_3 > AlCl_3$] धोखा
size of anion के Acc. ⇒ $AlCl_3 > Al_2O_3$]

शायद है कि $AlCl_3$ covalent है — ①

ΔEN can be judging too in these cases. — ②

- **SOLUBILITY ⇒**

a) Solubility of M+NM compound –

→ During hydration, L.E. is given to break ionic bond and H.E. is released due to hydration.

→ $MX(s) \xrightarrow{H_2O} M^+(aq.) + X^-(aq.) \qquad \Delta S = \oplus$

$\Delta G = \Delta H \underbrace{- T\Delta S}_{\ominus}$

– LE < HE ⇒ $\Delta H = \ominus$ ⇒ $\Delta G = \ominus$ ⇒ soluble

– insoluble ⇒ $\Delta G = \oplus$ ⇒ $\Delta H = \oplus$ ↑↑ ⇒ L.E. >> H.E.

→ $\boxed{\text{Solubility} \propto \dfrac{HE}{LE}}$ Mainly for s-block compounds

– If common ion is smaller, like $F^-, O^{2-}, OH^-, Li^+, Na^+$, II A cation ⇒ LE dominant.

– If common ion is larger, like I^-, Br^-, Cs^+, Rb^+, polyatomic anions ⇒ HE dominant.

Size : $\text{II A cations} < \underbrace{K^+ < Cl^-}_{\text{isoelectronic}}$ ← large

- LiF NaF KF RbF CsF

⟶ size ↑ ⇒ L.E. ↓ ⇒ ~~solubility~~ solubility ↑

⟶ size ↑ ⇒ H.E ↓ ⇒ solubility ↓

⇒ F^- = smaller ⇒ LE dominant ⇒ solubility ↑

→ $\boxed{\text{Solubility} \propto \dfrac{1}{\text{Polarisation / Cov. char.}}}$

applicabe for Be halides, p and d block compounds, and L ⟶ R solubility.

Polarisation ↑ ⇒ individual charge on atoms (ions) ↓ ⇒ attraction by H_2O ↓ ⇒ solubility ↓.

→ $\boxed{\text{Solubility in organic solvent} \propto \text{polarisation / cov. char.}}$

- $LiF < NaF < KF < RbF < CsF$ (LE)* Solubility

- $BeCO_3 > MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$ Solubility HE*

- $BaF_2 < BaCl_2 < BaBr_2 < BI_2$ LE*

- $BeCl_2 > MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$ HE*

** → Common ion smaller ⇒ Solubility ↑ down a group.
Common ion larger ⇒ Solubility ↓ down a group.

- $BeSO_4$ ⟶>>>> $BaSO_4$

- Li_2O <<<<⟵ Cs_2O

- $LiClO_4$ ⟶ → → → $CsClO_4$

- $Be(OH)_2 < < < < Ba(OH)_2$
- $BeF_2 > BeCl_2 > BeBr_2 > BeI_2$ (Pol.)*
- $AgF > AgCl > AgBr > AgI$ —''—
- $PbF_2 > PbCl_2 > PbBr_2 > PbI_2$ —''—
- $HgF_2 > HgCl_2 > HgBr_2 > HgI_2$ —''—
- $\underbrace{\overset{+1}{Na_2}\overset{-2}{S} > \overset{+2}{Cu}\overset{-2}{S}} \; \underbrace{< \overset{+2}{Zn}\overset{-2}{S}}$

  Δ block pol. power ↑↓ ⇒ Pol. ↑↓ ⇒ sol. ↓   cation size ↑ ⇒ pol. ↓ ⇒ sol. ↑

  ⇒ $Na_2S > ZnS > CuS$

- $LiCl > NaCl$ acetone / pyridene / ϕ

  covalent ↑   ionic ↑

- $Ag_2O > Ag_2S$
- $NaF < NaBF_4$ Na^+ small ⇒ LE* ⇒ anion size ↑ ⇒ L.E. ↓
- $SnCl_2 > SnCl_4$ charge ↑ ⇒ ~~cation~~ pol. ↑ ⇒ sol. ↓
- $Fe(OH)_2 > Fe(OH)_3$ (p and d)
- $MgF_2 < MgCl_2 < MgBr_2 < MgI_2$ Mg^{2+} ⇒ small.
- $\underbrace{LiCl > NaCl > KCl}_{Cl^- \text{ larger}} < \underbrace{RbCl < CsCl}_{Cl^- \text{ smaller}}$

– $Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$

~~HE~~* LE* dependent on crystal structure properties.

– $NaHCO_3 < KHCO_3 < RbHCO_3 < CsHCO_3$

~~HE~~* ~~LE~~* H bonding ↑ ⇒ energy req. for solubility ↑ ⇒ solubility ↓.

– $MgF_2 < CaF_2 < SrF_2 < BaF_2 < BeF_2$

Highest HE

Explaination: ΔEN of Be – F ↑↑ ⇒ bond polarity ↑ ⇒ solubility ↑ in polar solvent (although BeF_2 is covalent)

b) Facts –

→ All alkali metal salts are H_2O soluble except LiF, Li_2CO_3, $Li_2C_2O_4$, Li_3PO_4.

→ All metals nitrates are H_2O soluble.

→ All metal sulphates are H_2O soluble except $CaSO_4$, $SrSO_4$, $BaSO_4$, $PbSO_4$.

→ s-block metal sulphides are H_2O soluble. Rest are insoluble.

→ II A carbonates are insoluble in water.

→ I A hydroxides and $Ba(OH)_2$ are H_2O soluble. Rest hydroxides are insoluble or sparingly soluble.

→ Generally metal halides are H_2O soluble except chloride, bromide, iodide of Ag, Hg, Pb.

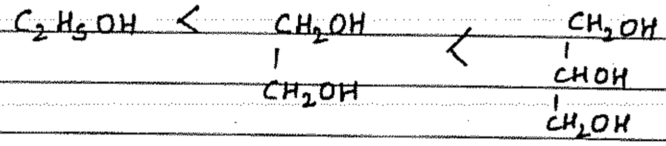
Q. Which of the following is least soluble in water-

a) Na_2CO_3 b) KNO_3
[✓ c)] $SrSO_4$ d) $BaCl_2$

c) Solubility of organic compounds -

→ Solubility of organic compounds in H_2O ↑ with ↑ing possibility of H-bonding with H_2O.

Q. Incorrect solubility order is -

a) $CH_3-OH > C_2H_5-OH > C_3H_7-OH$ (Hydrophobic ↑ ⇒ solubility ↓)
b) $CH_3-OH > CH_3-O-CH_3 > C_2H_5-O-C_2H_5$ (—"—; not +I)
c)

$C_2H_5OH < \begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array} < \begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$

[✓ d)] o-nitrophenol > p-nitrophenol

→ Solubility ⇒ intermolecular H-bond > intramolecular H-bond

- **MP and BP :-**

→ MP Diamond (s) > NaCl (s) > H_2O(s) > CO_2 (s)
Highest = 4000°C ionic H-bond VW

⇒ MP of M+NM compounds -

⇒ MP ∝ L.E. applicable for Na^+, K^+, Rb^+, Cs^+, or F^-, O^{2-}, H^-, N^{3-}, C^{4-}.

⇒ $MP \propto \dfrac{1}{\text{Polarisation / Covalent char.}}$ for others.

⇒ MP : ionic > covalent except giant molecules like diamond, silica, borazone $(BN)_x$, Carborundum (SiC), Norbide (B_4C).

⇒ Hardness : $\underset{\text{natural}}{\text{Diamond}} > \underset{\text{artificial}}{B_4C} > SiC > Al_2O_3$ (corrundum)

- $BeCl_2 < MgCl_2 < CaCl_2 < SrCl_2 < BaCl_2$
- $CaF_2 > CaCl_2 > CaBr_2 > CaI_2$
- $NaF < MgF_2 < AlF_3$
- $NaCl > MgCl_2 > AlCl_3$
- $\overset{+1}{Na_2O} < \overset{+2}{MgO} < \overset{+3}{Al_2O_3}$
- $\underset{s}{\overset{+}{NaCl}} \underset{\text{pol.}}{>} \underset{d}{\overset{+}{CuCl}} \underset{\text{charge pol.}}{>} \underset{d}{\overset{+2}{CuCl_2}}$
- $NaCl > KCl > RbCl > CsCl > \underset{\text{covalent}}{LiCl}$

CH_3-N_3 = Methyl Azide
N_3H = Hydrazoic Acid

- $MgF_2 > CaF_2 > SrF_2 > BaF_2 > \underline{BeF_2}$
  covalent

- Metal $\overset{-1}{\text{fluoride}}$ < Metal $\overset{-2}{\text{oxide}}$

- $\overset{+2}{Sn}Cl_2 > \overset{+4}{Sn}Cl_4$

- $AlF_3 > \underline{AlCl_3}$
  covalent

- $\overset{+}{Na}F < \overset{++}{Mg}O < \overset{+++}{Sc}N < \overset{++++}{Ti}C$ charge↑ LE↑

→ MP of NM compound =

⇒ With increasing intermolecular force, MP ↑
BP ↑
ST ↑
Viscosity ↑
Tc ↑

but Volatility ↓ ; VP ↓ .

- $CH_3-O-CH_3 < C_2H_5-OH$ BP
  (VWA) (H Bond)
  तेरा तेरे साथ

- $CH_3-N_3 < HN_3$ BP
  (VWF) (H-B)

- $\underbrace{H_2 < CO_2}_{\text{VWA}} < \underset{\text{(HB)}}{H_2O}$ Tc

HNMO ⇒ oxyacid ; H bonded to O

- $CH_3-OH < H_2O$ ST (Extent)

- $H_2O < D_2O$ BP

- $HCl < \underbrace{HNO_3 < H_3PO_4}_{EXTENT}$ MP
  VWF

- $C_2H_5-OH < \begin{array}{l}CH_2-OH\\ |\\ CH_2-OH\end{array} < \begin{array}{l}CH_2-OH\\ |\\ CH-OH\\ |\\ CH_2-OH\end{array}$ Viscosity

- $CH_4 < SiH_4 < GeH_4 < SnH_4$ BP

- $CO_2 < SiO_2$ MP (SiO_2 = 3D silicate)
  VWF Covalent giant

- $\overset{\delta+}{I}\overset{\delta-}{Cl} > Br_2$ BP
  Keesome London

- ONP > PNP Volatility
  VWF

- $\underbrace{HCl < HBr < HI}_{VWF;\ M_w} < \underset{H\ Bond}{HF}$ BP

- $\underbrace{H_2S < H_2Se < H_2Te}_{VWF;\ M_W} < \underset{HB}{H_2O}$ MP / BP

- $\underbrace{PH_3 < AsH_3 < SbH_3}_{VWF} < \underset{HB}{NH_3}$ MP

- $NH_3 < HF < H_2O$ Heat of Vaporisation / BP
  2 2 4

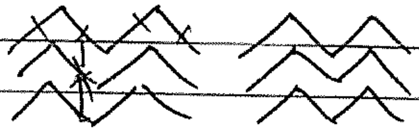
- $HF < NH_3 < H_2O$ Heat of fusion / MP

HF

~~v.v. less~~
Some H bond break
Chain breaks there

↓ MP

Mass of chain ↓
VWF ↓ ⇒ MP ↓
main ↳ fast conversion to liq.



But then in BP, max. no. of H bond needs to be broken, as in NH_3, now only VWA needs to be broken ⇒ BP HF > BP NH_3

** - $HCl < HBr < HF < HI$ MP

** - $PH_3 < AsH_3 < \underline{NH_3} < \underline{SbH_3}$ BP

weak H bond VWF dominates, as mass ↑↑.

Already H bond of NH_3 is weakest amongst all H bonds. Further, in liquid state, partial lp donation does not occur due to KE (movement). So, strength decreases further.

- $H_2 < D_2 < T_2$
- $He < Ne < Ar < Kr < Xe$
- $F_2 < Cl_2 < Br_2 < I_2$
- $N_2 < P_4 < As_4$
- $O_2 < S_8 < Se_8 < Te_8$

mass ↑
VWF ↑
BP ↑, MP ↑

- H_2 > He BP — London more effective (by chance creation of charge) in molecule.

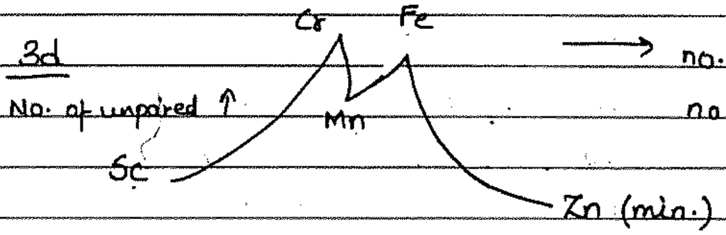
→ **MP of metals** — MP ∝ MBS

- Li > Na > K > Rb > Cs size ↑ MBS ↓.

- 3d < 4d < 5d Z_{eff} ↑ MBS ↑ (Heat of Atomisation)

- Zn > Cd > Hg Volatile metals.

no. of paired $e^{\ominus}$ ↑ ⇒ inter $e^{\ominus}$ repulsion b/w pairs ↑ ⇒ MBS ↓ ⇒ inter atomic/nuclear dist. ↑ ⇒ size ↑.
no unpaired $e^{\ominus}$ here, so this can't be related with others, as every where no. of unpaired $e^{\ominus}$ ↑, but NO.

- 

⟶ no. of unpaired ↓; no. of paired ↑

- Be > Ca > Sr > Ba > Mg (MP) बे कार सर बालन माँगो

inner d is vacant
↳ High participation of resonating $e^{\ominus}$ (delocalizing) there, which ↑ stability (Pauling Theory). Mg doesn't have vacant d, so it is less stable ⇒ less MP.
Be has size ↓↓ ⇒ MBS ↑↑.

⇒ Min. MP in all elements = He
Max. MP in all elements = C (diamond)
Max. MP in metals = W
Min. MP in metals = Hg

- Min. MP in B family = Ga (Ga_2)
  Max. MP in B family = B (B_{12} = icosahedral covalent)

- THERMAL STABILITY :- (A) polyatomic anion

⇒ $\boxed{T.S. \propto \frac{1}{\text{pol. power}} \propto \frac{\text{size}}{\text{charge}}}$

→ $H_2O(l) \xrightarrow{100^\circ C} H_2O(g) \underset{\substack{\uparrow \\ \text{THERMAL DECOMPOSITION} \\ \text{TEMP.}}}{\xrightarrow{2200^\circ C}} H_2(g) + \frac{1}{2}O_2(g)$

→ $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

$\overset{2+}{M}\cdots\cdots \overset{-}{O} \not- \overset{\overset{O}{\|}}{C} - O^- \xrightarrow{\Delta} \overset{2+}{M}{\equiv}O^{2-} + CO_2(g)$

→ Carbonates, sulphates, hydroxides of Na^+, K^+, Rb^+, Cs^+ do not decompose even @ high temperature, due to larger size of cation. (only melt)

→ $LiHCO_3$ and II A bicarbonates do not exist in solid state (exist as sol^n) due to high pol. power of cation (TS ↓).

→ $BeCO_3$ is kept in CO_2 atmosphere due to less T.S.
$BeCO_3 \rightleftharpoons BeO + CO_2$; to keep $BeCO_3$ stable.

(B) Halides, Hydrides, Normal Oxides

⇒ $\boxed{T.S. \propto \frac{1}{\text{size}}}$

- $BeCO_3 \;\leftarrow\!\leftarrow\!\leftrightarrow\; BaCO_3$
- $LiNO_3 \;\leftarrow\!\leftarrow\!\leftrightarrow\; CsNO_3$
- $Be(OH)_2 \;\leftarrow\!\leftarrow\!\leftrightarrow\; Ba(OH)_2$
- $CaO_2 < SrO_2 < BaO_2$

polyatomic anion size ↑
T.S. ↑

- $Na_2SO_4 > MgSO_4 > Al_2(SO_4)_3$ size ↓ ⇒ T.S. ↓
- $HF > HCl > HBr > HI$
- $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
- $CCl_4 > SiCl_4 > GeCl_4 > SnCl_4 > PbCl_4$
- $SO_2 > SeO_2 > TeO_2$.

size ↑
T.S. ↓

- $NaF < MgF_2 < AlF_3$ size ↓ ⇒ L.E. ↑ (for ionic)
- $\underset{0.9}{NH_3} < \underset{1.4}{H_2O} < \underset{1.9}{HF}$ $\overset{L \to R}{\underline{\Delta EN}}$ ↑ ⇒ charge ↑ ⇒ B.S. ↑ ⇒ T.S. ↑
  <u></u>$\underline{\text{size}}$ ↓ ⇒ T.S. ↑ (Top to bottom)

- **HEATING EFFECT :-**

→ Metal $CO_3 \xrightarrow{\Delta}$ Metal O + CO_2 $(MCO_3 \xrightarrow{\Delta} MO + CO_2)$

→ $MOH \xrightarrow{\Delta} MO + H_2O$

→ $MNO_3 \xrightarrow{\Delta} MO + \underset{\text{BROWN PARAMAGNETIC}}{\underline{NO_2}} + O_2$

- except: Na, K, Rb, Cs nitrates $\xrightarrow[\text{temp}]{\text{low}}$ $MNO_2 + \frac{1}{2}O_2$

  (T.S. ↑ ; Δ = v.v. high temp. N=O breaks)

  $$MNO_2 \xrightarrow{\Delta} M_2O + \underline{\underline{N_2}} + O_2$$

→ $MSO_4 \cdot xH_2O \xrightarrow{<200^\circ C} MSO_4 \cdot H_2O \xrightarrow[-H_2O]{>200^\circ C} MSO_4$

$$MSO_4 \xrightarrow{\Delta} MO + SO_2 + O_2$$

$MSO_4 \xrightarrow{\Delta\uparrow} MO + SO_3$

$SO_3 \xrightarrow{\Delta\uparrow} SO_2 + O_2$ (readily)

→ a) Ammonium salts having strong oxidising anions like MnO_4^-, $Cr_2O_7^{2-}$, NO_2^-, NO_3^- give N_2 or N_2O gas on decomposition

b) Ammonium salts having weak or non oxidising anions like SO_4^{2-}, PO_4^{3-}, CO_3^{2-}, X^-, give NH_3 gas on decomposition

→ High O.S. Chloride $\xrightarrow{\Delta}$ Low O.S. Chloride + Cl_2 (g)

→ a) Hydrated ionic chlorides $\xrightarrow{\Delta}$ Anhydrous ionic chloride + H_2O ↑

b) Hydrated covalent chlorides $\xrightarrow{\Delta}$ MO

→ Metal salts having strong oxidising anions like MnO_4^-, $Cr_2O_7^{2-}$, NO_3^-, ClO_3^-, etc give O_2 (g)

→ ~~Met.~~ $MHCO_3 \underset{\text{low temp.}}{\overset{\Delta}{\rightleftharpoons}} MCO_3 + CO_2 + H_2O$

→ Some less stable MO like Ag_2O, HgO further decompose into $M + O_2$

– $PbCO_3 \xrightarrow{\Delta} PbO + CO_2$
CERRUCITE

– $ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$
CALAMINE

– $FeCO_3 \xrightarrow{\Delta} FeO + CO_2$
SIDERITE

– $MgCO_3 \cdot CaCO_3 \xrightarrow{\Delta} MgO + CaO + 2CO_2$
DOLOMITE

– $CuCO_3 \cdot Cu(OH)_2 \xrightarrow{\Delta} CuO + CO_2 + CuO + H_2O$
MELACHITE GREEN
BASIC CUPRIC CARBONATE

– $Na_2CO_3 \cdot 10H_2O \xrightarrow[-9H_2O]{\text{ROOM}} Na_2CO_3 \cdot H_2O \xrightarrow{\Delta} Na_2CO_3$ No decomp.
WASHING SODA "efflorescence" NATRON SODA ASH Only wt. loss.
K_2CO_3 = PEARL ASH

– $Pb(NO_3)_2 \xrightarrow{\Delta} PbO + NO_2 + \frac{1}{2}O_2$

– $Zn(NO_3)_2 \xrightarrow{\Delta} ZnO + NO_2 + \frac{1}{2}O_2$

– $Ca(NO_3)_2 \xrightarrow{\Delta} CaO + NO_2 + \frac{1}{2}O_2$

– $LiNO_3 \xrightarrow{\Delta} Li_2O + NO_2 + \frac{1}{2}O_2$

- $NaNO_3 \xrightarrow{400^\circ C} NaNO_2 + \frac{1}{2}O_2$

$$\begin{tikzcd} NaNO_2 \arrow[d, "800^\circ C"'] \\ Na_2O + N_2 + O_2 \end{tikzcd}$$

- $AgNO_3 \xrightarrow{\Delta} Ag_2O + NO_2 + \frac{1}{2}O_2$

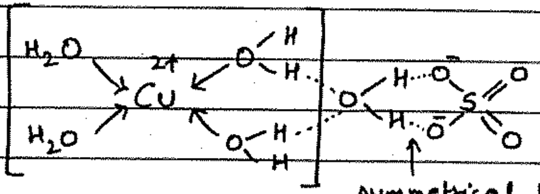
LUNAR CAUSTIC

$$\begin{tikzcd} Ag_2O \arrow[d, "\Delta = 300^\circ C"] \\ 2Ag + \frac{1}{2}O_2 \end{tikzcd}$$

- $CuSO_4 \cdot 5H_2O \xrightarrow{<200^\circ C} CuSO_4 \cdot H_2O \xrightarrow{>200^\circ C} CuSO_4$

BLUE VITRIOL

$$\begin{tikzcd} CuSO_4 \arrow[d, ">800^\circ C"] \\ CuO + SO_2 + \frac{1}{2}O_2 \end{tikzcd}$$



symmetrical H-bond; near to covalent (strength)

- $ZnSO_4 \cdot 7H_2O \xrightarrow{<200^\circ C} ZnSO_4 \cdot H_2O \xrightarrow{>200^\circ C} ZnSO_4$

WHITE VITRIOL

$$\begin{tikzcd} ZnSO_4 \arrow[d, "\Delta"] \\ ZnO + SO_2 + \frac{1}{2}O_2 \end{tikzcd}$$

Same for $MgSO_4 \cdot 7H_2O$

- $FeSO_4 \cdot 7H_2O \xrightarrow{<200^\circ C} FeSO_4 \cdot H_2O \xrightarrow{>200^\circ C} FeSO_4$

GREEN VITRIOL

$$\begin{tikzcd} FeSO_4 \arrow[d, "750^\circ C"] \\ Fe_2O_3 + SO_2 + SO_3 \end{tikzcd}$$

<u>Stability</u> $\underset{d^5}{Fe^{3+}} > \underset{d^6}{Fe^{2+}}$

$$\begin{tikzcd} 2FeSO_4 \arrow[r, "\Delta"] & 2\overset{+2}{Fe}O \arrow[d, "{[O]}"] & + & \overset{+6}{S}O_3 \arrow[d] \arrow[ll, bend left] & + & SO_3 \arrow[d] \\ & Fe_2O_3 & + & \overset{+4}{S}O_2 & + & SO_3 \end{tikzcd}$$

* $NH_3 \longrightarrow$ ~~SBH3~~ SbH_3 ⇒ size ↑ , TS ↓ ⇒ Hydrogen losing tendency ↑
⇒ oxidation tendency ↑ ⇒ R.A. better.
⇒ NH_3 = weak RA.
SbH_3 = strong RA

$$\overset{+3}{Fe_2}(SO_4)_3 \xrightarrow{<750^\circ C} Fe_2O_3 + SO_3$$

SO_4^{2-} = polyatomic anion
charge +3 > +2
pol. power $Fe^{3+} > Fe^{2+}$
T.S. $Fe^{3+} < Fe^{2+}$
Temp $Fe^{3+} < Fe^{2+}$

— $$\underset{\text{GLAUBER'S SALT}}{Na_2SO_4 \cdot 10H_2O} \xrightarrow{\Delta} Na_2SO_4 \cdot H_2O \xrightarrow{\Delta} \underset{\text{(only wt. loss)}}{Na_2SO_4} \xrightarrow{\Delta} X$$

— $$\underset{\text{GYPSUM}}{2(CaSO_4 \cdot 2H_2O)} \xrightarrow[-3H_2O]{120^\circ C} (CaSO_4)_2 \cdot H_2O \xrightarrow{>200^\circ C} \underset{\text{DEAD PLASTER}}{CaSO_4}$$

or $CaSO_4 \cdot \frac{1}{2}H_2O$
(POP)

$$CaSO_4 \xrightarrow{\Delta \uparrow} CaO + SO_2 + O_2$$

(QUICK LIME)

— $$\underset{\text{(POP)}}{CaSO_4 \cdot \frac{1}{2}H_2O} \xrightarrow[\text{(PASTE)}]{3/2\ H_2O} \underset{\text{GYPSUM}}{CaSO_4 \cdot 2H_2O}$$

↳ (HARD MASS) = SETTING OF POP

Acceleration → put NaCl (Catalysts)
Retardation → Borax or Alum

— $$\underset{RA.}{(\overset{-3}{N}H_4)_2}\ \underset{O.A.}{\overset{+6}{Cr_2}O_7} \xrightarrow{\Delta} \underbrace{\overset{+3}{Cr_2}O_3}_{\text{GREEN RESIDUE}} + \overset{0}{N_2} + 4H_2O$$

— $$\underset{RA.}{\overset{-3}{N}H_4}\ \underset{O.A.}{\overset{+3}{N}O_2} \xrightarrow{\Delta} \overset{0}{N_2} + 2H_2O$$

— $$\overset{-3}{N}H_4\ \overset{+5}{N}O_3 \xrightarrow{\Delta} N_2O + 2H_2O$$

LAUGHING GAS ; DENTISTS USE AS ANAESTHETIC

— $$(\overset{-3}{N}H_4)_2CO_3 \xrightarrow{\Delta} 2NH_3 + CO_2 + H_2O$$

— $$NH_4Cl \xrightarrow{\Delta} NH_3 + HCl$$

* Hg^+ exists as dimer Hg_2^{2+} $[Hg^{+}\cdot * \cdots * Hg^{+}]$ = Diamagnetic.

* PbO = Litharge ZnO = Philosopher's wool

PbS = Galena ZnS = Black Jack

- $Ba(N_3)_2$ OR $NaN_3 \xrightarrow{\Delta} Ba$ OR $Na + \underline{N_2}$

  (N_3^- = AZIDE) PUREST MOP

- $\overset{+4}{Pb}Cl_4 \xrightarrow{\Delta} \overset{+2}{Pb}Cl_2 + Cl_2$

- $FeCl_3 \xrightarrow{\Delta} FeCl_2 + \frac{1}{2}Cl_2$

- $2HgCl_2 \xrightarrow{\Delta} Hg_2Cl_2 + Cl_2$

  CORROSIVE SUBLIMATE CALOMEL

- $AuCl_3 \xrightarrow{\Delta} AuCl + Cl_2$

- $PCl_5 \xrightarrow{\Delta} PCl_3 + Cl_2$

- $MgCl_2 \cdot 6H_2O \xrightarrow{\Delta} MgO + H_2O\uparrow + HCl$ (Hydrolysis)

$$Mg\begin{matrix} Cl \\ Cl \end{matrix} + H-OH \xrightarrow[-HCl]{} Mg\begin{matrix} OH \\ Cl \end{matrix} \xrightarrow[-HCl]{H-OH} Mg\begin{matrix} OH \\ OH \end{matrix} \xrightarrow{\Delta} MgO + H_2O$$

- $AlCl_3 \cdot 6H_2O \xrightarrow{\Delta} Al_2O_3 + HCl + H_2O$

- $CaCl_2 \cdot 6H_2O \longrightarrow CaCl_2 + 6H_2O\uparrow$ (ionic)

- $BaCl_2 \cdot 2H_2O \xrightarrow{\Delta} BaCl_2 + 2H_2O\uparrow$ (ionic)

- $FeCl_3 \cdot 6H_2O \xrightarrow{\Delta} Fe_2O_3 + HCl + H_2O$

  [covalent]

- $K\overset{+7}{Mn}\overset{-2}{O_4} \xrightarrow{\Delta} K_2\overset{+6}{Mn}O_4 + \overset{+4}{Mn}O_2 + \overset{0}{O_2}$ MOP of O_2

- $K_2\overset{+6}{Cr_2}O_7 \xrightarrow{\Delta} K_2\overset{+6}{Cr}O_4 + \overset{+3}{Cr_2}O_3 + \overset{0}{O_2}$ MOP of O_2

$$\text{Acid} + \text{Base} \longrightarrow \underset{\substack{\text{Cation} \quad \text{Anion}\\ \text{fm. Base} \quad \text{fm. Acid}}}{\underline{\text{Salt}}} + H_2O$$

$2\,K\overset{+5}{Cl}O_3 \xrightarrow{\Delta} 2\,K\overset{-1}{Cl} + 3\,O_2$ — MOP of O_2

$\underset{+4}{PbO_2}$ OR $\underbrace{Pb_3O_4}_{2PbO+\underset{+4}{PbO_2}}$ OR $\underbrace{Pb_2O_3}_{PbO+\underset{+4}{PbO_2}} \xrightarrow{\Delta} PbO + O_2$ — MOP of O_2

- $2\,NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$
- $CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$

→ SOLVAY AMMONIA SODA PROCESS / Preparation of $NaHCO_3$ or Na_2CO_3

- $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$
- $NH_3 + H_2O + CO_2 \longrightarrow (NH_4)_2CO_3$
- $(NH_4)_2CO_3 + H_2O + CO_2 \longrightarrow 2\,NH_4HCO_3$
- $2\,\overset{+}{NH_4}\overset{-}{HCO_3} + 2NaCl \longrightarrow 2\,NaHCO_3 + 2\,NH_4Cl$
- $2\,NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$
- There is no ammonia consumption in Solvay's process

$\underset{\hookrightarrow (aq.)}{CaO} + 2\,NH_4Cl \longrightarrow CaCl_2 + 2\,NH_3 + H_2O$

- Solvay's process is not used for preparation of K_2CO_3, as ~~highly~~ $K_2CO_3 \dashrightarrow KHCO_3$ ⇒ highly soluble

↳ 3 pages

Q. Anhydrous $MgCl_2$ can be obtained by -

covalent

a) $MgCl_2 \cdot 6H_2O \xrightarrow{\Delta} MgO + HCl$

b) ✓ $MgCl_2 \cdot 6H_2O \xrightarrow[\text{HCl gas}]{\Delta} MgCl_2\ (\text{anhydrous}) + HCl\uparrow + H_2O\uparrow$

↳ backward ↑

c) $Mg + \text{dil} \cdot 2HCl \longrightarrow MgCl_2 + H_2$

↳ hydrated (dil.)

d) ✓ $\overset{+2}{Mg}\overset{-2}{O} + \underset{R.A.}{C} + Cl_2 \xrightarrow{\Delta} MgCl_2\ (\text{anhydrous}) + CO\uparrow$

REDUCTIVE CHLORINATION ~~Carbon ⊖ SRP metal oxide~~ की oxygen ~~chlorine~~ की ~~मदद से हटाता~~ है

- $BeO + C + Cl_2 \xrightarrow{\Delta} BeCl_2 + CO\uparrow$

- $Al_2O_3 + 3C + 3Cl_2 \xrightarrow{\Delta} AlCl_3 + 3CO\uparrow$

- $B_2O_3 + 3C + 3Cl_2 \xrightarrow{\Delta} 2BCl_3 + 3CO\uparrow$

doesn't dimerise

Q. Which of the following contain 2 s-block metals -

a) Super Phosphate	$CaSO_4 + Ca(H_2PO_2)_2$
b) Microcosmic Salt	~~$NaNH_4(HPO_4)$~~ $Na(NH_4)HPO_4$
c) Lithophone	$ZnS + BaSO_4$
d) ✓ Fusion Mixture	$Na_2CO_3 + K_2CO_3$

→ MP of mixture of 2 salts is less than MP of individual salts due to interionic attraction b/w ions of those salts

→ Soda lime = $(NaOH + CaO)$

→ Aq. sol^n of $Ca(OH)_2$ = Lime water

Date
Page

→ Suspension of $Ca(OH)_2$ = Milk of Lime

→ Suspension of $Mg(OH)_2$ = Milk of magnesia ; antacid

\- $CaO + H_2O \longrightarrow \underset{\text{SLAKED LIME}}{Ca(OH)_2}$ Slaking of Lime

* COVALENT BOND :-

- A chemical bond is formed to decrease P.E., or to gain stability.

- OCTET RULE :- KOSSEL LEWIS CONCEPT
Each atom tries to complete 8 $e^{\ominus}$ in its outermost shell, by loss or gain of $e^{\ominus}$, or by sharing of $e^{\ominus}$.

→ EXCEPTIONS -

① $e^{\ominus}$ deficient species / hypovalent compounds (These are Lewis A.)

BeH_2, $BeCl_2$ (g), $AlCl_3$ (g), B_2H_6, $ZnCl_2$, BF_3, etc.

② super octet / hypervalent compounds

PCl_5, SF_6, IF_7, XeF_2, SF_4, etc.

③ all ~~deficient~~ odd $e^{\ominus}$ species are exceptions of Octet Rule

NO, NO_2, $\dot{C}H_3$, ClO_2, ClO_3, OF, etc.

④ All odd $e^{\ominus}$ species are paramagnetic.

Q. which of the following is not an exception of octet rule

a) CH_4 b) SO_4^{2-} [✓ c) AlF_3] d) B_2H_6
(ionic)

$$AlF_3 = \underset{(2,8)}{Al^{3+}} + \underset{(2,8)}{3F^-}$$

Q. which of the following is an exception of octet rule but not $e^{\ominus}$ deficient

✓ a) $LiAlH_4$ = $\overset{+}{\underset{②}{Li}}[\underset{8}{AlH_4}]^-$

b) $NaBH_4$ = $\overset{+}{\underset{8}{Na}}[\underset{8}{BH_4}]^-$

c) SiH_4 = 8

d) $AlCl_3$ (g) = $\underset{6}{Al}^{+} \cdot Cl_3$

- VALENCY ⇒

→ ELECTROVALENCY = Charge of ions

→ COVALENCY = No. of ~~coordinate~~ covalent bond + coordinate bonds

→ Valency increases fm. IA to VII A wrt O

→ Valency increases fm. IA to IV A and then decreases wrt H.

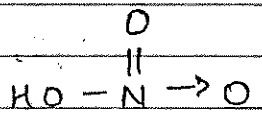
→ No. of covalent bonds = No. of unpaired $e^{\ominus}$ in G.S. or in E.S.

→ Max. covalency of II ~~A~~ period elements is 4.

→ III period elements can extend their covalency (> 4) due to presence of vacant d orbitals

→ Covalency increases by 2 with each excitation for s and p block elements

→ Covalency increases by 1 for d-block elements ($FeCl_2$, $FeCl_3$).

→ 

$HO-\overset{\overset{O}{\|}}{N}\rightarrow O$ Covalency of N = 4   (Max.)

Max. O.S. of N = +5

→ CH_2Cl_2 C covalency = 4   C O.S. = 0.

→ $C = \underset{2s}{\boxed{\uparrow\downarrow}}\ \ \underset{2p}{\begin{array}{|c|c|c|}\hline \uparrow & \uparrow & \; \\ \hline\end{array}}$ G.S. ⇒ 2 $:C\overset{\leftarrow}{\equiv}O:$; $H-N\overset{\rightarrow}{\equiv}C$

$C^* = \boxed{\uparrow}\ \ \begin{array}{|c|c|c|}\hline \uparrow & \uparrow & \uparrow \\ \hline\end{array}$ E.S. ⇒ 4 CCl_4

→ $B = \boxed{\uparrow\downarrow}\ \ \begin{array}{|c|c|c|}\hline \uparrow & \; & \; \\ \hline\end{array}$ G.S. ⇒ 1   ✗

$B^* = \boxed{\uparrow}\ \ \begin{array}{|c|c|c|}\hline \uparrow & \uparrow & \; \\ \hline\end{array}$ E.S. ⇒ 3 BCl_3

→ $N = \boxed{\uparrow\downarrow}\ \ \begin{array}{|c|c|c|}\hline \uparrow & \uparrow & \uparrow \\ \hline\end{array}$ G.S. ⇒ 3 NCl_3 NCl_5 ✗ NO E.S.

→ $O = \boxed{\uparrow\downarrow}\ \ \begin{array}{|c|c|c|}\hline \uparrow\downarrow & \uparrow & \uparrow \\ \hline\end{array}$ G.S. ⇒ 2 OF_2 OF_4, OF_6 ✗ NO E.S.

→ $P = \boxed{\uparrow\downarrow}\ \ \begin{array}{|c|c|c|}\hline \uparrow & \uparrow & \uparrow \\ \hline\end{array}\ \ \begin{array}{|c|c|c|c|c|}\hline \; & \; & \; & \; & \; \\ \hline\end{array}$ G.S. ⇒ 3 PCl_3 (PCl_4 ✗)

$P^* = \boxed{\uparrow}\ \ \begin{array}{|c|c|c|}\hline \uparrow & \uparrow & \uparrow \\ \hline\end{array}\ \ \begin{array}{|c|c|c|c|c|}\hline \uparrow & \; & \; & \; & \; \\ \hline\end{array}$ E.S. ⇒ 5 PCl_5

→ $S = \boxed{\uparrow\downarrow}\ \ \begin{array}{|c|c|c|}\hline \uparrow\downarrow & \uparrow & \uparrow \\ \hline\end{array}\ \ \begin{array}{|c|c|c|c|c|}\hline \; & \; & \; & \; & \; \\ \hline\end{array}$ G.S. ⇒ 2 SF_2

$S^* = \boxed{\uparrow\downarrow}\ \ \begin{array}{|c|c|c|}\hline \uparrow & \uparrow & \uparrow \\ \hline\end{array}\ \ \begin{array}{|c|c|c|c|c|}\hline \uparrow & \; & \; & \; & \; \\ \hline\end{array}$ E.S. ⇒ 4 SF_4

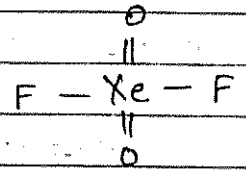
$S^{**} = \boxed{\uparrow}\ \ \begin{array}{|c|c|c|}\hline \uparrow & \uparrow & \uparrow \\ \hline\end{array}\ \ \begin{array}{|c|c|c|c|c|}\hline \uparrow & \uparrow & \; & \; & \; \\ \hline\end{array}$ E.S. ⇒ 6 SF_6

→ Cl / Br / I $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow \,|\, \uparrow\downarrow \,|\, \uparrow}$ $\boxed{\ \ |\ \ |\ \ |\ \ |\ \ }$

$G.S. = 1$ $ES_1 = 3$ $ES_2 = 5$ $ES_3 = 7$

$H-Cl$ ClF_3 ClF_5 Cl_2O_7

→ $\underline{XeO_2F_2}$ ES of Xe = ?



$$F - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Xe}} - F$$

$Xe = 5s^2 5p^6 \Rightarrow G.S \Rightarrow 0$

Covalency = 6 $ES_1 \Rightarrow 2$

$ES_2 \Rightarrow 4$

$\underline{\underline{ES_{\textcircled{3}}}} \Rightarrow 6$

- **<u>SIDGWICK RULE</u>** – Atom which has vacant orbitals in its outermost shell can extend its covalency.

→ $BeF_2 + 2F^- \longrightarrow BeF_4^{2-}$ ✓

$Be^* = \underset{\checkmark}{\boxed{\uparrow}}\ \underset{\checkmark}{\boxed{\uparrow}}\boxed{\underset{\ddot{F}^-}{\uparrow\downarrow}}\boxed{\underset{\ddot{F}^-}{\uparrow\downarrow}} = BeF_4^{2-} \Rightarrow$ possible

→ $BeF_2 + 3F^- \longrightarrow BeF_5^{3-}$ ✗

→ $BF_3 + F^- \longrightarrow BF_4^-$ ✓

→ $BF_3 + 3F^- \longrightarrow BF_6^{3-}$ ✗

→ $AlF_3 + 3F^- \longrightarrow AlF_6^{-3}$ ✓

→ $CF_4 + 2F^- \longrightarrow CF_6^{2-}$ ✗

→ $SiF_4 + 2F^- \longrightarrow SiF_6^{2-}$ ✓

→ $F-F + F^- \longrightarrow F_3^-$ ✗

→ $Cl-Cl + Cl^- \longrightarrow Cl_3^-$ ✗ Should have been possible. Vacant $\oplus$. But size ↓ ⇒ $\ominus$ charge density ↑ ⇒ inter lp repulsion ↑ ⇒ bond stability ↓

→ $Br-Br + \ominus Br^- \longrightarrow Br_3^-$ ✓

→ $I-I + \ominus I^- \longrightarrow I_3^-$ ✓

→ $\overset{\delta+}{I}-\overset{\delta-}{Cl} + \ominus Cl^- \longrightarrow ICl_2^-$ ✓

5d ✓

POLYHALIDE

→ $KI_3 = K^+ + I_3^-$ ⇒ ionic + covalent + coordinate

→ $KNO_2 = K^+ + O^- - N = O$ → ionic + covalent

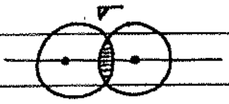
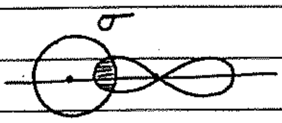
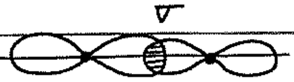
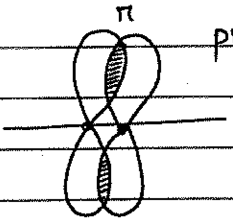
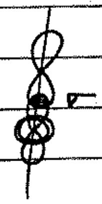
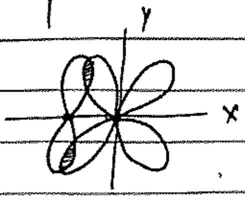
→ $CH_3NO_2 = CH_3 - \overset{\displaystyle O}{\underset{}{N}} \rightarrow O$ ⇒ covalent + coordinate

- **VBT** :- Hitler and London

→ Any atom which undergoes covalent bond formation, tries to pair up its unpaired $e^\ominus$ in G.S. or E.S. This ~~pair~~ pairing of $e^\ominus$ takes place by the combination of atomic orbitals of 2 bonded atoms. This combination is known as overlapping:

a) Axial overlapping (Head to Head)

b) Colateral / Sideways overlapping.

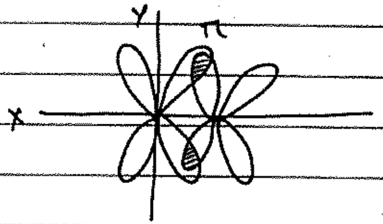
	OVERLAPPING	INTER NUCLEAR AXIS	TYPE OF BOND	EXAMPLE
1.	$s + s$	Any	σ	
2.	$s + p_x$	X	σ	
	$s + p_y$	Y	σ	
	$s + p_z$	Z	σ	
	Any other	s-p overlapping	not possible	
3.	$p_x + p_x$	X	σ	
	$p_y + p_y$	Y	σ	
	$p_z + p_z$	Z	σ	
4.	$p_x + p_x$	Y or Z	π	 $p\pi - p\pi$
	$p_y + p_y$	X or Z	π	
	$p_z + p_z$	X or Y	π	
	Any other	p-p overlapping	not possible	
5.	$p_z + d_{z^2}$	Z	σ	
6.	$p_x + d_{xy}$	Y	π	
	$p_y + d_{xy}$	X	π	
	$p_z + d_{xy}$	ANY	NONE	

* >3 bonds possible b/w 2 atoms : Re_2 Re≣Re (1σ, 2π, 1δ)

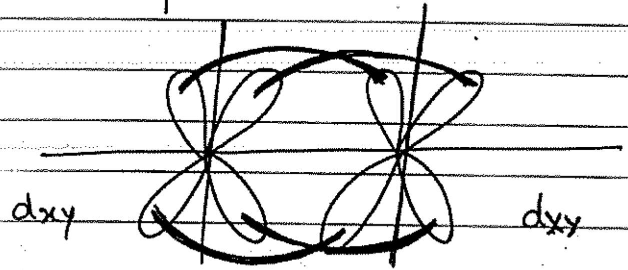
7.	$p_y + d_{yz}$	Z	π
	$p_z + d_{yz}$	Y	π
8.	$p_x + d_{xz}$	Z	π
	$p_z + d_{xz}$	X	π

Any other p-d overlapping is not possible.

→ d-d overlapping-



dπ-dπ



Z axis = internuclear

δ-bond

Q. Which of the following orbital can form only δ bond:

a) d_{yz} b) d_{z^2} [✓ c) $d_{x^2-y^2}$]   d) d_{xy}

- OVERLAPPING & BOND STRENGTH :- (applicable only when orbitals are given)

⟹ $\boxed{B.S. \propto \frac{1}{\text{shell no. of orbitals}}}$

– $1s-2p > 1s-3p > 1s-4p$ B.S.

⟹ If shell no. of orbitals are same,

$\boxed{B.S. \propto \text{extent of overlapping} \propto \text{directional property}}$

– $\underset{\text{Axial}}{2p-2p} > \underset{\text{Axial}}{2s-2p} > \underset{\text{Axial}}{2s-2s} > \underset{\text{Colateral}}{2p-2p}$ BS

⟹ π B.S. order : $\underset{\text{(Strongest)}}{2p\pi-2p\pi} > \underset{\text{(stable)}}{2p\pi-3d\pi} > 2p\pi-3p\pi$ (v. weak) $> 3p\pi-3p\pi$ X

a) O=O exists but S=S doesn't at room temperature.

Ans O=O = $\underset{\text{stable}}{2p\pi-2p\pi}$ S=S = $\underset{\text{not possible generally}}{3p\pi-3p\pi}$

b) N≡N exists but P≡P doesn't.

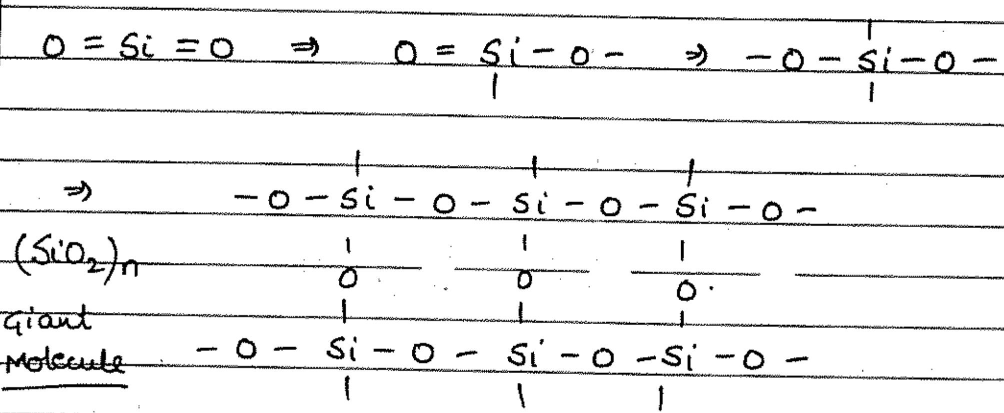
Ans N≡N = $2p\pi-2p\pi$ P≡P = $3p\pi-3p\pi$

c) O=C=O stable but O=Si=O doesn't exist.

Ans O=C=O = $2p\pi-2p\pi$ O=Si=O = $2p\pi-3p\pi$ (v. weak)

→ Tendency of polymerisation decreases with increasing π-bond strength.

→ Weak π bond tend to break them and convert to some more stable structure (polymer)



→ $O=Si=O \Rightarrow O=Si-O- \Rightarrow -O-Si-O-$

$\Rightarrow -O-Si-O-Si-O-Si-O-$

$(SiO_2)_n$

Giant Molecule

→ All giant molecules are covalent solids.

→ Dry ice = molecular solid (CO_2 have VWA b/w 'em)

Q. Which of these is a molecular solid –

a) B_4C = Norbide = Giant = Covalent
b) NH_4Cl = Ionic
c) $Cu(s)$ = Metallic Solid
d) Rhombic Sulphur = S_8 ⇒ VWA b/w S_8s = Molecular.

Q. Which of these has least tendency of polymerisation?

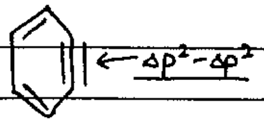
a) SiO_4^{4-} b) PO_4^{3-} c) SO_4^{2-} ~~d)~~ ClO_4^-
Si–O P–O S–O Cl–O

⟶ size ↓ ; B.L. ↓ ; overlapping ↑ ; π B.S. ↑ ; polymer ↓

* HYBRIDISATION :- By pauling; hypothetical.

- Endo
- Explaination of geometry / shape, not reason of it.
- Mixing of atomic orbitals of an atom to form new orbitals having same energy and same shape.
- Half filled, full filled, or vacant orbitals can participate in hybridisation as it is mixing of orbitals, not $e^{\ominus}$.
- Orbitals having almost same energy but different shape can participate in hybridisation.
- Hybrid orbitals always form σ bond, except Benzyne.

Benzyne :



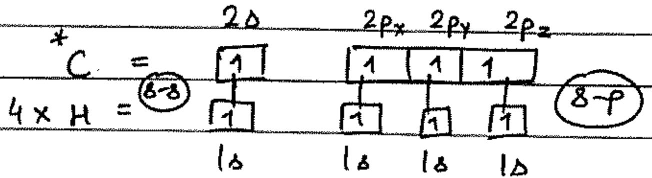
- Size / energy / directional properties of hybrid orbitals $\propto \frac{1}{s\text{-character}}$

→

sp	sp^2	sp^3
50% s	33% s	25% s
50% p	67% p	75% p

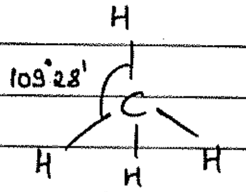
→ p character ↑ ⇒ size ↑ ; energy ↑ ; directional property ↑.

- **CH_4**



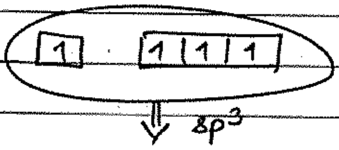
s-s <ⁿ s-p (B.S.) ⇒ All s-p should have B.A = 90°.

But



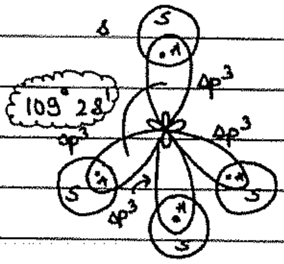
Tetrahedral; B.S., B.L (all) equal.

Just before overlapping



4 ×

(sp^3)



All 4 = identical = $sp^3 - s$ overlapping.

- Endothermic because $e^\ominus$ density present at different places and axes need to be mixed, overcoming that initial ~~bp~~ $e^\ominus$ repulsion, so that they can become less repulsive after hybridisation. That energy comes from work done by system (energy released) when C and H come closer, to form bond.

- HYBRIDISATION & $e^\ominus$ GEOMETRY —

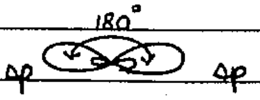
→ Arrangement of mixed up $e^\ominus$ cloud around central atom is $e^\ominus$ geometry.

* $4s, 4p, 4d = sp^3d$

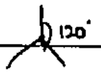
$4s, 4p, 3d = dsp^3 \Longrightarrow$ coordinate compounds

* Hyb. मे वो orbitals participate करते है जिनकी Mixing आसान हो → 1° = On same axis
→ 2° = on same plane

1. sp → linear



2. sp^2 → trigonal planar



If $s + p_x, p_y \Rightarrow$ in xy plane (sp^2)

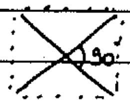
3. sp^3 → tetrahedral

$s + p_x, p_y, p_z \Rightarrow$ 3D

6 angles of 109°28'

4. $dsp^2 = (n-1)d_{x^2-y^2}, ns, np_x, np_y$ [in same plane (dsp^2)]

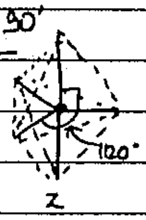
↳ square planar

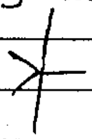


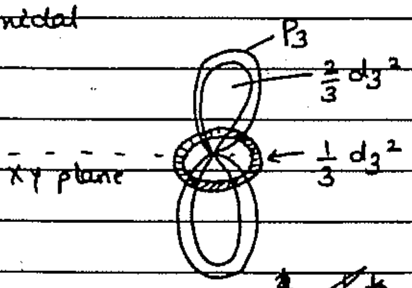
5. $sp^3d / dsp^3 = s + p_x, p_y, p_z + d_{z^2}$

6 angles of 90°

~~Trigonal Bi Pyramidal~~



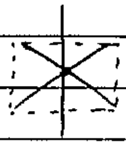




On z axis = $\frac{1}{3}s + p_z + \frac{2}{3}d_{z^2} = \underline{\underline{2}}$

in xy plane = $\frac{2}{3}s + \frac{1}{3}d_{z^2} + p_x + p_y = \underline{\underline{3}}$

6. $sp^3d^2 / d^2sp^3 = s + p_x + p_y + p_z + d_{z^2} + d_{x^2-y^2}$

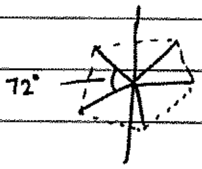


Square Bi Pyramidal = Octahedral

2 axial, 4 equatorial. Which can't be determined.

12 90° angles.

7. sp^3d^3 / d^3sp^3 = $s + p_x + p_y + p_z + d_{z^2} + d_{x^2-y^2} + d_{xy}$



Pentagonal Bi Pyramidal

10 90' angles.

- PREDICTION OF HYBRIDISATION –

⟹ Steric number = No. of σ + No. of lp

↓ No. of Terminal atoms (T.A.)

Covalency of T.A. =	H	X	OH	O	S	N	–R
	1	1	1	2	2	3	1

– XeO_2F_2 σ = 4 lp = 1 s.no. = 5 sp^3d.

– XeF_5^- σ = 5 lp = 2 sp^3d^3

– I_3^+ σ = 2 lp = 2 sp^3

– N_3^- σ = 2 lp = 0 sp (lp = 0 as octet of T.A ⇒ completion)

– H_3BO_3 σ = 3 lp = 0 sp^2

– ~~X4~~ H_4XeO_6 ⇒ oxyacid ⇒ 4 × OH (no. of H) + 2 O.
perxenic acid
σ = ~~8~~6 lp = 0 sp^3d^2

– SO_4^{2-} σ = ~~8~~4 lp = 0 sp^3

- I_3^- $\sigma = 2$ $lp = 3$ sp^3d
- H_3PO_4 $\sigma = 3+1 = 4$ $lp = 0$ (M.B.) sp^3
- XeF_3^+ $\sigma = 3$ $lp = 2$ sp^3d

- **VSEPRT** – Gilespi and Nyhom.

→ Shape of a molecule depends upon total no. of lp and bp around C.A.

→ These $e^\ominus$ pairs tend to occupy such a place that they have minimum repulsion.

→ Repulsion order :

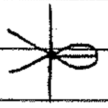
a) lp – lp > lp – bp > bp – bp

b) MB – MB > MB – SB > SB – SB. (Multiple and single)

→ Position of lp and M.B. ⇒

a) sp, sp^2, sp^3 = anywhere

b) sp^3d = always @ equatorial



c) sp^3d^2 = always @ axial

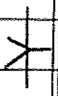
d) sp^3d^3 = → one lp = @ equatorial
→ 2 lp = @ axial.

→ 'V', 'T' shape, linear, trigonal planar, square planar, pentagonal planar are planar shapes. Rest shapes are non-planar.

→

Hybridisation state	π - bond with O
sp	Max. 2 pπ-pπ.
sp^2	1 pπ-pπ; others pπ-dπ.
sp^3, sp^3d, sp^3d^2	Only pπ-dπ

(O की तरफ से pure p ही π बनाता है। Rest of hyb. CA.)

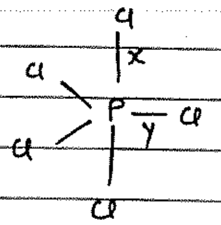
→  sp^3d : axial B.L > equatorial B.L.
90° 120°

→  sp^3d^3 : equatorial B.L > axial B.L.
72° 90°

Terminal atoms are same.

Angle ↓ Repulsion ↑ BL ↑

– PCl_5 = sp^3d.

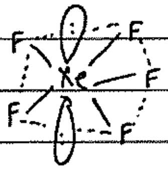


B.L.x > B.L.y

Irregular geometry
(all B.A, B.L. not same)

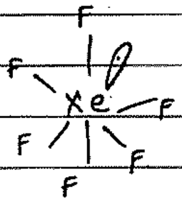
Q. Find out :
1. no. of σ and lp
2. Hyb.
3. $e^{\ominus}$ geometry
4. position of lp and MB
5. Molecular geometry (geometry) / shape
6. Planar or non planar
7. pπ-pπ or pπ-pdπ bond.
8. all B.L. are identical or not

1. XeF_5^- $\sigma = 5$ $lp = 2$ sp^3d^3 PBP



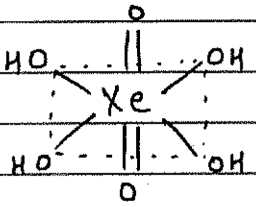
pentagonal planar ; ~~all pπ-dπ~~, all B.L. identical.

2. XeF_6 $\sigma = 6$ $lp = 1$ sp^3d^3 PBP



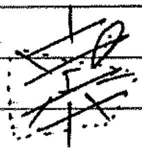
Octahedral (distorted) [all angles not same]
non planar; all B.L. not identical.
(axial <> equatorial)

3. H_4XeO_6 $\sigma = \cancel{4}6$ $lp = 0$ sp^3d^2 SBP

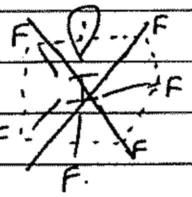


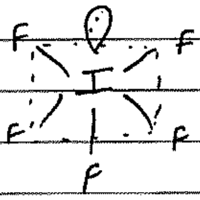
SBP ; non planar; B.L. not equal.
2 pπ-dπ.

4. IF_5 $\sigma = 5$ $lp = 1$ sp^3d^2 SBP

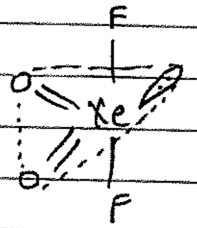


~~distorted octahedral~~
square pyramidal.
non planar.
B.L. not equal.
No perfect 90° BA. almost 90° = 4.





5. XeO_2F_2 $\sigma = 4$ $lp = 1$ sp^3d TBP

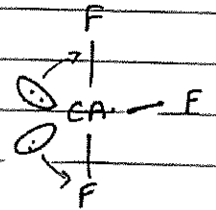


distorted tetrahedral

see saw / π / K   non planar

pπ–dπ ; all B.L. not identical.

6. ClF_3 / BrF_3 $\sigma = 3$ $lp = 2$ sp^3d TBP

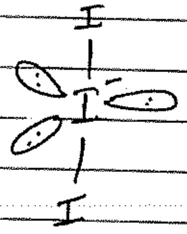


T = Bent T shape

planar

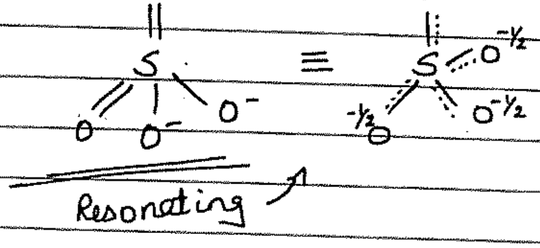
all B.L. not identical.

7. I_3^- $\sigma = 2$ $lp = 3$ sp^3d TBP



= linear ; planar, all B.L. identical

8. SO_4^{2-} $\sigma = 4$ $lp = 0$ sp^3 Tetrahedral



Non planar

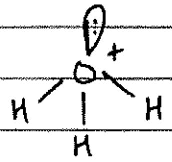
pπ–dπ

all B.L. identical

Formal charge on O = $-1/2$

B.O. = $\frac{6}{4}$ = 1.5.

9. H_3O^+ / NH_3 / CH_3^- $\sigma = 3$ $lp = 1$ sp^3 Tetrahedral



= Pyramidal ; non planar ; all B.L. identical

10. SF_4

11. NO_3^-

12. NO_2^-

13. SO_3

14. NO_2^+

15. $HgCl_2$

16. IF_7

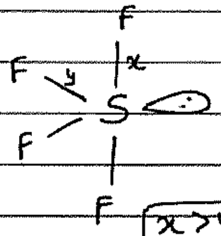
17. I_3^+

18. SO_2Cl_2

19. S_3^{2-}

20. XeF_4

10. SF_4 $\sigma = 4$ $lp = 1$ sp^3d TBP



$\boxed{x > y}$

π / [illegible] / Bent K / Distorted tetrahedral

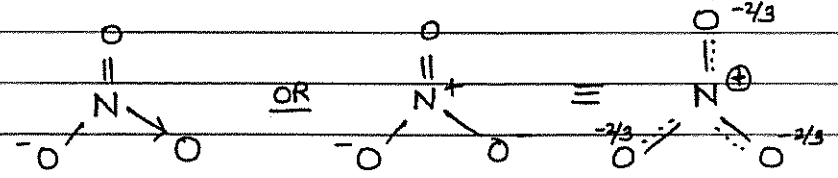
~~planar~~ non planar

no π

all B.L. not identical.

11. NO_3^- $\sigma = 3$ $lp = 0$ sp^2 Trigonal Planar

N = $\boxed{1\downarrow}$ $\boxed{1|1|1}$ NO_2^- $\sigma = 2$ $lp = 1$

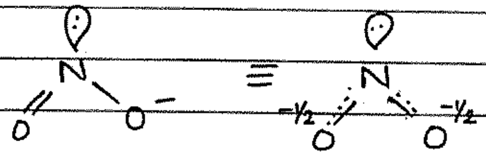


Formal Charge on O = $-2/3$

Bond Order = $\frac{4}{3}$ Trigonal planar ; planar ; pπ-pπ.

All B.L. are identical.

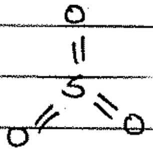
12. **NO_2^-** $\sigma = 2$ $lp = 1$ sp^2 Trigonal Planar



V / Bent / Angular; planar; pπ – pπ
all B.L. identical.

F.C. = $-\frac{1}{2}$ B.O. = $\frac{3}{2}$

13. **SO_3** $\sigma = 3$ $lp = 0$ sp^2 Trigonal Planar



Trigonal planar; planar;
1 pπ–pπ, other (2) pπ–dπ.
All B.L. identical, by internal resonance b/w $p_\perp$ and $d_\perp$ of S and $p_\perp$ of O (⊥ to plane of SO_3)

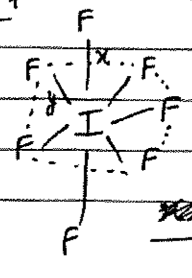
14. **NO_2^+** $\sigma = 2$ $lp = 0$ sp linear

$O = \overset{+}{N} = O$ Linear, planar, both pπ–pπ;
all B.L. identical

15. **$HgCl_2$** $\sigma = 2$ $lp = 0$ sp linear

Cl – Hg – Cl Linear, planar, No π,
all B.L. identical.

16. **IF_7** $\sigma = 7$ $lp = 0$ sp^3d^3 PBP



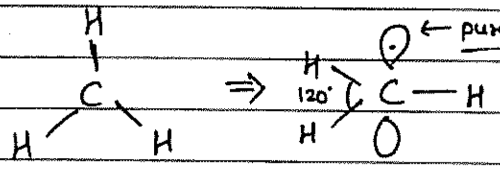
PBP; non planar; no π

y > x

HYBRIDISATION OF ODD $e^{\ominus}$ SPECIES –

1. $\dot{C}H_3$ $\sigma = 3$ $lp = 0.5$ steric no. = 3.5 ⇒ sp^2

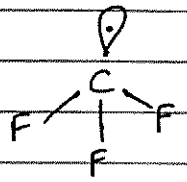
If T.A. has EN < 2.5 ⇒ 3.5 → 3 ⇒ sp^2 ✓(Here)
If T.A. has EN > 2.5 ⇒ 3.5 → 4 ⇒ sp^3



← pure p left after sp^2 contains F.R.

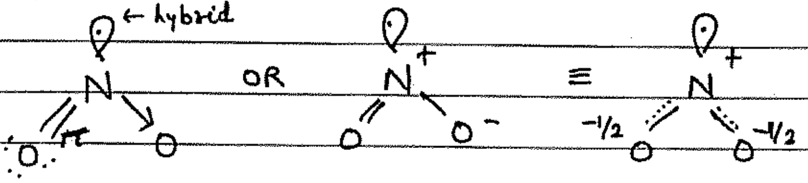
Trigonal planar

2. $\dot{C}F_3$ $\sigma = 3$ $lp = 0.5$ ⇒ sp^3 Tetrahedral



Pyramidal. B.A. > 109°28', as repulsion is caused by 1 $e^{\ominus}$, not lp.

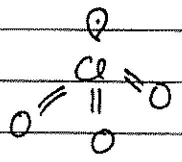
3. NO_2 $\sigma = 2$ $lp = 0.5$ ⇒ sp^{2} Trigonal planar
V shaped.



B.A = 134°
(>120°)

C.A. का octet is incomplete, even then it donates lp to T.A.

4. ClO_3 $\sigma = 3$ $lp = \cdot 5$ ⇒ sp^3

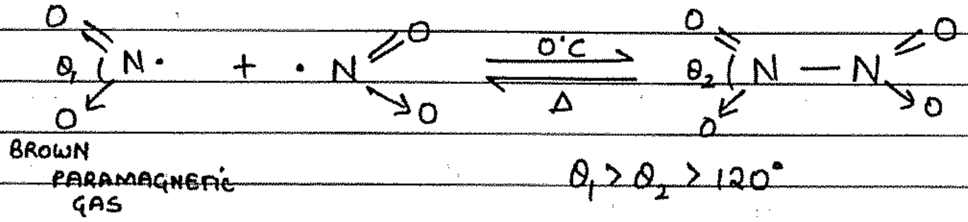


Pyramidal; B.A. > 109°

5• $\underline{ClO_2}$ $\sigma = 2$ $lp = 1.5 \Rightarrow sp^3$

→ All odd $e^{\ominus}$ species tend to dimerize at low temperatures

-



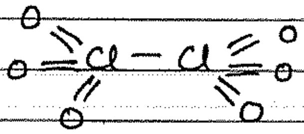
$\theta_1 > \theta_2 > 120°$

- $\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3-CH_3$ $sp^3 \simeq 109°$

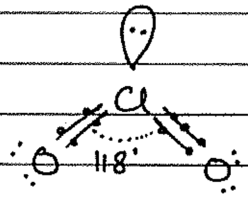
$sp^2 = 120°$

- $\dot{C}F_3 + \dot{C}F_3 \longrightarrow F_3C-CF_3$

- $\dot{C}lO_3 + \dot{C}lO_3 \longrightarrow$



→ If like above examples, ClO_2 had 1 non bonded unpaired $e^{\ominus}$, it would've dimerized. But that $1e^{\ominus}$ forms $3e^{\ominus}$ bond.



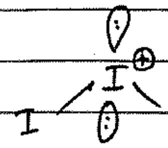
$2\sigma, 1lp \Rightarrow sp^2$; V shape

$\boxed{B.O. = 1.75.}$ unpaired $e^{\ominus}$ in ABMO.
so, it reduces B.O by 0.5 ⇒ 0.25 both.

→ ClO_2 does not dimerize.

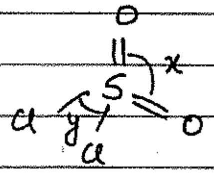
→ Cl_2O_4 exists ⇒ $ClO^+ + ClO_3^-$

17. I_3^+ $\sigma = 2$ $lp = 2$ sp^3 Tetrahedral



V shape ; planar; No π ; all B·L· identical.

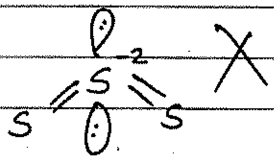
18. SO_2Cl_2 $\sigma = 4$ $lp = 0$ sp^3 Tetrahedral



Tetrahedral; non planar; 2 pπ-pπ ; all B·L· not identical.

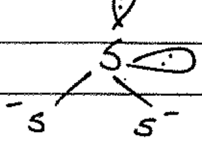
$x > y$

19. S_3^{2-} $\sigma = 2$ $lp = 2$ sp^3 Tetrahedral



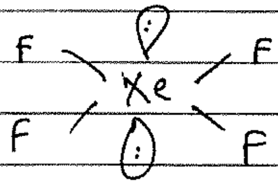
as 3pπ-3pπ is v. weak.
as $-2 + 2$ lp on C·A· = $e^{\ominus}$ density ↑↑↑
⇒ reactivity ↑↑↑; stability ↓↓↓.

⇒



V shape ; ~~non~~ planar; no π. all B·L· identical.

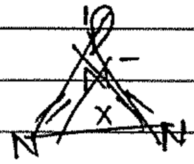
20. XeF_4 $\sigma = 4$ $lp = 2$ sp^3d^2 SBP



Square Planar; planar; no π ; all B·L· identical.

21. N_3^- ~~$\sigma = 2$ $lp = 1$ sp^2 Trigonal planar~~

Azide (pseudohalide)



$\sigma = 2$ $lp = 0$ sp linear

($3 - 3\ e^\ominus$ involved in completing octet of T.A)

$N - N - N \Rightarrow$

$:N \equiv N \rightarrow \ddot{N}:^\ominus \quad = \quad N \equiv N \rightarrow N^\ominus \quad = \quad :N \equiv \overset{+}{N} - \ddot{N}:^{-2}$

(octet of T.A. completed)

$\updownarrow$

$^{2-}:\ddot{N} - \overset{+}{N} \equiv N: \quad \leftrightarrow \quad :\overset{-}{N} = \overset{+}{N} = \overset{-}{N}:$

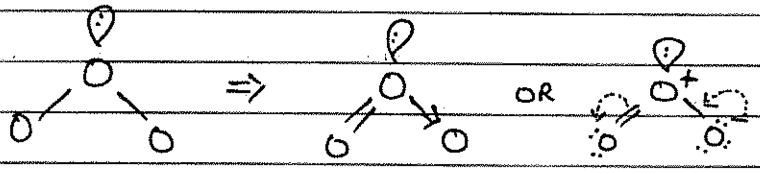
Resonating hybrid, or

most stable Resonating structure

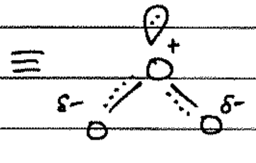
Sets of F.C. possible = 3 ⇒ (0, +1, −2), (−1, +1, −1), (−2, +1, 0)

Planar, linear, 2 pπ−pπ ; all B.L. identical.

22. O_3 $\sigma = 2$ $lp = 1$ sp^2 Trigonal Planar



F.C. on O = 0, +, −



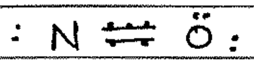
F.C. on O = $-\frac{1}{2}, +1, -\frac{1}{2}$

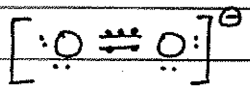
$\delta- = -\frac{1}{2}$

$B.O = \frac{3}{2}$

V shape ; planar ; pπ−pπ bond ; all B.L. identical.

⇒ NO and O_2^- also exist.





→ Orbitals having non bonded unpaired $e^{\ominus}$ and ~~or~~ d orbitals are present at higher energy level. They can participate in hybridisation only when orbital contraction is possible, in presence of T.A.s having high EN (+ on nucleus ↑ ⇒ orbital having $e^{\ominus}$ comes near = contraction). That EN > 2.5

→

EXISTENCE	NON EXISTENCE	
PCl_5, SF_4, XeF_2, SF_6,	PH_5, SH_4, XeH_2, ClI_3	= sp^3d
XeF_4, IF_7, ClF_3,	SH_6, XeH_4	= sp^3d^2
XeF_6, all exist as d	IH_7, XeH_6	= sp^3d^3
orbital participates as	do not exist as d orbital	
T.A. has high E.N.	can't participate in hyb. as	
(EN > 2.5)	T.A. has less EN.	

- BOND LENGTH, BOND STRENGTH, FORMAL CHARGE, RESONANCE —

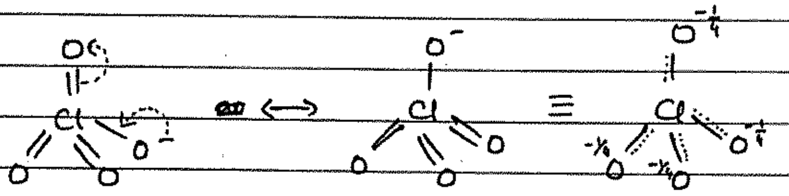
⇛ $B.S.$ or $B.E.$ or $BDE \propto \frac{1}{B.L.} \propto \frac{1}{size} \propto$ s character $\propto B.O.$

→ B.E. / B.D.E. (not B.L.) of 2nd period single bonded atoms also depend upon lp – lp repulsion.

— $Cl_2 > Br_2 > F_2 > I_2$ BE / BDE

→ If species has equally stable resonating structures, then B.L, BO, BA, FC etc. depend upon resonance hybrid

– $\frac{ClO_4^-}{sp^3}$



F.C. = $\frac{-1}{4}$ B.O. = $\frac{7}{4}$ = 1.75

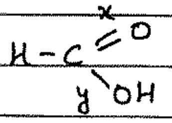
→ Catenation ∝ B.E.

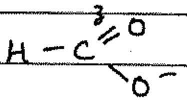
Q. Compare :

1. $H_2O_2 > O_3 > O_2$ (O–O B.L.)
1 1.5 2 B.O

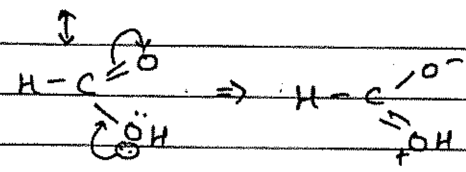
2. $NO_2^+ > NO_2^- > NO_3^-$ (N–O B.S.)
2 1.5 1.33 B.O.

3.



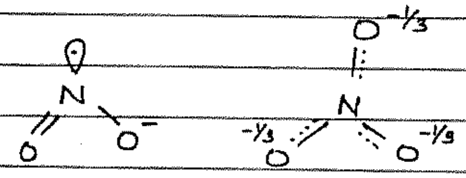


(B.L.) (x < z < y)



V. less stable. So, Ans acc to more stable resonating structure, as that structure has main contribution in forming hybrid

2. $O=\overset{+}{N}=O$



4. $-\underset{|}{\ddot{N}}-\underset{|}{\ddot{N}}- \;<\; -\underset{|}{P}-\underset{|}{P}-$ BE/BDE

5. $\underset{sp}{\equiv C-H} \;<\; \underset{sp^2}{=\overset{|}{C}-H} \;<\; \underset{sp^3}{-\overset{|}{\underset{|}{C}}-H}$ B.L.

6. $\underset{sp\;\;sp}{\equiv C-C\equiv} \;>\; \underset{sp^2\;\;sp^2}{=\overset{|}{C}-\overset{|}{C}=} \;>\; \underset{sp^3\;\;sp^3}{-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-}$ B.S.

7. $C-C > Si-Si > Ge-Ge > Sn-Sn$ (Catenation)
$\longrightarrow$ size ↑ ⇒ B.E. ↓ ⇒ catenation ↓.

8. $F_2 < Cl_2 < Br_2 < I_2$ (B.L.)

9. $H-\underset{-1}{\overset{\delta-}{O}}-\underset{-1}{\overset{\delta-}{O}}-H \;>\; F-\underset{+1}{\overset{\delta+}{O}}-\underset{+1}{\overset{\delta-}{O}}-F$ (O−O B.L.)
~~→ ⊕ charge ↑ ⇒ size ↓ ⇒ B.L. ↓~~

10. $C=C < C=O < C\equiv C < C\equiv O$ (B.S.)
size ↓; ΔEN ↑ $\quad = < \equiv \quad$ size ↓; ΔEN ↑
~~Same period ⇒ size ≃ equal.~~

11. $O-O < S-S$ (Catenation)

→ Strongest single bond in diatomic species = $H-F$ (ΔEN ↑↑)

→ Strongest bond in diatomic species = $C\equiv O$ (≡ + ΔEN ↑)

- BOND ANGLE ⇒

① Hybridisation. eg. $CO_2 > CO_3^{2-} > CCl_4$
$sp > sp^2 > sp^3$

- eg. $XeF_2 > XeO_3 > XeF_4$
  $sp^3d > sp^3 > sp^3d^2$
  180° ≃109° 90°

→ **DRAGO'S RULE** – Elements of 3rd period and lower (4th ...) do not show hybridisation when they are bonded with less E.N. atom like H (EN < 2.5).

→ This rule is applicable only when C.A. has lp.

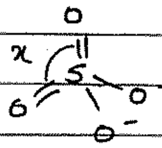
$NH_3 = 107°$	$H_2O = 104.5°$		
$PH_3 = 93° - 94°$	$H_2S = 92°$	B.A. ≃ 90°	
$AsH_3 = 92°$	$H_2Se = 91°$	No HYB.	
$SbH_3 = 91°$	$H_2Te = 90°$		

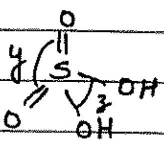
② $B.A. \propto \frac{1}{\text{no. of } lp}$

eg. $NH_4^+ > NH_3 > NH_2^-$
sp^3 sp^3 sp^3
0 lp 1 lp 2 lp

③ MB – MB and MB – SB repulsion

e.g.

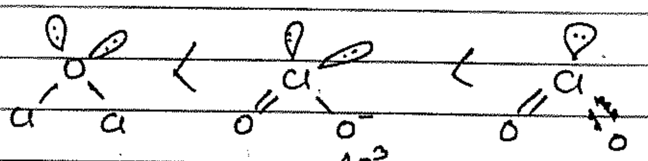




equally stable R.S.
$x = 109°28'$

R.S. forming other than this is highly unstable. So, acc. to this,
~~y > z~~ $y > 109°28' > z$
$y > x > z$

eg. OCl_2 ClO_2^- ClO_2



sp^2

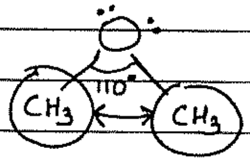
sp^3
2lp (SB–SB)

sp^3
2lp
partial (MB – MB)

④ B.A. ∝ $\frac{\text{EN of CA}}{\text{size of CA}}$ (size of CA ↑ steric repulsion ↓ BA ↓ as lp-lp or/and lp-bp takes over)

eg. $NCl_3 > PCl_3 > AsCl_3 > SbCl_3$

⑤ B.A. ∝ $\frac{\text{size of TA}}{\text{EN of TA}}$



eg. $PF_3 < PCl_3 < PBr_3 < PI_3$

eg. $OF_2 < H_2O < OCl_2$ sp^3, 2 lp, main = O.

size of T.A : $H_2O < OF_2 < OCl_2$
EN of T.A : $OF_2 < OCl_2 < H_2O$

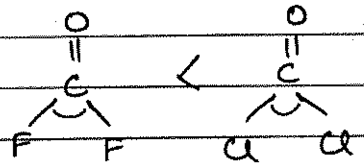
for F, see EN; rest ⇒ size (if size and EN are opp.)

→ CA and TA factors are applicable only when C.A. has lp or forms different types of bonds.

- e.g. $\underbrace{BF_3 = BCl_3 = BBr_3}$ = 120°

sp^2; 0 lp; C.A. = B; size of TA ↑ ⇒ not applicable.

e.g.



sp^2, 0 lp on C, C.A. = C, size of T.A. ↑ ⇒ B.A. ↑

Q. Compare B.A.

1. $BF_3 > CF_4 > XeF_4$
2. $\overset{+}{N}O_2 > NO_2 > \overset{-}{N}O_2$
3. $XeF_4 > ClF_3 > BrF_3$
4. $H_2S < SF_2 < SCl_2$
5. $NF_3 < NH_3 < NCl_3$
6. $PO_4^{3-} = SO_4^{2-} = ClO_4^-$
7. $SOF_2 < SOCl_2 < SOBr_2$ $\quad X-\hat{S}-X$
8. $BCl_3 = AlCl_3 = GaCl_3$
9. $H_2O < NH_3 < O(CH_3)_2$
10. $PH_3 < PF_3 < PCl_3$
11. $ClO_3^- > BrO_3^- > IO_3^-$

* Best lp donors belong to 2p. In 3p, size ↑ ⇒ $e^{\ominus}$ density ↓.

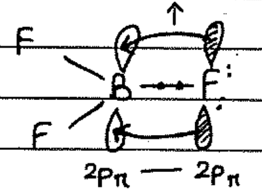
12. $CH_4 = CF_4 = CCl_4$

* BACK BONDING ⇒

Occurs between 2 adjacent covalently bonded atoms in which -

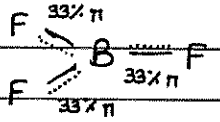
a) 1 atom should have lp (generally this atom is from 2nd period)
b) another atom should have vacant orbital (generally this atom is from 2nd or 3rd period)

[coordinate π = back bond]



$^*B$ = [↑] [↑|↑|]
F = [↑↓] [↑↓|↑↓|↑]

≡

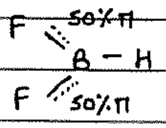


Due to B.B., B.S. ↑, B.L. ↓.

Q. Strongest B − F is present in :-

a) BF_4^- ↓ NO B.B.

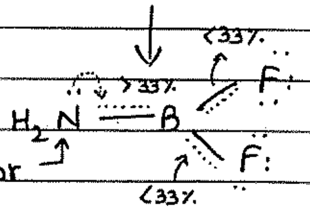
e) HBF_2 ✓ ↓



b) $H_3N \rightarrow BF_3$ ↓ NO B.B.

c) BF_3 ↓ 33 % π

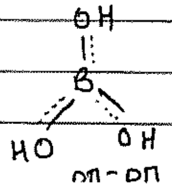
d) $H_2N - BF_2$ ↓



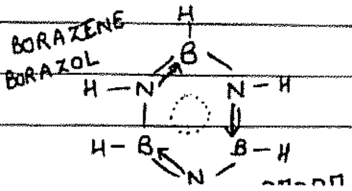
EN ↓ ⇒ better donor
(tendency to give ↑)

q. pπ−dπ BB is present in:

a) H_3BO_3



inorganic benzene
b) $B_3N_3H_6$



Methyl Isocyanate
c) $CH_3-N=C=O$
NO BB

Silyl isocyanate
d) H_3Si-N
$O=C$

d) $H_3Si \Leftarrow \ddot{N} = C = O$
pπ−dπ

* In $H_3Si-N=C=O$, max. 4 atoms in 1 line
max. 5 atoms in 1 plane.

~~Q. Which of the followin~~

→ If lp of CA participates in B.B., then it is not considered as hybrid $e^{\ominus}$ pair. In this condition, LBS also decreases. (Lewis Base Strength)

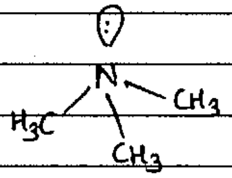
a) $(CH_3)_3-\ddot{N}$ TRIMETHYL AMINE

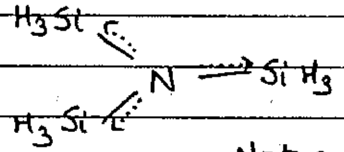
$(H_3Si)_3-\ddot{N}$ TRISILYL AMINE

$\sigma = 3$; $lp = 1 \Rightarrow sp^3$

$(p\pi-d\pi)$ B.B. present.

$\sigma = 3$ $lp = 0$ $\Rightarrow sp^2$





Trigonal Planar

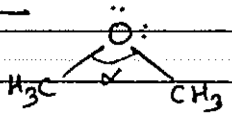
pyramidal
Acts as L.B.

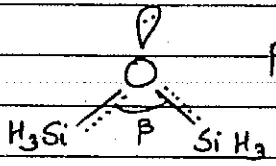
Not a L.B.

b) $(CH_3)_2-\ddot{O}:$

$(H_3Si)_2-\ddot{O}:$

NO BB





$p\pi-d\pi$ BB

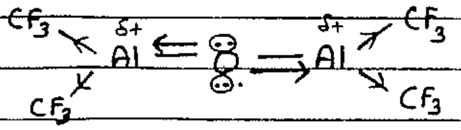
$\alpha < \beta$

sp^3, V shape
Acts as L.B.

>

sp^2, V shape
Acts as L.B.

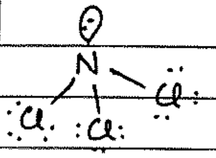
Generally, neutral atom donates only 1 lp to BB, cuz after that, $e^{\ominus}$ density on that atom itself is highly reduced. Rare example of 2 lp donation:

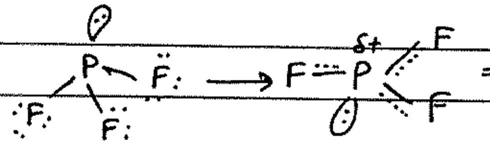


Q. Which of the following molecule is planar due to BB

a) NCl_3 b) PF_3 c) BF_3 ~~d)~~ None

~~2pπ-3dπ ⇒ X~~ ~~2pπ-3dπ ⇒ X~~ already was planar



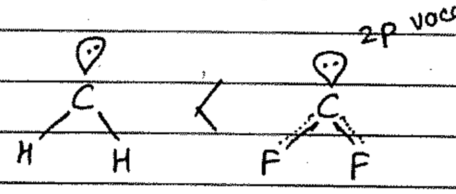


⇒ pyramidal.
Weak B.B. due to +δ on P.

3d = vacant; but no BB due to ↑ inter $e^\ominus$ repulsion.

Q. Compare stability ⇒

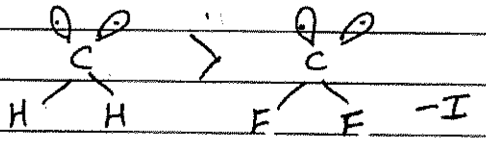
a)



singlet carbene $C = \boxed{\uparrow\downarrow}\ \boxed{\uparrow}\boxed{\uparrow}\boxed{\ }$
(reason for unstability : $e^\ominus$ deficiency)

I effect पर BB dominant है as it ↑ stability.

b)



triplet carbene $C = \boxed{\uparrow}\ \boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

Q. Compare Lewis Acid Strength :

a) $BF_3 < BCl_3 < BBr_3 < BI_3$ (extent of BB ↓)
$2p-2p > 2p-3p > 2p-4p > 2p-5p$

b) $BeF_2 < BeCl_2 < BeBr_2 < BeI_2$

Q• Compare acidic strength.

a) $CH_3-OH < SiH_3-OH$

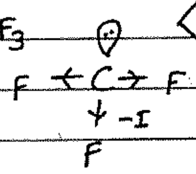
$\downarrow \qquad \downarrow$

$CH_3-O^{\ominus} < SiH_3 \leftarrow O^{\ominus}$ stability

3d

b) $CHF_3 < CHCl_3$

$\downarrow \qquad \downarrow$

$^{\ominus}CF_3$  $< \ ^{\ominus}CCl_3$ BB ✓ (I पर BB dominant)

$$\begin{array}{c} \ominus \\ F \leftarrow C \rightarrow F \\ \downarrow -I \\ F \end{array}$$

($p\pi-d\pi$) [d orbital resonance]

Q)· Compare strength of H-Bond.

a) $(CH_3)_3-C-OH < (CH_3)_3-Si \leftarrow \ddot{O}-H$

$e^{\ominus}$ density $\downarrow$ ⇒ attracts more from H ⇒ more $\delta+$ on H ⇒ better H bond

---

→ Why BB is present in $^{\ominus}CCl_3$ but not in NCl_3 ?

Q. Compare B.L.

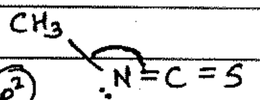
a) $B-(NR_2)_3 > HB-(NR_2)_2 > H_2B-NR_2$ (B – N B.L.)

33% MB 50% MB 100% M.B.

⟶ steric crowding ↓

** Energy barrier for free rotation ~~decreases~~ increases (⟶)

Q. Compare B.A. around N :-



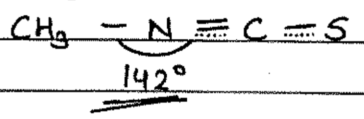
sp^2 (Methyl Thio Isocyanate)

↕

$CH_3 - \overset{\oplus}{N} \equiv C - \overset{\ominus}{S}$

sp Though it has charge, and is less stable, it has significant contribution, as a weak (very) bond gets broken = $2p\pi - 3p\pi$ between C and S.

||| (Bent)



$H_3Si \leftarrow \ddot{N} = C = S$ (Silyl Thio Isocyanate)

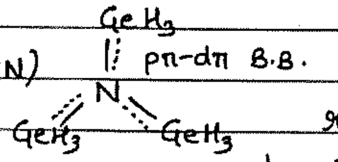
lp of N gets involved in both BB ($p\pi - d\pi$) and resonance = Double Conjugation (⟵ ⊙ ⟶). So, lp is fully delocalized. ∴ lp is not considered in Hyb.

⇒ Hyb. of N = sp = linear

180°

An example where donor is of 2nd period and acceptor of 4th:

(sp^2N)



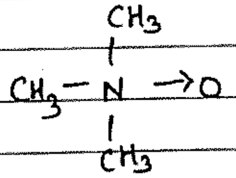
GeH_3 is very big, so steric repulsion ↑ ⇒ to minimize, B.A. ↑

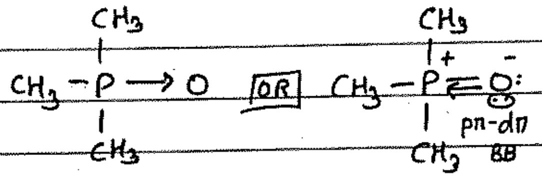
⇒ ≃ 120° ⇒ BB ✓ (simultaneous)

Q. Compare dipole moment:

a) $(CH_3)_3-NO$ $(CH_3)_3-PO$

$(CH_3)_3-NO \quad > \quad (CH_3)_3-PO$


$CH_3-\overset{CH_3}{\underset{CH_3}{N}}\rightarrow O$


$CH_3-\overset{CH_3}{\underset{CH_3}{P}}\rightarrow O$ $\boxed{OR}$ $CH_3-\overset{CH_3}{\underset{CH_3}{\overset{+}{P}}}\rightleftarrows\overset{-}{\ddot{O}}:$ pπ-dπ BB

$(CH_3)_3-\overset{\longmapsto}{\overset{\oplus}{N}-\overset{\ominus}{O}} \quad > \quad (CH_3)_3-P\rightleftarrows O$

---

* BENT RULE →

A) More EN atom occupies that position of hybrid orbitals which has less s character or more p character, and vice-versa.

B) lp and MB occupy that position of hybrid orbitals which has more s character

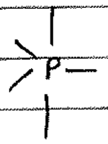
C) lp ~~ks~~ will always have more s character than bp or MB.

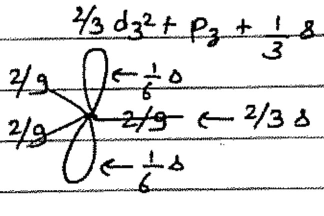
D) For fixed C.A. and T.A.s, and for same hyb. state,

$$B.S. \propto \frac{1}{B.L.} \propto s\ char. \qquad B.A. \propto s\ char$$

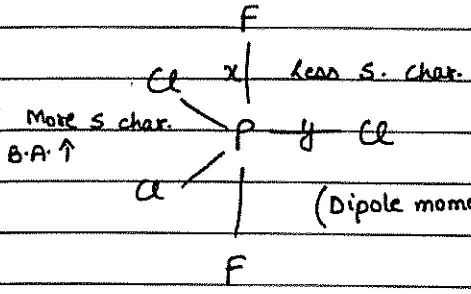
For % s or % p character, $\cos\theta = \frac{s}{s-1} = \frac{p-1}{p}$

- PCl_3F_2 sp^3d





$\frac{2}{9} > \frac{1}{6}$



(Dipole moment = 0)

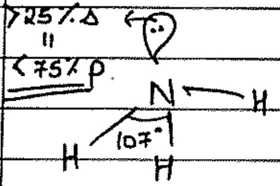
F is ↑ EN. It wants to be where EN ↓ so it can attract more.
EN ∝ s char. So, EN ↑ F @ axial.
So, already weak axial gets charge induced ⇒ B.S. ↑
⇒ more stability.

Bond length : x < y (Cl is bigger than F ⇒ B.L. ↑)
At equatorial, Cl–Cl repulsion is ↓↓ as B.A. is ↑↑ = 120°.

Q. % p character @ lp of NH_3 –

a) > 75% [✓ b) < 75%] c) 75% d) 100%

Ans



all are sp^3 ⇒ all bonds are same (similar)
Bent rule : lp वहाँ आएगा जहाँ s char. ↑ होगा
= lp जहाँ आएगा वहाँ s char ↑ हो जाएगा

$\cos 107 = \frac{s}{s-1} \Rightarrow -0.3 = \frac{s}{s-1} \rightarrow -0.3s + 0.3 = s$

$0.3 = 1.3s \rightarrow s = \frac{3}{13}$

$s = 0.23$

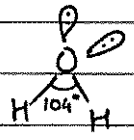
Total s char. = 1 (1 s was there)

s char. @ lp = 1 − 3(0·23) = 1 − 0·69 = 0·31. = >25%

p char. @ lp = 1 − 0.31 = 0·69 = < 75%

Q. Get s character @ lp of H_2O. ($\cos 104° = -0.25$)

Ans

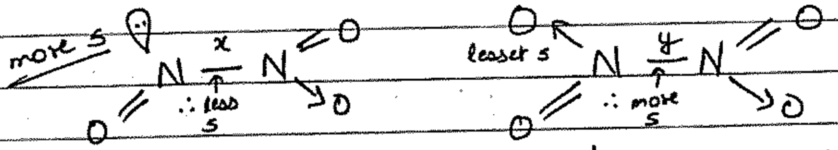


all are sp^3 ⇒ lp → >25% s each.

$\cos 104 = \frac{s}{s-1} \Rightarrow -0.25 = \frac{s}{s-1} \Rightarrow s = 0.2$

s char. @ lp = 1 − 3(0·2) = 1 − 0·6 = 0·4 = >25%.
(40%) each

Q.• Compare N−N B.L. of N_2O_3 and N_2O_4.

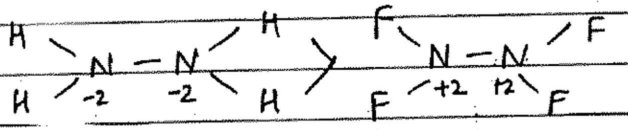


s char. $\propto \frac{1}{B.L}$ ⇒ $\underline{\underline{x > y}}$ | In such condition of bent rule, check O.S. of C.A. $N_2O_3 \Rightarrow +3$; $N_2O_4 \Rightarrow +4$

$\oplus \uparrow \Rightarrow$ size $\downarrow \Rightarrow B.L. \downarrow \Rightarrow N_2O_3 > N_2O_4$

Q. Compare B.L.

a)



(N−N B.L.)

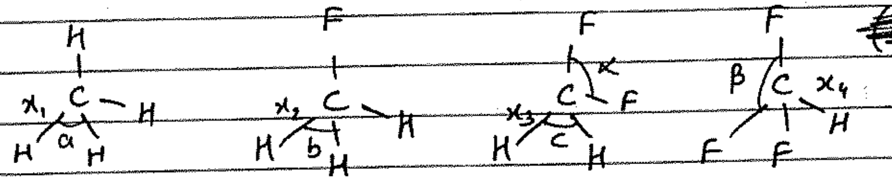
$\oplus \uparrow \Rightarrow$ size $\downarrow \Rightarrow B.L. \downarrow$.

b) $H-\underset{-1}{O}-\underset{-1}{O}-H > F-\underset{+1}{O}-\underset{+1}{O}-F$ (O−O)

c) $H_3C-CH_3 > F_3C-CF_3$

Q. Compare given properties −

a)



a) $x_1 > x_2 > x_3 > x_4$ (BL)

b) ~~a > b > c~~ a < b < c

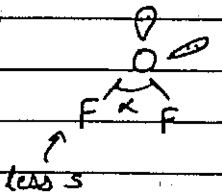
c) β > α

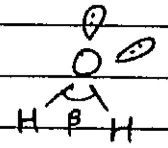
CH_4 = Methane
SiH_4 = Silane
GeH_4 = Germane
SnH_4 = Stannane

PbH_4 = Plumbane

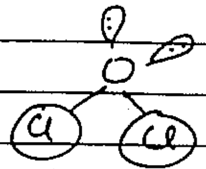
Q. Compare B.A.

a)





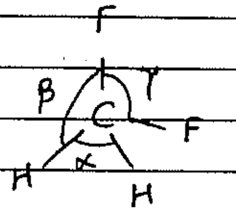
$\alpha < \beta$

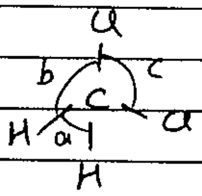


Steric repulsion.
Bent rule not applicable.

$H_2O < OCl_2$ (BA)

Q. b)

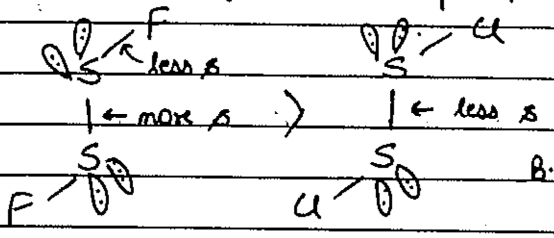




$\gamma < \beta < \alpha$ (Bent rule)

$a < b < c$ (Steric repulsion)

Q. Compare energy barrier for free rotation @ S–S bond.



$\Delta \propto$ B.S.

B.S. ↑ ⇒ energy barrier for free rotation ↑

* DIMERISATION ⇒

A) BY BANANA BONDING / 3C-2$e^{\ominus}$ bond / $e^{\ominus}$ deficient bond

- B_2H_6 = diborane

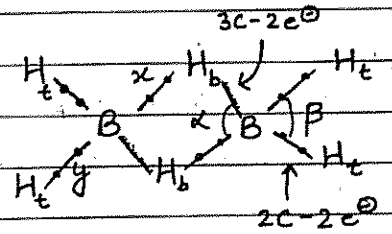
$$\underset{(g)}{2BH_3} \underset{\Delta}{\xrightleftharpoons{\text{ROOM TEMP.}}} \underset{(g)}{B_2H_6}$$

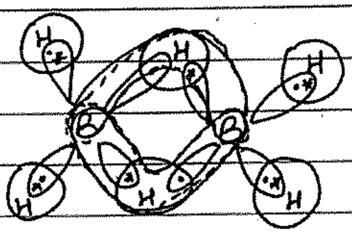
$\Delta S = \ominus$
$-T\Delta S = \oplus$

But dimerisation ✓ ⇒ $\Delta G = \ominus$ ⇒ ΔH is highly $\ominus$.

* whenever 1 orbital of an atom is involved in bonding with 2 or more orbitals of other atom, always occurs delocalization of $e^{\ominus}$.

- BORANE $\longrightarrow$ NIDOBORANE = B_nH_{n+4} = B_2H_6
  $\longrightarrow$ ARCHANOBORANE = B_nH_{n+6} = B_4H_{10}





Hyb. = sp^3

→ B.A. $\alpha < \beta$
$\simeq 97°$ $\simeq 120°$

Whenever dimerisation occurs, leading to formation of ring by banana bond, in the ring, B.A is ↓ and B.L. is ↑.

→ B.L. $x > y$

Incomplete octet ⇒ Acts as L.A.

→ $[BH_2^+][BH_4^-] \longleftrightarrow [BH_4^-][BH_2^+]$ complete delocalization at a point of time
I II I II

→ B.E. ⇒ $2c-2e^{\ominus}$ bond < $3c-2e^{\ominus}$ bond

→ Non planar, Non polar molecule ($\mu/\vec{p} = 0$)

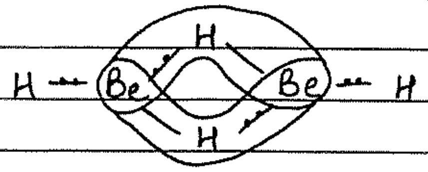
→ All H_t are in same plane, both H_b are ⊥ that plane

→ Max. no. of atoms in same plane = 6

→ If substitution reaction takes place, only 4 H_t will be substituted.

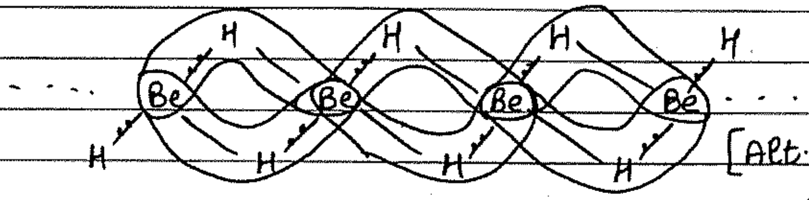
$$B_2H_6 + 4\ CH_3-Cl \longrightarrow B_2H_2(CH_3)_4 + 4\ H-Cl$$

- Be_2H_4 = dimer of BeH_2 in vapour form.



sp²; planar; incomplete octet

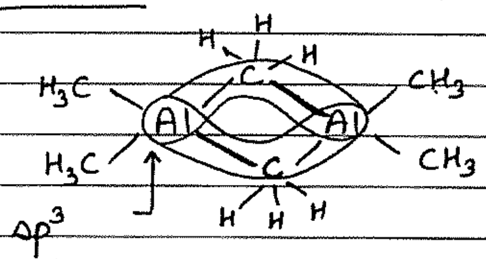
- $(BeH_2)_n$ = ~~da~~ polymer of BeH_2 in solid state



sp³
Non planar
[Alt. rings are in same plane]

All Bonds are 3c – 2e⊖ bonds; all B.L. identical

- $Al_2(CH_3)_6$ = dimer of $Al(CH_3)_3$



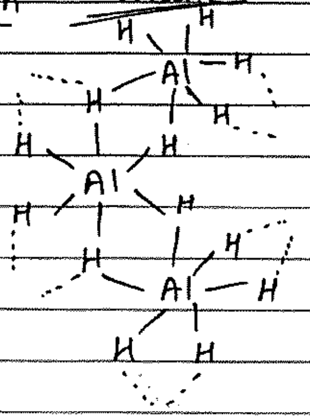
$C_t = C_b = sp^3$. (No change)

Non planar ⇒ incomplete octet

Same for $Ga_2(CH_3)_6$

- $(AlH_3)_n$ = Alane

C.N. / Covalency of Al = 6

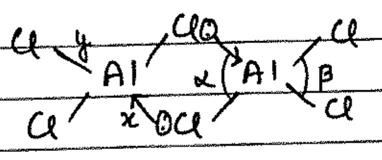


sp^3d^2; non planar

OTHERS ⇒ $Be(BH_4)_2$
$Al(BH_4)_3$

3) **BY COORDINATE BOND** — 3c – 4 $e^{\ominus}$ bond (No delocal.)

- Al_2Cl_6 = dimer of $AlCl_3$ $AlCl_3$ (g) = monomer



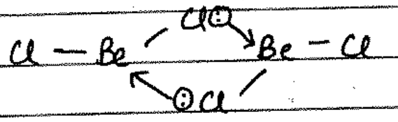
sp^3 Non planar

COMPLETE OCTET

$\alpha < \beta$ $x > y$

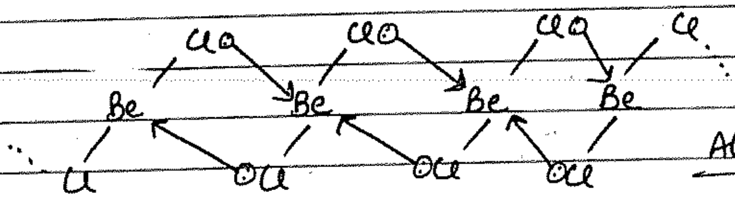
Same for Ga_2Cl_6 , Al_2Br_6

- Be_2Cl_4 = dimer of $BeCl_2$ in vapour state



sp^2, planar [Incomplete Octet]

- $(BeCl_2)_n$ = polymer of $BeCl_2$ (Δ)

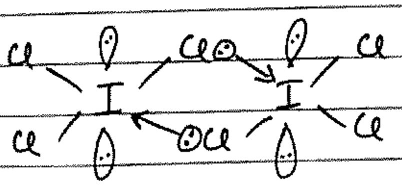


sp^3 Non planar

COMPLETE OCTET

All B.L. identical

- I_2Cl_6 = dimer of ICl_3 (@ room temp.)



sp^{3}d^2 planar

super octet

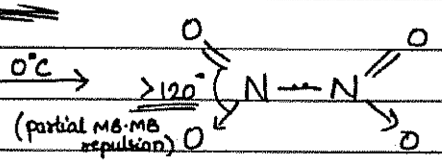
- Others — Fe_2Cl_4 , Fe_2Cl_6

- BCl_3, BBr_3, BI_3 do not form dimer due to smaller size of B and larger size of halogen, steric repulsion ↑

- BF_3 does not form dimer due to B.B.

c) <u>IN ODD $e^{\ominus}$ species</u>

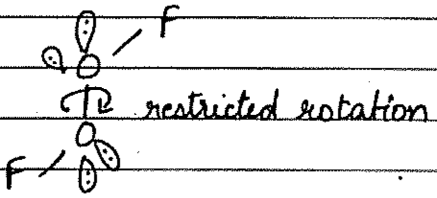
- $\dot{N}O_2 + \dot{N}O_2 \xrightarrow{0°C}$

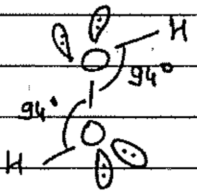


<u>all N are sp^2</u>

All N-O bonds are identical due to resonance.

- $\dot{O}F + \dot{O}F \longrightarrow O_2F_2$ Half-open book like <u>(S_2F_2, S_2Cl_2)</u>

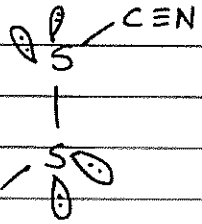




<u>DIHEDRAL ANGLE</u> gas = 110.2°
solid = 90.5°

- <u>$(SCN)_2$</u> = Thiocyanogen ; example of pseudohalogen.

NC−S−S−CN



Max. no. of atoms in same plane = 4

Same for $(OCN)_2$
OXYCYANOGEN;
pseudohalogen.

- $(CN)_2$ = cyanogen (pseudohalogen)

  $N\equiv C-C\equiv N$ sp; linear ; $\sigma : \pi :: 3 : 4$

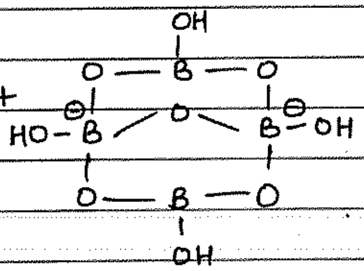
- SCN^-, OCN^-, CN^- = pseudohalide

⇛ SOME IMP. CYCLIC & POLYCENTRIC COMPOUNDS –

1) BORAX / TINCAL / SUHAGA

$Na_2B_4O_7 \cdot 10H_2O$ || OR || $Na_2B_4(O)_5(OH)_4 \cdot 8H_2O$

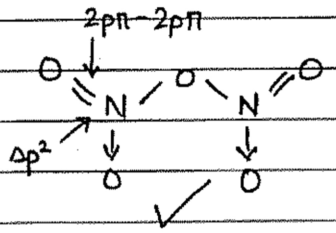
$2Na^+ +$

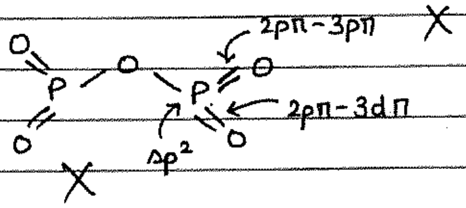


No. of sp³ units = 11
(9 O + 2 B⊖)
No. of tetrahedrals = 2
No. of trigonal units = 2
No. of bridging O = 5

2) P_4O_6, P_4O_{10}

→ Oxides of P, As, Sb exist in dimer form

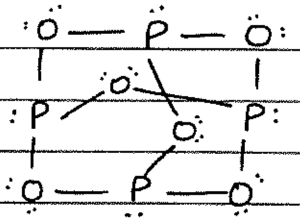




(monomer)

$2\ P_2O_5 \longrightarrow P_4O_{10}$

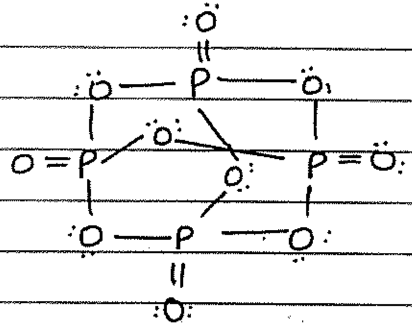
→ **P_4O_6**



Hyb. of P = sp^3
No. of lp = 16
No. of bridging O = 6
No. of 6 membered ring = 4

All P are present @ corners of tetrahedral.

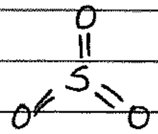
→ **P_4O_{10}**



Hyb. of P = sp^3
No. of lp = 20
No. of bridging O = 6
Smaller P–O = 4
Larger P–O = 12
pπ – pπ = 0

③ SOLID SO_3 / TRIMER OF SO_3 / S_3O_9

SO_3 (g) = monomer



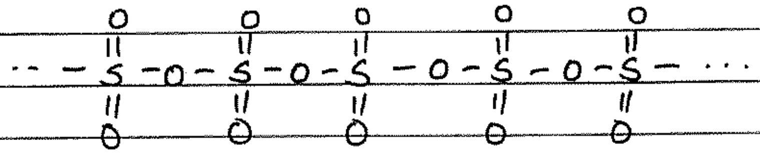
sp^2, planar,
$2p\pi - 3p\pi = 1$
$2p\pi - 3d\pi = 2$

All B.L. identical due to d-orbital resonance.
All 3 π bonds have character of both 2pπ-3pπ and 2pπ-3dπ.

2pπ-3pπ is v. weak, can be broken.

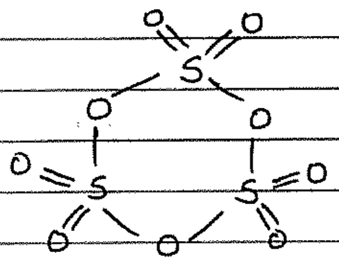
$\boxed{SO_3}$
→ α – SO_3 = cross linked sheet polymer
→ β – SO_3 = chain polymer
→ γ – SO_3 = Cyclic trimer

- β-SO_3 =



$$\cdots - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}} - O - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}} - O - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}} - O - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}} - O - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}} - \cdots$$

- γ-SO_3



Hyb. of S = sp^3 ; Non planar
$p\pi - p\pi = 0$
$p\pi - d\pi = 6$
$S - O \rightarrow S = 3$

④ Calcium Cyanamide [$CaCN_2$]

$$CaC_2 + N_2 \xrightarrow{\Delta} \underbrace{CaCN_2 + C}_{\text{NITROLIM}}$$

, used as fertiliser.

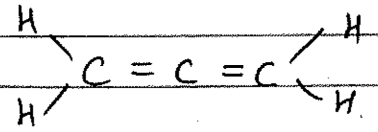
- CaC_2 is used for fixation of atmospheric N_2.

- $CaCN_2$ $\quad Ca^{2+} + CN_2^{2-}$ $\quad [\overset{-1}{N} = C = \overset{-1}{N}]$ (linear)

⑤ Carbon Suboxide [C_3O_2]

$O = C = C = C = O$ (linear) $\quad \sigma : \pi :: 1 : 1$

⑥ Allene [C_3H_4]



non planar

⇛ COMPOUNDS WHICH CHANGE STRUCTURE IN (s) ⇒

10 covalent   10 covalent + 1 ionic attraction. LE released ↑
⇒ ΔH highly ⊖

① $2PCl_5 (s) \longrightarrow PCl_4^+ + PCl_6^-$

sp^3d; irregular geometry sp^3 sp^3d^2 regular geometry   (1 axial Cl is transferred)

② $PBr_5 (s) \longrightarrow PBr_4^+ + Br^-$ PBr_6^- doesn't exist (due to steric repulsion)

③ $2PF_5 (s) \cancel{\longrightarrow} PF_4^+ + PF_6^-$ Not possible due to Berry pseudo rotation.

when X rays are incident on PF_5 for B.L detection, spherical rotation of all bonds start. So, at a pt of time, all bonds ⇒ regular geometry. But all B.L not identical

④ $2IF_5 (l) \longrightarrow IF_4^+ + I_6^-$

shows conductivity (ions form in liquid state)

⑤ $N_2O_5 (s) \longrightarrow NO_2^+ + NO_3^-$

NITRONIUM NITRATE   NITRONIUM   NITRATE

⑥ $N_2O_4 (s) \longrightarrow NO^+ + NO_3^-$

NITROSONIUM

⑦ $Cl_2O_6 (s) \longrightarrow ClO_2^+ + ClO_4^-$

⑧ • $I_2Cl_6\ (l) \longrightarrow ICl_2^+ + ICl_4^-$

⑨ $XeF_6\ (l) \longrightarrow XeF_5^+ + F^-$

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

⑩ $3I_2\ (l) \longrightarrow I_3^+ + I_3^-$

V shape $\quad$ linear

PBr_6^-, PI_6^-, SCl_6, SBr_6, SI_6, $SiCl_6^{2-}$, $SiBr_6^{2-}$, SiF_6^{2-},
$AlCl_6^{2-}$, $AlBr_6^{3-}$, AlI_6^{3-}, ICl_7, IBr_7, II_7

$\Downarrow$

all do not exist.

If T.A. are 6 or 7, mainly fluorides exist. (PCl_6^- too)

---

* **DIPOLE MOMENT :- (μ)**

- μ is product of charge and internuclear distance.
- Unit = Debye. $\quad$ 1 Debye = 10^{-18} esu·cm
  1 Debye = 3.3×10^{-30} C·m
- Charge of $e^{\ominus}$ = 4.8×10^{-10} esu
- μ is a vector quantity and directed ** $\oplus$ atom ⟶ $\ominus$ atom
  less EN ⟶ more EN

- ~~Pola~~ Polarity of a bond depends on ΔEN, while polarity of molecule depends on μ.

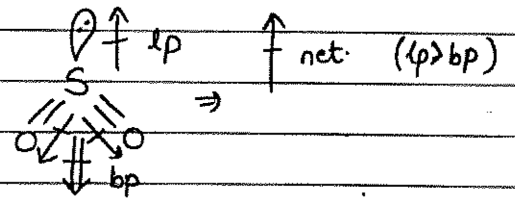
- μ of a molecule is vector sum of bond moments and lp moments.

- Generally lp moment > bp moment.

- lp moments : $sp > sp^2 > sp^3$

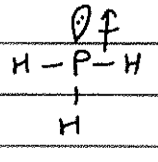
  % p ↑ ⇒ size of hybrid ↑ ⇒ charge density ↓ ⇒ tendency to shift ↓ ⇒ q ↓ ⇒ p ↓

→



- If everything's same, θ angle b/w μ_1 and μ_2 (μ of 2 bonds), θ ↑ ⇒ μ ↓.

— $\underset{\longleftarrow}{O=}C\underset{\longrightarrow}{=O}$ polar bonds, non polar molecule

— 

$\underline{\Delta EN = 0}$ non polar bonds, polar molecule

1. If C.A. has no lp, and all T.A. are same, $\mu = 0$

e.g. CS_2, BF_3, CCl_4, PCl_5, SF_6, IF_7, B_2H_6, Al_2Cl_6, ...

2. If molecule has V shape, T shape, pyramidal, $\mu \neq 0$

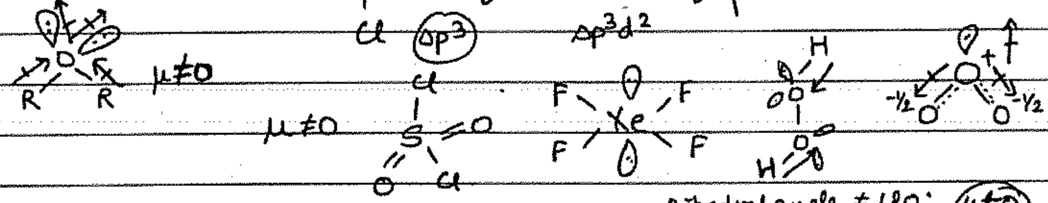
e.g. SO_2, H_2S, SF_2, NH_3, ClF_3, PF_3, BrF_3, ...

3. If C.A. has only 1 lp, then $\mu \neq 0$ (polar molecule ✓)

e.g. XeF_6, SF_4, PCl_3, $TeCl_4$, NF_3, ...

Q. Which of the following molecule is non polar?

a) $\overrightarrow{R-}\overleftarrow{O-R}$ b) $O=\overset{Cl}{\underset{Cl}{S}}=O$ c) XeF_4 ✓ ~~d)~~ H_2O_2 e) O_3



Dihedral angle ≠ 180° $\mu \neq 0$

Q. Which of these nitrogen oxides is non polar -

a) N_2O
b) N_2O_3
~~c)~~ N_2O_4
d) N_2O_5

① N_2O $\sigma = 2$ $lp = 0$ linear

~~$N \equiv N = O \Rightarrow \overset{-}{N} \equiv \overset{+}{N} = O$~~

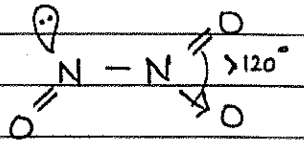
$N \equiv N \rightarrow O \Rightarrow N \equiv \overset{+}{N} - \overset{-}{O}$

$\Updownarrow$

$\overset{-}{N} = \overset{+}{N} = O = \underset{-}{N} = \overset{+}{N} = O$

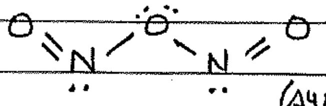
$\mu \neq 0$ polar. Resulting μ isn't too high,
as it gets lesser due to reso.

- ② N_2O_3



(Asymmetrical)

$1\,lp \Rightarrow \mu \neq 0$



(Symmetrical)

V shape around bridging O

$\mu \neq 0$

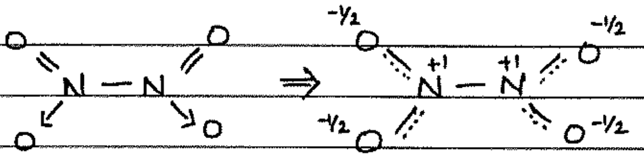
Also, N has only 1 lp ⇒ $\mu \neq 0$

$NO_2 + NO \xrightarrow[-23^\circ C]{250\ K} N_2O_3$

BROWN GAS @ 25°C — COLORLESS — (BLUE SOLID)

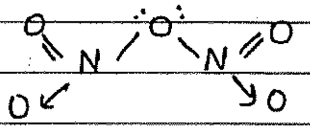
N_2O_3 @ 25°C = Blue liquid

③ N_2O_4



$\mu = 0$

④ N_2O_5



V around O_b ⇒ $\mu \neq 0$

Q. Which of these Nitrogen oxides has least N−N B.L.?

✓a) N_2O b) N_2O_3 c) N_2O_4 d) N_2O_5.

- μ and GEOMETRY ⇒

⇒ AX_2; $\mu = 0$ ⇒ Linear ⇒ sp, sp^3d

$sp \downarrow CO_2$

$sp^3d \downarrow XeF_2$

⟹ AX_2 ; $\mu \neq 0$ V shape ⇒ sp^2 sp^3

$$\begin{tikzcd} sp^2 \arrow[d] & sp^3 \arrow[d] \\ SO_2 & H_2O \end{tikzcd}$$

⟹ AX_3 $\mu = 0$ ⇒ Trigonal Planar = sp^2 (BCl_3)

$\mu \neq 0$ ⇒ Pyramidal = sp^3 (NH_3)

T = sp^3d (ClF_3) (1 lp)

⟹ AX_4 $\mu = 0$ ⇒ 90° = Square Planar = sp^3d^2, dsp^2 (XeF_4)

109°28' = Tetrahedral = sp^3 (CCl_4)

$\mu \neq 0$ ⇒ Distorted tetrahedral = sp^3d (SF_4)

⟹ AX_5 $\mu = 0$ ⇒ TBP = sp^3d (PCl_5)

Pentagonal Planar = sp^3d^3 (XeF_5^-)

$\mu \neq 0$ ⇒ Square pyramidal = sp^3d^2 (IF_5) (1 lp)

⟹ AX_6 $\mu = 0$ ⇒ SBP = sp^3d^2 (SF_6)

$\mu \neq 0$ ⇒ Distorted octahedral = sp^3d^3 (XeF_6) (1 lp)

⟹ AX_7 $\mu = 0$ ⇒ PBP = sp^3d^3 (IF_7)

$\mu \neq 0$ ⇒ not possible

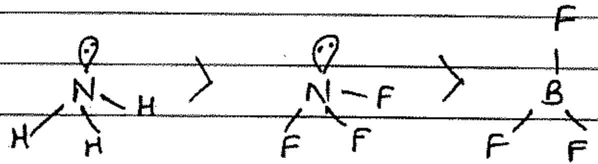
Q. Compare μ.

1. HF > HCl > HBr > HI

$$\xrightarrow{\hspace{2cm}} \quad \mu = q \times d \Rightarrow \underbrace{q \uparrow\downarrow}_{\Delta EN \downarrow} \underbrace{d \uparrow}_{size \uparrow} \Rightarrow {}^{*}\underline{\Delta EN}^{*}$$

2. $CH_3-Cl > CH_3-F > CH_3-Br > CH_3-I$

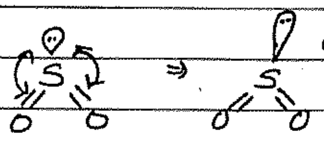
* size * * [illegible]

3. 

ⓐ see geometry
ⓑ see direction of all μ
ⓒ check ΔEN
ⓓ see 'θ' ($\theta \uparrow \; \mu \downarrow$)
e) reso, coordinate affect too.

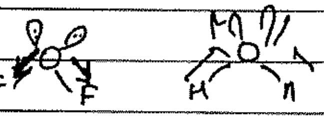
EXCEPT ⇒ $NH_3 < SO_2$

lp↑↑bp   lp↑↓bp.



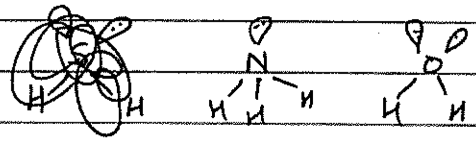
d ↑ ⇒ ↑ lp

4. $OF_2 < H_2O$

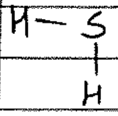


5. $H_2S < NH_3 < H_2O < HF$

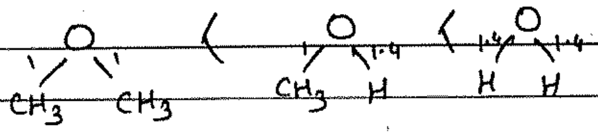
ⓐ all are polar
ⓑ $\Delta EN \uparrow$



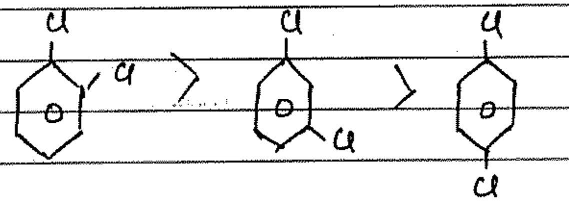
H — F



⑥ • ~~$O-CH_3$~~



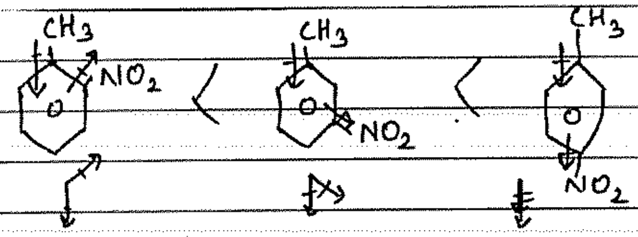
7.



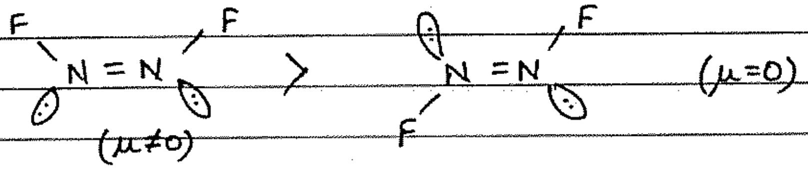
If both $e^\ominus$ withdrawing / $e^\ominus$ donor groups are present, then $\mu \Rightarrow$ o > m > p.

If one is $e^\ominus$ withdrawing and other is $e^\ominus$ donor, then $\mu \Rightarrow$ p > m > o.

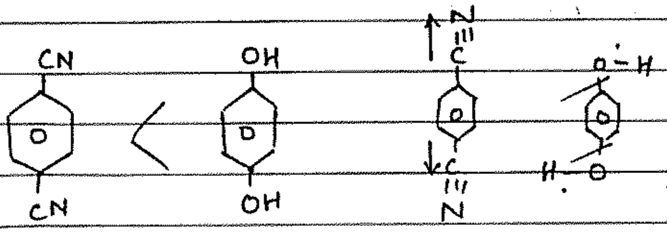
8.



9.



ɔ.



[illegible] can rotate.

$\mu \neq 0$

11. $(CH_3)_3-N\rightarrow O$ > $(CH_3)_3-P=O$

$(CH_3)_3-\overset{+}{N}-O^-$

12. $CH_3-\overset{\delta+}{C}\equiv\overset{\delta-}{N}$ < $CH_2=CH-\overset{\delta+}{C}\equiv\overset{\delta-}{N}$

$\updownarrow$ Add

$\overset{\oplus}{C}H_2-CH=C=N^{\ominus}$ Charge separation

13. C_2H_5-OH < $CH_3-C(=O)-\ddot{O}H \leftrightarrow CH_3-C(-\bar{O})=\overset{+}{O}H$

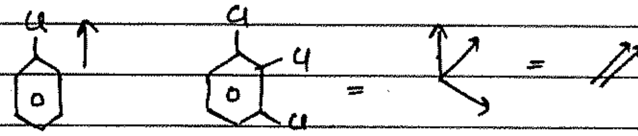
14. CH_3-F < CD_3-F (D is more ⊕ than H ; vibrational th.)

15. CH_3-Cl > CH_2-Cl_2 > $CH-Cl_3$ > CCl_4

1.8D 1.6D 1D $\mu=0$

Q) If μ of chloro ϕ is x, get μ of 1,2,3,-trichloro ϕ.

Ans



$= 2x$

Q. In which of these molecules $\mu\uparrow$ due to resonance:

a) $C\equiv O$

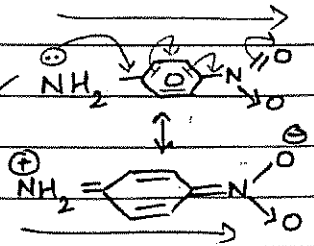
$\overset{-}{C}\equiv\overset{+}{O}$

$\mu = 0.112$ D

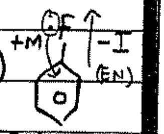
b) $CH_2=\overset{\delta+}{CH}-\overset{\delta-}{Cl}$

$\overset{\ominus}{C}H_2-CH=Cl^{\oplus}$

c) ✓



d)



$-I > +M$

* $\% \text{ i.c.} = 16(\Delta EN) + 3.5(\Delta EN)^2$

* $1\,D = 10^{-18}$ esu·cm $= 3.3 \times 10^{-30}$ C·m

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

- % ionic character $= \frac{\mu_{OBS.}}{\mu_{TH.}} \times 100$ (only for diatomic)

→ for A − B, $q_{TH.} = 1e$ $(A^+ B^-)$
for A = B, $q_{TH.} = 2e$

* **MOLECULAR ORBITAL THEORY :-**

- Drawbacks of VBT ⇒

→ It can't explain paramagnetic nature of O_2.

→ It can't explain bonding of odd $e^\ominus$ species.

→ —— " —— formation of H_2^+, He_2^+, etc.

- Both VBT and MOT are based on wave nature of $e^\ominus$.

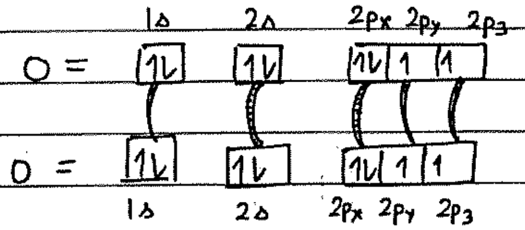
- —— " —— are based on combination of atomic orbitals.

- Acc. to VBT, atomic orbitals having unpaired $e^\ominus$ can combine with each other. But acc. to MOT, all atomic orbitals which have almost same energy and have same symmetry can combine with each other.
structural, not electronic.

- Acc. to VBT, 1 A.O + 1 A.O = 1 M.O.

- Acc. to MOT, 1 A.O + 1 A.O = 2 M.O $\left\{ \begin{array}{l} \rightarrow \text{ABMO (energy} \uparrow) \\ \rightarrow \text{BMO (energy} \downarrow) \end{array} \right.$

- MOT is based on linear combination of atomic orbitals.



- when 2 $e^{\ominus}$ waves (orbitals) combine ⇒

→ constructive ⇒ A_{net} ↑ ⇒ $I \propto A^2$ ⇒ I ↑ ⇒ E ↑ released.

probability to find $e^{\ominus}$ ↑ ↵

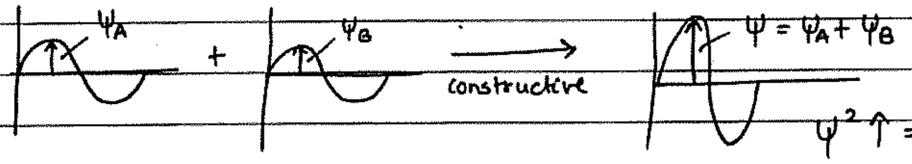
↳ bond formation

↳ BMO.

⇓

$E_{possess}$ ↓ ⇒ BMO (less energy)

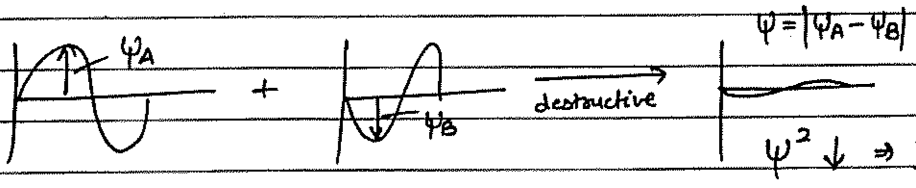
→ destructive ⇒ opposite. probability ↓ ⇒ no bond ⇒ ABMO.



ψ^2 ↑ ⇒ I ↑

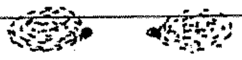
BMO

⇒ $e^{\ominus}$ density b/w nuclei ↑



ψ^2 ↓ ⇒ I ↓

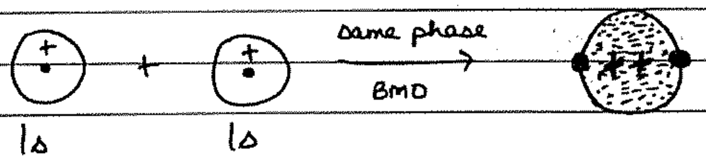
⇒ $e^{\ominus}$ density b/w nuclei ↓



ABMO

LINEAR COMBINATION OF ATOMIC ORBITALS ⇒

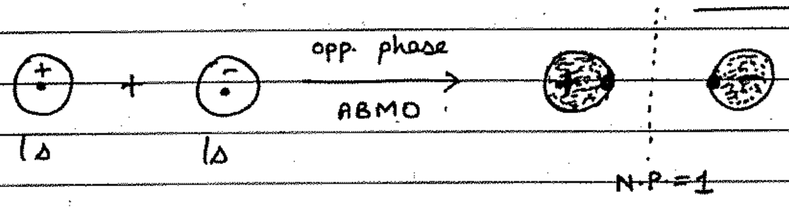
1. 1s – 1s axial →



σ_{1s} GERADE (symmetrical M.O.)

Nodal plane = 0

UNGERADE (asymmetrical M.O.)



σ^*_{1s}

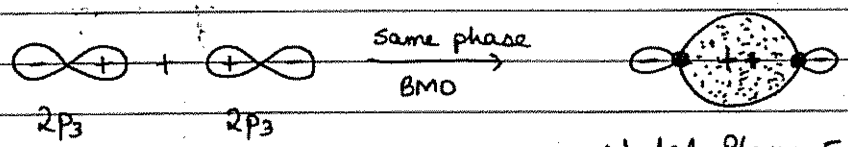
No. of NP = 0 or even = Gerade.
No. of NP = odd = Ungerade.

first flip MO along 180° INA, then 180° ⊥ INA.
If signs change ⇒ Ungerade

2. 2s – 2s axial →

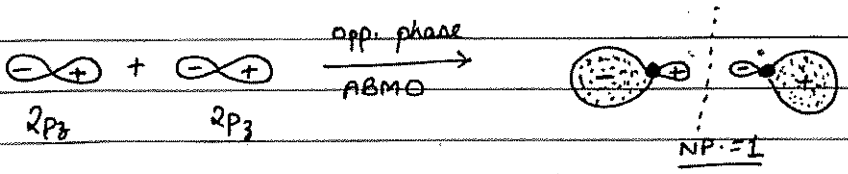
$2s + 2s = 2\ MO$ → σ^*_{2s}, σ_{2s}

3. $2p_z - 2p_z$ axial → z axis = INA



σ_{2p_z}

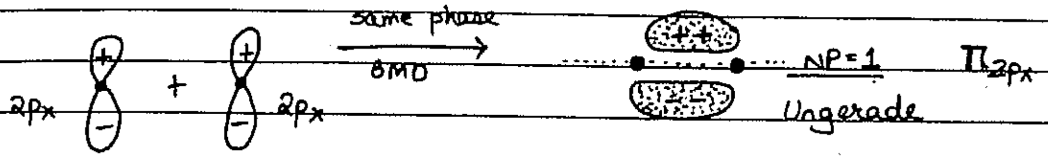
Nodal Plane = 0 Gerade

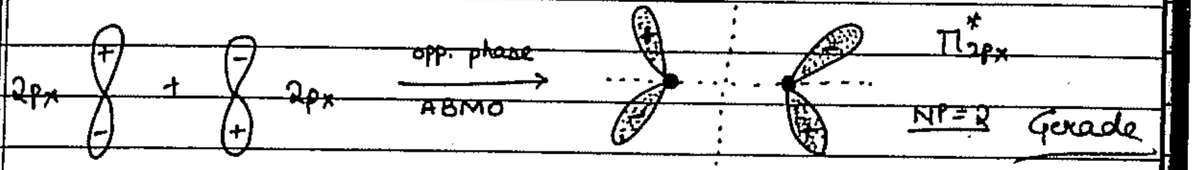


$\sigma^*_{2p_z}$

Ungerade

4. $2p_x - 2p_x$ colateral → Z = INA

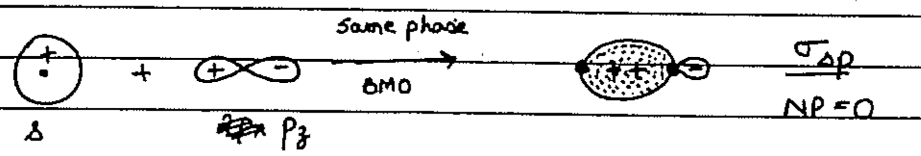


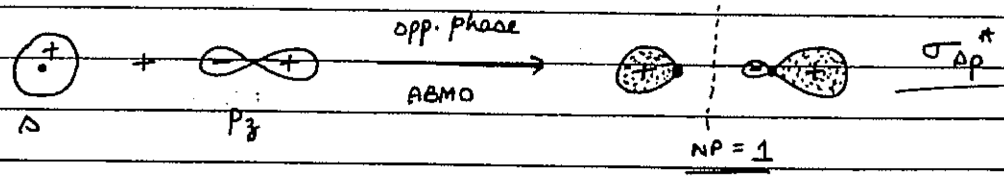


5. $2p_y - 2p_y$ colateral → Z = INA

$2p_y + 2p_y = 2$ M.O. $\to \pi^*_{2py}$, π_{2py}

6. $s + p_z$ (axial) → Z = INA





Q. Pair of degenerate orbitals are: (Energy levels perfectly orbital) [n+l]

a) 1s, 2s
b) 2s, $2p_z$
c) $2p_x$, $2p_y$
d) $3d_{z^2}$, $3d_{x^2-y^2}$
e) π_{2px}, π_{2py} ($p_x - p_y$ colateral BMO)
f) σ_{2p_z}, $\sigma^*_{2p_z}$ ($\sigma_{2p_z} < \sigma^*_{2p_z}$)
g) π^*_{2px}, π^*_{2py}
h) σ_{2p_z}, π_{2px} (colateral - axial)

• • ENERGY LEVELS OF M.O. ⇒

A) for molecular species having $Z \geq 8$ (14 $\overset{2\uparrow}{\cancel{\text{or}}}$ more $e^{\ominus}$)

$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \underline{\underline{\sigma_{2p_z} < \pi_{2p_x} = \pi_{2p_y}}} < \pi^*_{2p_x} = \pi^*_{2p_y} < \sigma^*_{2p_z}$

B) For molecular ~~[illegible]~~ species having $Z < 8$ (≤ 14 $e^{\ominus}$)

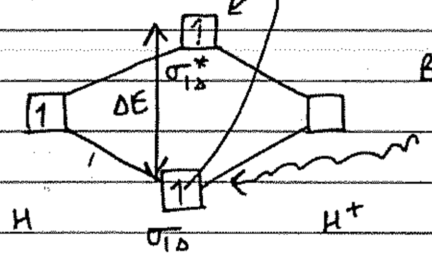
$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \underbrace{\pi_{2p_x} = \pi_{2p_y} < \sigma_{2p_z}}_{s-p_z \text{ mixing}} < \pi^*_{2p_x} = \pi^*_{2p_y} < \sigma^*_{2p_z}$

• BOND ORDER ⇒ ⊕, ⊖, 0 or fractional

⇒ $B.O. = \dfrac{N_{BMO} - N_{ABMO}}{2}$

→ B.O. negative: only at a pt. of time.

H_2^+



B.E. > ΔE

$\Rightarrow BO. = \dfrac{0-1}{2} = \dfrac{-1}{2}$

(w/o bond break)

→ For diatomic species $BL \propto \dfrac{1}{BO}$

$BS \propto \text{Stability} \propto BO$

→ Isoelectronic species have same B.O. and magnetic nature but BL and BS differ.

classmate
Date
Page

→

No. of $e^{\ominus}$	10	11	12	13	14	15	16	17	18	19	20
B.O.	1	1.5	2	2.5	3	2.5	2	1.5	1	0.5	0
Mag. nature			Dia		Dia				Dia		X
No. of unpaired $e^{\ominus}$	2	1	0	1	0	1	2	1	2	1	X

→ B.E. $N\equiv N < C\equiv O$ both have 14 $e^{\ominus}$; B.O. = 3; dia

→ If 2 molecular species (having same atoms) have same B.O.; then species which has less ABMO $e^{\ominus}$, is more stable.

Q. Write $e^{\ominus}$ config. Of O_2 and explain its paramagnetism.

Ans $O_2 = 16\,e^{\ominus} \Rightarrow \sigma_{1s}^{2}\ \sigma_{1s}^{*2}\ \sigma_{2s}^{2}\ \sigma_{2s}^{*2}\ \sigma_{2p_z}^{2}\ \pi_{2p_x}^{2} = \pi_{2p_y}^{2}\ \underbrace{\pi_{2p_x}^{*1} = \pi_{2p_y}^{*1}}_{\text{paramagnetic}}\ \sigma_{2p_z}^{*0}$

$Z=8$

$$B.O. = \frac{BMO - ABMO}{2} = \frac{10-6}{2} = \underline{\underline{2}} \qquad O=O$$

HOMO = Highest occupied MO = $\pi^{*}_{2p_x}$ or $\pi^{*}_{2p_y}$
LUMO = Lowest unoccupied MO = $\sigma^{*}_{2p_z}$

Q. Compare stability of H_2, H_2^+ and H_2^-.

Ans

H_2	H_2^+	H_2^-	
$2e^{\ominus}$	$1e^{\ominus}$	$3e^{\ominus}$	
σ_{1s}^{2}	σ_{1s}^{1}	$\sigma_{1s}^{2}\ \sigma_{1s}^{*1}$	
1	0.5	0.5	B.O.

Stability: $H_2 > H_2^+ > H_2^-$

Q. • ~~Assert~~ Assertion : B_2 is paramagnetic (B)

Reason : HOMO for B_2 is π_{2p_x}

Ans $B_2\ (10\ e^{\ominus}) \Rightarrow \sigma_{1s}^2\ \sigma_{1s}^{*2}\ \sigma_{2s}^2\ \sigma_{2s}^{*2}\ \underbrace{\pi_{2p_x}^1 = \pi_{2p_y}^1}_{HOMO}\ \underbrace{\sigma_{2p_z}}_{LUMO}$

$B.O. = \frac{6-4}{2} = \underline{\underline{1}} \quad \left[\underset{\underline{(\pi)}}{B - B}\right]$

Q. Compare ~~the~~ C−C B.S. of C_2 and C_2H_4.

Ans $C_2 = 12e^{\ominus} = \sigma_{1s}^2\ \sigma_{1s}^{2*}\ \sigma_{2s}^2\ \sigma_{2s}^{2*}\ \pi_{2p_x}^2\ \pi_{2p_y}^2$

$B.O. = \frac{4}{2} = 2 \Rightarrow \underline{C = C}$ (both are π)

$\underline{B.S.}\quad \underset{2\pi}{C = C} < \underset{1\sigma,\ 1\pi}{H_2C = CH_2}$

Q. Pair of species which do not exist :

a) H_2^+, H_2^-

b) He_2, Li_2 $\quad He_2$ doesn't exist. Li_2 exists in vapour ~~state~~ state.

~~c)~~ Be_2, Ne_2

d) He_2^+, S_2 $\quad S_2 \Rightarrow B.O = 2$, like O_2 ; exists in vapour state

---

Q. which of these is not correct :-

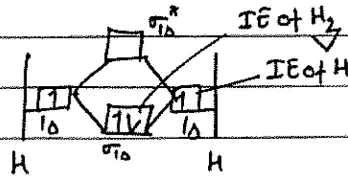
a) $H_2 > H$ IP

b) $O_2 < O$ IP

c) $NO > NO^+$ Magnetic moment

d) $KO_2 < O_2^+[AsF_6]^-$ O−O B.S.

✓e) $CO < CO^+$ B.L.



$\underset{15e^{\ominus}}{NO} > \underset{14e^{\ominus}}{NO^+}$ spin M.M. $= \sqrt{n(n+2)}$

KO_2 < $O_2^+[AsF_6]^-$ B.S.
$17e^\ominus$ (1.5) $15e^\ominus$ (2.5)

CO > CO^+ B.L. 9^{th} and 10^{th} $e^\ominus$ of 2^{nd} shell enter
$14e^\ominus$ (3) $13e^\ominus$ ($\cancel{2.5}$) into NBMO. in CO. As 1 $e^\ominus$ is
$\boxed{3.5}$ taken out of CO for CO^+, it is taken out of NBMO. So, $\overset{G_1 \text{(due to NBMO)}}{\text{bekaar}}$ ka $\overset{\text{inter}}{e^\ominus}$ repulsion ↓ ⇒ attraction ↑ ⇒ BL ↓. This NBMO also has some ABMO character as Energy diff. is ↓↓. So, as that $e^\ominus \longrightarrow$ ⇒ B.O ↑ by 0.5 and B.L. ↓.

Q. Compare B.O., magnetic nature, B.L., B.S. and IE.

1.

O_2	O_2^+	O_2^-	O_2^{2-}
16	15	17	18
2	2.5	1.5	1
Para	Para	Para	Dia.
$\pi^{*1}_{2px}/\pi^{*1}_{2py}$	π^{*1}_{2px}	$\pi^{*2}_{2px}=\pi^{*1}_{2py}$	$\pi^{*2}_{2px}=\pi^{*2}_{2py}$

HOMO (all ABMO; for IP)

None are O.A. (No one wants to get more $e^\ominus$ in ABMO to lower stability).
All are R.A.

B.L. ⇒ $O_2^+ < O_2 < O_2^- < O_2^{2-}$ B.S. ⇒ $O_2^+ > O_2 > O_2^- > O_2^{2-}$
IE ⇒ $O > O_2^+ > O_2 > O_2^- > O_2^{2-}$
(charge)

2.

N_2	N_2^+	N_2^-	N_2^{2-}
14	13	15	16
3	2.5	2.5	2
Dia	Para	Para	Para
σ^2_{2pz}	σ^1_{2pz}	π^{*1}_{2px}	$\pi^{*1}_{2px}=\pi^{*1}_{2py}$

HOMO

N_2^+ = O.A.
N_2^-, N_2^{2-} = R.A.

Stability : $N_2 > N_2^+ > N_2^- > N_2^{2-}$ (B.O)
B.L. : $N_2 < N_2^+ < N_2^- < N_2^{2-}$
IP : $N_2^+ > N_2 > N > N_2^- > N_2^{2-}$

$\boxed{IP \propto \frac{\oplus}{\ominus}}$

3.

NO^+	NO	NO^-	NO^{2-}
14	15	16	17
3	2.5	2	1.5
Dia	Para	Para	Para
$\sigma_{2p_z}^2$ ~~$\pi^{*1}_{2p_x} = \pi^{*1}_{2p_y}$~~	$\pi^{*1}_{2p_x}$ ~~$\pi^{*}_{2p_y}$~~	$\pi^{*1}_{2p_x} = \pi^{*1}_{2p_y}$	$\pi^{*2}_{2p_x} = \pi^{*1}_{2p_y}$

HOMO(acc. to N)

O.A. = None
R.A. = NO, NO^-, NO^{2-}

Stability/BO :- $NO^+ > NO > NO^- > NO^{2-}$ >N>
B.L ⇒ $NO^+ < NO < NO^- < NO^{2-}$ I.P. :- $NO^+ \geq NO > NO^- > NO^{2-}$

Q. O_2 and N_2^{2-} differ in :-

✓a) BL   b) BO   c) Magnetism   ✓d) Energy level of σ_{2p_z} and π_{2p_x}

Q. If sp$_z$ mixing is not observed, then which of these change their magnetic nature?

a) B_2	✓b) C_2	c) C_2^{2-}	d) N_2^+	e) O_2	f) B_2^+
Para	Dia	~~Para~~ Dia	Para	Para	Para
			$13e^\ominus$		$9e^\ominus$
			always para		always para

$B_2 = \sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p_z}^2$ dia

$C_2 =$ ———"——— $2p_z^2$ $\pi^1_{2p_x} = \pi^1_{2p_y}$ para

$C_2^{2-} =$ ———"——— $\sigma 2p_z^2$ $\pi^2_{2p_x} = \pi^2_{2p_y}$ dia

Q. Color of halogens is due to :

a) d-d transition
~~b)~~ $e^\ominus$ transition from HOMO to LUMO
c) polarisation
d) presence of unpaired $e^\ominus$

F_2 = light yellow
Cl_2 = greenish yellow
Br_2 = reddish brown
I_2 = violet

* **OXYACIDS :-** $\boxed{C.A} - OH$

$\uparrow$ NM or Cr^{6+} or Mn^{7+}

- Acidic oxide + $H_2O \longrightarrow$ oxyacid.

- $SO_3 + H_2O \longrightarrow H_2SO_4$
- $Cl_2O_7 + H_2O \longrightarrow 2\,HClO_4$
- $Mn_2O_7 + H_2O \longrightarrow 2\,HMnO_4$
- $CrO_3 + H_2O \longrightarrow H_2CrO_4$ [CHROMIC ACID]
- $N_2O_3 + H_2O \longrightarrow 2\,HNO_2$

No change in O.S.

- $\overset{+4}{N_2O_4} + H_2O \longrightarrow \overset{+3}{HNO_2} + \overset{+5}{HNO_3}$ (<u>Disproportionation</u>)
  (2 NO_2)
  $\downarrow$
  ~~$HNO_3 + NO$~~
- $\overset{+6}{Cl_2O_6} + H_2O \longrightarrow \overset{+7}{HClO_4} + \overset{+5}{HClO_3}$ (— " —)

- oxyacid − $H_2O \longrightarrow$ oxide
  (anhydride of parent oxyacid)

- N_2O_5 is anhydride of ? ⇒ $N_2O_5 + H_2O \rightarrow 2\,HNO_3$
  ⇒ anhydride of nitric acid

- Anhydride of HNO_2 = ? $2\,HNO_2 \mp H_2O \rightarrow N_2O_3$ = nitric oxide

- N_2O_4 is anhydride of ? ⇒ It is a mixed anhydride of
  (or NO_2) HNO_2 and HNO_3 both.

- pyro ···· acid

→ 2 mol oxyacid $- H_2O \longrightarrow$ pyro···acid

- $2\ H_2SO_4 - H_2O \longrightarrow H_2S_2O_7$

sulphuric acid pyrosulphuric acid

→ All pyroacids contain oxy linkage $(X-O-X)$ except pyrosulphurous acid. $(H_2S_2O_5)$

- Hypo ···· ic acid

→ pyro ····ic acid $- [O] \longrightarrow$ Hypo ···· ic acid

$[X-O-X]$ $[X-X]$

Q. Classify oxyacids which can form their pyroacids –

H_3BO_3, HNO_3, H_3PO_3, H_4SiO_4, $HClO_4$, $HClO_2$

✓ ✗ ✓ ✓ ✗ ✗

(At least 2 H should be there in oxyacid.)

- meta ····acid

→ oxyacid $- H_2O \longrightarrow$ meta···acid

- $H_3PO_4 - H_2O \longrightarrow HPO_3$

(ortho) phosphoric acid metaphosphoric acid

If any parent oxyacid is capable of creating meta··acid, then ortho prefix can be used before name of parent oxy acid.

Q* Classify oxyacids which have ortho prefix -

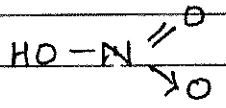
H_3BO_3, H_3PO_3, H_2SO_4, HNO_2, $HClO_3$, H_4SiO_4.

✓ ✓ X X X ✓

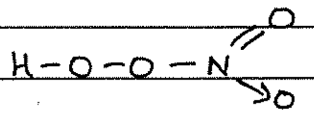
(At least 3H should be there in parent)

• per-oxyacid - which contains peroxy linkage $[\overset{\delta-}{-O}-\overset{\delta-}{O}-]$

→ $HNO_3 \xrightarrow{+[O]} HNO_4$



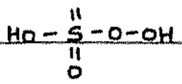
Nitric Acid



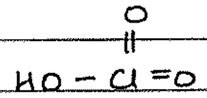
Pernitric acid

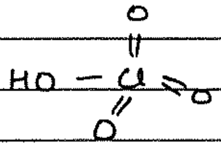
→ $H_2SO_4 \xrightarrow{+[O]} H_2SO_5$ peroxy sulphuric acid or

[CARO'S ACID] persulphuric acid



→





(But not true per…acid)

+5 Chloric Acid $\xrightarrow{O.S.\ High}$ +7 Perchloric acid ✓

→ $\overset{+6}{H_2MnO_4}$ $\overset{+7}{HMnO_4}$ (C.A. की O.S. ic acid से ज्यादा ⇒ per-ic acid बोल सकते हैं)

~~Magnic Acid~~ ~~permagnic acid~~

~~Q. peroxy linkage is absent in:~~

~~a) H_3PO_5~~ ~~b) CrO_5~~ ~~c) H_3O_2~~ ~~d) O_2F_2~~

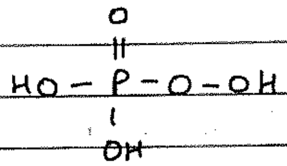
~~Calculated O.S. = +7~~ ~~Cal. = +10~~

~~Max O.S. = +5~~ ~~Max = +6~~

~~⇒ 1 peroxy~~ ⇒ 2 peroxy

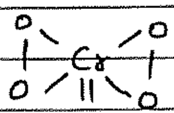
Q.• peroxy linkage is absent in:-

a) H_3PO_5 Cal. O.S. = +7 Max OS = +5



$HO-P(=O)(OH)-O-OH$

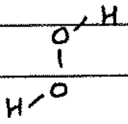
b) CrO_5 Cal. = +10 Max = +6



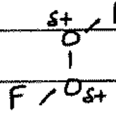
cyclic (NO H) PEROXIDE (PEROXY IN OXIDE)

(highly unstable 3 memb. ring)

c) H_2O_2

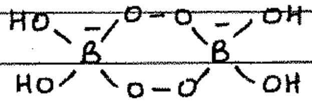


~~d)~~ O_2F_2



(not true peroxy)

e) $B_2(O)_4(OH)_4^{2-}$



$$\text{No. of peroxy linkage (one C.A.)} = \frac{\text{Cal. O.S.} - \text{Max. O.S.}}{2}$$

$$\text{No. of peroxy linkage (2 C.A.)} = \text{Cal. O.S.} - \text{Max. O.S.}$$

- If an element makes oxyacids only from 1 O.S., then ⇒ ... ic acid [B(+3), C(+4), Si(+4)]

- If an element makes oxyacids from 2 O.S., then less O.S. [-ous acid], more O.S. [-ic acid] [S(+4), S(+6)]

- If an element makes oxyacids from 3 O.S., then

	least O.S.	middle O.S.	more O.S.
	[hypo ....ous]	[....ous]	[... ic]
N, P ⇒	+1	+3	+5

•• If an element makes oxyacids from 4 O.S., then

Cl/Br/I +1 +3 +5 +7
[Hypo .... ous] [.... ous] [.... ic] [per .... ic]

• .... ous acide $\xrightarrow{-\text{all } H^+}$ .... ite

— $\overset{+1}{HOCl} \xrightarrow{-H^+} {}^-OCl$
Hypo Chlorous acid Hypochlorite

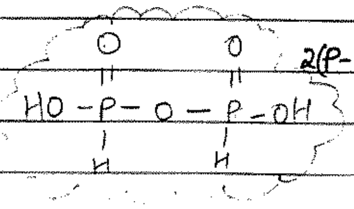
• .... ic acid $\xrightarrow{-\text{all } H^+}$ .... ate

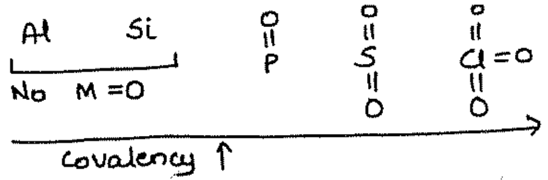
— $H_4P_2O_7 \xrightarrow[+4\,NaOH]{-4H^+} P_2O_7^{-4}$
Pyrophosphoric acid
$\downarrow$ 2 NaOH
$\underbrace{2Na^+ + H_2P_2O_7^{2-}} + 2H_2O$
Sodium dihydrogen pyrophosphate

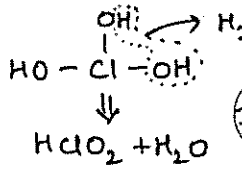
— $H_2CO_3 \xrightarrow{-H^+} HCO_3^- \xrightarrow{-H^+} CO_3^{2-}$
bicarbonate
OR
hydrogen carbonate

• Basicity of oxyacid = No. of H atoms <u>except</u>

$H_4P_2O_5$, H_3BO_3, H_3PO_3, H_3PO_2,
2(P-H) ② ①(L.A.) ② 1(P-H) ② 2(P-H)



* 



12↑gt ⇒ ΔS = (+)

Bonds strong ⇒ ΔH = (−)
अत
ΔG = (−)

Oxyacids of N :

(+1) Hyponitrous acid

(+3) Nitrous acid

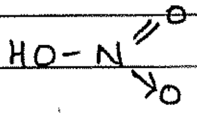
(+5) Nitric acid

HO − N = N − OH

$H_2N_2O_2$

HO − $\ddot{N}$ = O

HNO_2



HNO_3

Oxyacids of Cl :

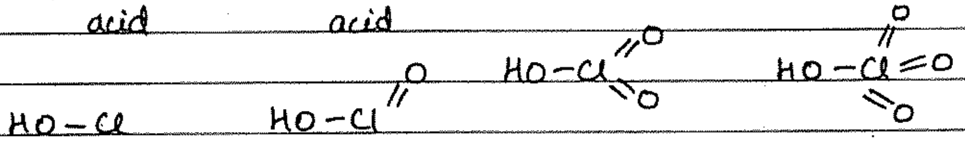
(+1) HypoChlorous acid

(+3) Chlorous acid

(+5) Chloric acid

(+7) Perchloric acid

(sp³ all)



HOCl $HClO_2$ $HClO_3$ $HClO_4$

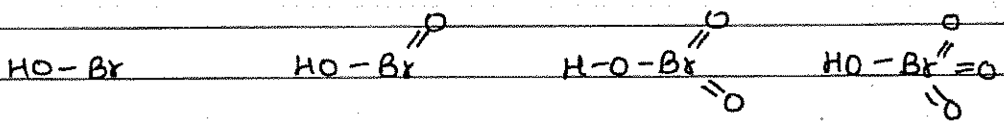
Oxyacids of Br :

(+1) Hypobromous

(+3) Bromous

(+5) Bromic

(+7) Perbromic



HOBr $HBrO_2$ $HBrO_3$ $HBrO_4$

Oxyacids of I :

(+1) Hypoiodous

(+3) Iodous

(+5) Iodic

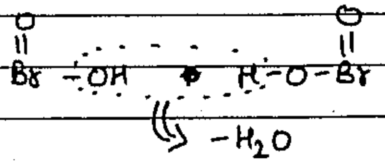
(+7) Periodic

HOI ~~HIO~~ HIO_2 HIO_3 HIO_4

→ $HBrO_2$ and HIO_2 exist only in solution form, not in (Δ).

$HBrO_2\ (aq.) \rightleftharpoons H^+ + BrO_2^-$

$HBrO_2\ (\Delta) \Rightarrow$



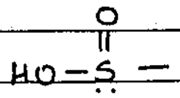
$\overset{\overset{O}{\|}}{Br}-OH + H-O-\overset{\overset{O}{\|}}{Br} \xrightarrow{-H_2O}$

→ Only possible oxyacid of F is HOF (max. covalency = 1)
F ⇒ O.S. = −1   O ⇒ O.S. = 0.   Hypoflorous acid (acc. to others)

- Oxyacids of S : sp^3, always

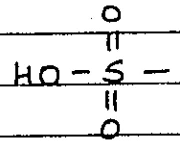
Common O.S.		③ +3	+5
+4	+6	Thionous	Thionic
Sulphurous	Sulphuric	[S – S bond]	

-ous acid :-



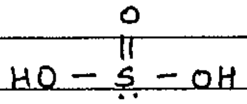
$HO-\overset{\overset{O}{\|}}{\underset{\cdot\cdot}{S}}-$

-ic acid :-



$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-$

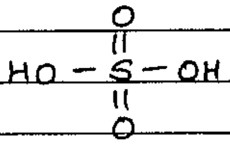
→ Sulphurous acid :



$HO-\overset{\overset{O}{\|}}{\underset{\cdot\cdot}{S}}-OH$

H_2SO_3
doesn't exist in (Δ)
exists only in aq.

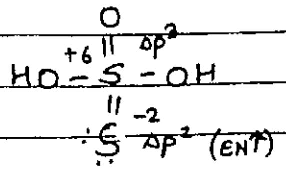
→ Sulphuric acid :



$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$

H_2SO_4

→ Thio Sulphuric acid :

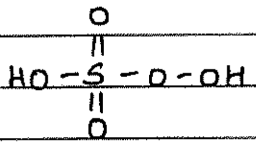


$HO-\overset{\overset{O}{\|}\ sp^3}{\overset{+6}{S}}-OH$, $\underset{\cdot\cdot}{\overset{\|}{S}}\ \overset{-2}{sp^2}$ (EN↑)

$H_2S_2O_3$
$\big\downarrow -2H^+$
Thio sulphate ⇒ $S_2O_3^{2-}$

Av. O.S. = +2
(Min. O.S. in oxyacid)

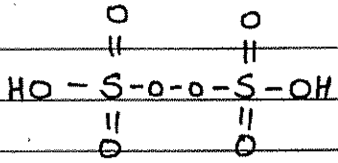
→ • H_2SO_5 Cal. O.S. = +8 Max = +6 ⇒ peroxy = 1



$HO-\underset{\underset{O}{\parallel}}{\overset{\overset{O}{\parallel}}{S}}-O-OH$ [Caro's Acid = Peroxy Sulphuric Acid]

→ Peroxy disulphuric acid

~~-o-o- 2S ic~~



$HO-\underset{\underset{O}{\parallel}}{\overset{\overset{O}{\parallel}}{S}}-O-O-\underset{\underset{O}{\parallel}}{\overset{\overset{O}{\parallel}}{S}}-OH$

$H_2S_2O_8$
MARSHALL ACID

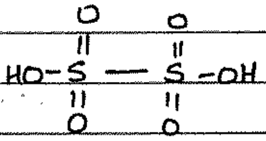
→ Thionous Acid

$OH-\overset{\overset{O}{\parallel}}{\ddot{S}}-\overset{\overset{O}{\parallel}}{\ddot{S}}-OH$

$H_2S_2O_4$

→ $H_2S_2O_6$ Cal. O.S. = ~~+10~~ +5 ~~Max = +6 ⇒ peroxy = 4~~

Thionic Acid

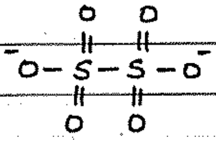


$HO-\underset{\underset{O}{\parallel}}{\overset{\overset{O}{\parallel}}{S}}-\underset{\underset{O}{\parallel}}{\overset{\overset{O}{\parallel}}{S}}-OH$

(Hypo sulphuric Acid)

$\downarrow -2H^+$

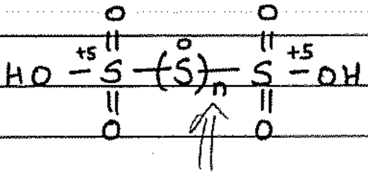
$S_2O_6^{2-}$
THIONATE



$^-O-\underset{\underset{O}{\parallel}}{\overset{\overset{O}{\parallel}}{S}}-\underset{\underset{O}{\parallel}}{\overset{\overset{O}{\parallel}}{S}}-O^-$

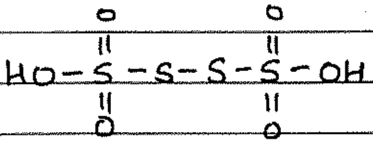
only 1 kind of bond (S-O) ⇒ resonance.

→ Poly thionic Acid



$HO-\underset{\underset{O}{\parallel}}{\overset{\overset{O}{\parallel}}{\overset{+5}{S}}}-(\overset{0}{S})_n-\underset{\underset{O}{\parallel}}{\overset{\overset{O}{\parallel}}{\overset{+5}{S}}}-OH$

- Tetra thionic acid



$HO-\underset{\underset{O}{\parallel}}{\overset{\overset{O}{\parallel}}{S}}-S-S-\underset{\underset{O}{\parallel}}{\overset{\overset{O}{\parallel}}{S}}-OH$

$H_2S_4O_6$

$\downarrow -2H^+$

Tetrathionate $S_4O_6^{2-}$

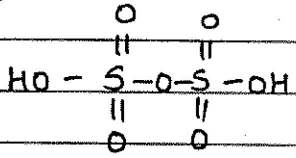
No. of S-S bond = $(n-1) = 4-1 = 3$

No. of S which show 0 O.S. = 2 $[(n-2)]$

→ Pyro sulphuric acid $2\ H_2SO_4 - H_2O \rightarrow H_2S_2O_7$

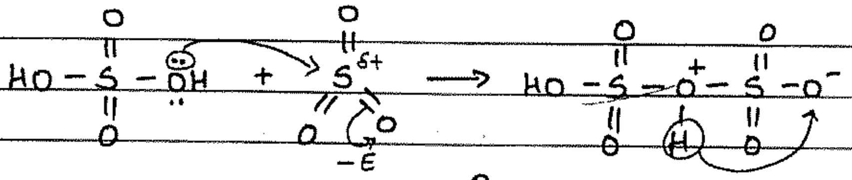
OLEUM

2S   ic

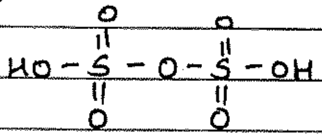

$HO-S(=O)_2-O-S(=O)_2-OH$

(All pyro have X−O−X except pyrosulphurous)

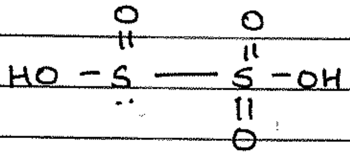
Preparation :



($H_2SO_4 + SO_3 \rightarrow H_2S_2O_7$)


$HO-S(=O)_2-O-S(=O)_2-OH$

→ Pyro Sulphurous Acid


$HO-S(=O)-S(=O)_2-OH$

$H_2S_2O_5$

2S   +4 = ~~ous~~

↓ +3 ous   ↓ +5 ic

→ $H_2S_2O_3$ → S have different o.s. Thio Sulphuric

$H_2S_2O_4$ (S−S)

$H_2S_2O_5$ → S have different o.s. Pyrosulphurous

$H_2S_2O_6$

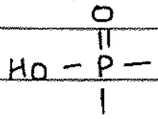
$H_2S_2O_7 \rightarrow$ (S−O−S) oleum $\xrightarrow{\text{hydrolysis}}$ H_2SO_4

$H_2S_2O_8 \rightarrow$ (O−O) Marshall's acid $\xrightarrow{\text{hydrolysis}}$ $H_2SO_4 + H_2O_2$

MOP

- Oxyacids of P :- sp^3

Always $\overset{O}{\overset{\|}{P}}$.

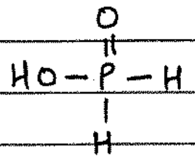

$HO-P(=O)-$

(+1)	(+3)	(+5)
Hypo····ous	····ous	····ic
[H−P−H]	[P−H]	[No P−H]

oxyacids of P that have P–H ⇒ **RA**

→ • **Hypophosphorous acid / Phosphinic acid**

+1



$HO-P(=O)(H)-H$

H_3PO_2 Basicity = 1

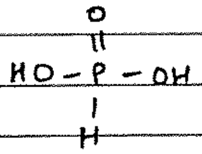
At time of O·S· calculation, in P–H, H is electropositive. So, O·S· of P = +1, not +3.

$H_3PO_2 \xrightarrow{-H^+} H_2PO_2^-$ (HYPOPHOSPHITE)

Tautomerism ✓

→ **Phosphorous acid / Phosphonic acid**

+3

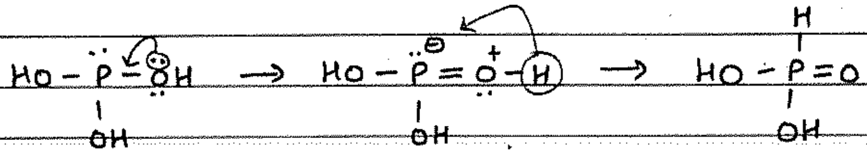


$HO-P(=O)(H)-OH$

H_3PO_3 **Basicity = +2**

Tautomerism ✓ in here

BB is good, as O·S· of P = +3 ⇒ $e^\ominus$ gain ↑

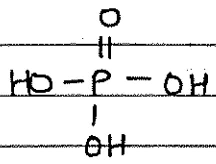


phosphorous acid

phosphonic acid (major)

→ **Phosphoric acid**

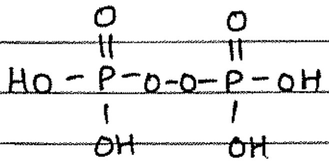
+5



$HO-P(=O)(OH)-OH$

Basicity = 3

→ **$H_4P_2O_8$** Cal. O·S· = ~~+7~~ +6 Max (real) = +5 ⇒ Peroxy = 1



$HO-P(=O)(OH)-O-O-P(=O)(OH)-OH$

peroxy di phosphoric acid

• • HEATING EFFECT OF H_3PO_4 ⇒

$$2\,H_3PO_4 \xrightarrow[-H_2O]{200^\circ C} \underset{\text{pyrophosphoric}}{H_4P_2O_7} \xrightarrow[-H_2O]{600^\circ C} H_2P_2O_6 = \underset{\text{meta phosphoric}}{2\,HPO_3}$$

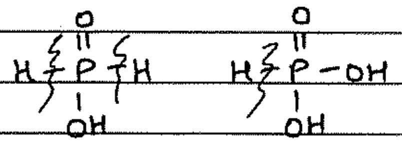
$$2\,HPO_3 \xrightarrow[-H_2O]{\Delta} P_2O_5$$

exists as P_4O_{10} ⇐ P_2O_5

• HEATING EFFECT OF H_3PO_2 and H_3PO_3 ⇒

→ Oxyacid of P which contains P–H can act as R.A. or give disproportionation reaction on heating.

$\Delta EN_{P-H} = 0$ ⇒ no additional B.S. ⇒ can be broken.



addition of O = removal of H = oxidation

RA

$$\overset{+1}{H_3PO_2} + AgNO_3 + 2H_2O \longrightarrow \overset{+5}{H_3PO_4} + Ag\downarrow + HNO_3$$

R.A. O.A. silver mirror

$$\overset{+3}{H_3PO_3} + Ag_2O \longrightarrow \overset{+5}{H_3PO_4} + 2Ag\downarrow \text{ (silver mirror)}$$

RA OA

$$Ag_2O \Leftarrow AgNO_3 + NH_4OH$$

$$\Downarrow$$

$$[Ag(NH_3)_2]^+NO_3^-$$ Tollen's reagent

→ Same for H_3PO_2

$$\underset{+3}{H_3PO_3} \xrightarrow{\Delta} \underset{+5}{H_3PO_4} + \underset{-3}{PH_3} \text{ (disproportionation)}$$

• HEATING EFFECT OF H_3BO_3

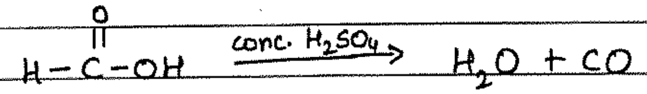
$$H_3BO_3 \xrightarrow[-H_2O]{170^\circ C} HBO_2$$ MetaBoric Acid

$$4HBO_2 \xrightarrow[-H_2O]{300^\circ C} H_2B_4O_7 \xrightarrow[-H_2O]{\Delta} 2\,B_2O_3$$ Boric Anhydride

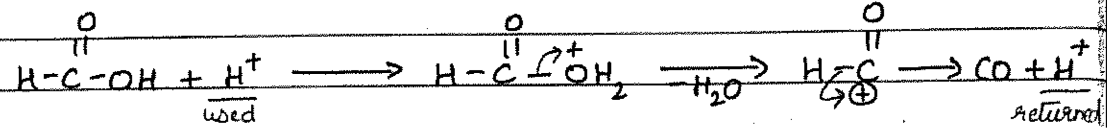
Boron Sesqui oxide

DEHYDRATING AGENT -

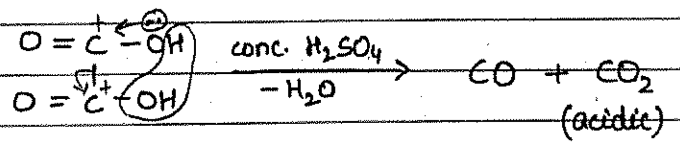
Conc. H_2SO_4, P_4O_{10}, anhydrous $CaCl_2$, ionic hydrides, etc act as dehydrating agents



→ $H-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{conc.\ H_2SO_4} H_2O + CO$

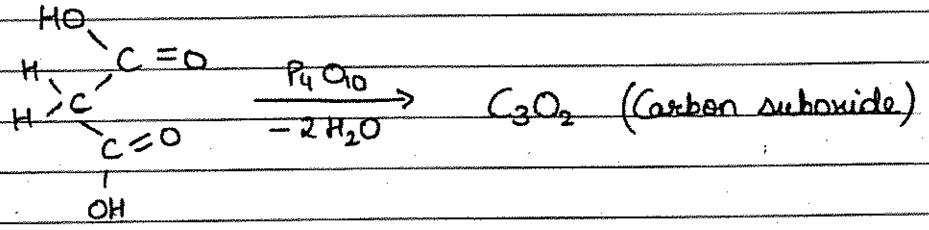


$H-\overset{O}{\overset{\|}{C}}-OH + \underset{used}{H^+} \longrightarrow H-\overset{O}{\overset{\|}{C}}-\overset{+}{O}H_2 \xrightarrow{-H_2O} H-\overset{O}{\overset{\|}{C}}{}^{\oplus} \longrightarrow CO + \underset{returned}{H^+}$



→ alic Acid

$\begin{matrix} O=\overset{+}{C}-\overset{\ominus}{O}H \\ O=\overset{+}{C}-OH \end{matrix} \xrightarrow[-H_2O]{conc.\ H_2SO_4} CO + \underset{(acidic)}{CO_2}$



→ alonic Acid

$\xrightarrow[-2H_2O]{P_4O_{10}}$ C_3O_2 (Carbon suboxide)

→ $2HClO_4 \xrightarrow[-H_2O]{P_4O_{10}} Cl_2O_7$

→ $2HNO_3 + P_4O_{10} \longrightarrow \underset{(MOP)}{\underline{N_2O_5}} + \underset{metaphosphoric\ acid}{HPO_3}$

→ $\underset{(sugar)}{C_{12}H_{22}O_{11}} \xrightarrow{conc.\ H_2SO_4} \underset{(black\ mass)}{12C} + 11H_2O$ [CHARRING OF SUGAR]

Q. Ammonia can be dried by : $NH_3 + H_2O$

a) anhydrous $CaCl_2 \xrightarrow{NH_3} CaCl_2 \cdot 6NH_3$ (ADDUCT) $[Ca(NH_3)_6]^{2+} + 2Cl^-$

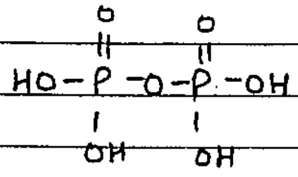
b) conc. $H_2SO_4 \xrightarrow{NH_3\ (LB)} (NH_4)_2SO_4$

c) $P_4O_{10} \xrightarrow{NH_3} (NH_4)_3PO_4$ (P_4O_{10} = acidic)

d) CaO (Basic) $CaO + H_2O \rightarrow Ca(OH)_2$ = insoluble.

→ Pyro phosphoric acid

2P +5

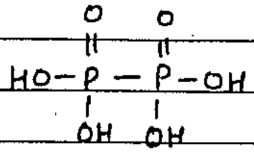


$$HO-\underset{OH}{\overset{O}{\overset{\|}{P}}}-O-\underset{OH}{\overset{O}{\overset{\|}{P}}}-OH$$

$H_4P_2O_7$

Basicity = 4.

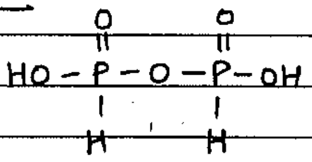
→ Hypophosphoric acid



$$HO-\underset{OH}{\overset{O}{\overset{\|}{P}}}-\underset{OH}{\overset{O}{\overset{\|}{P}}}-OH$$

Abnormal O.S. = +4
(only oxyacid of P to
have P–P bond)

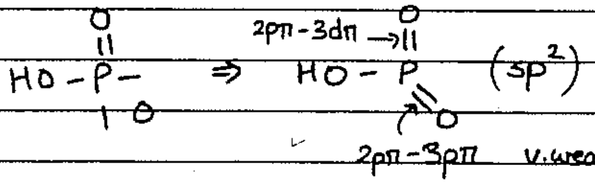
→ $H_4P_2O_5$ Cal. O.S. = +3 (avg) pyrophosphorous acid



$$HO-\underset{H}{\overset{O}{\overset{\|}{P}}}-O-\underset{H}{\overset{O}{\overset{\|}{P}}}-OH$$

→ Metaphosphoric acid $H_3PO_4 - H_2O \longrightarrow HPO_3$

O.S. = +5.

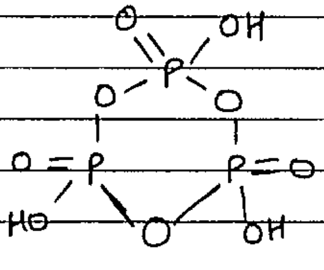


v.weak ⇒ polymerisation.

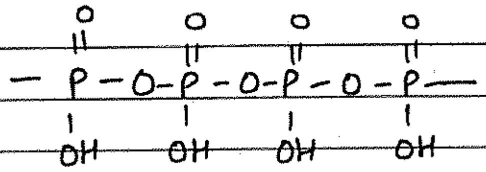
→ Trimetaphosphoric acid = $(HPO_3)_3$ OR $H_3P_3O_9$

C.A. = 3 3 – OH
3 = O ⇒ 3 – O –

All bond no. are multiple of no. of C.A. = cyclic



→ • Poly meta phosphoric acid = $(HPO_3)_n$ (as n ≠ defined, chain)

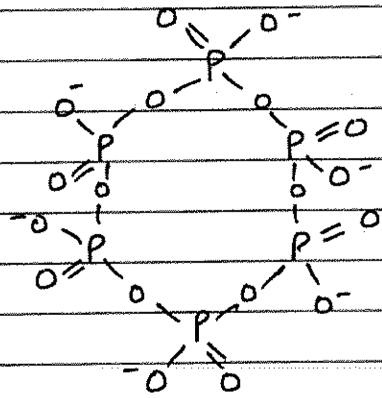


$$-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}-$$

→ CALGON ⇒ Sodium Hexa Meta phosphate

Hexa Meta phosphoric acid = $(HPO_3)_6$

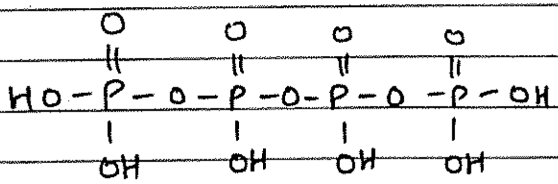
CA (P) = 6
OH = 6
=O = 6
−O− = 6] ⇒ CYCLIC



$+ 6\ Na^+$

→ $H_6P_4O_{13}$ Cal. O.S. = +5

P = 4
OH = 6
=O = 4
−O− = 3] not multiple ⇒ chain



$$HO-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}-OH$$

Q. Conc. H_2SO_4 is suitable drying agent for -

a) $H_2 \xrightarrow[\text{highly exothermic}]{\text{water vapour} + H_2SO_4} H_2$ ⇒ explodes.
b) NH_3
c) $H_2S\,(R.A.) \xrightarrow{\text{conc. } H_2SO_4\ (O.A)} S$
[✓ d)] Cl_2

* HYDROLYSIS :-

- CONDITIONS ⇒

1. Presence of vacant orbital
2. Covalent character
3. Absence of steric crowding

- $\boxed{\text{Extent of hydrolysis} \propto \text{covalent character}}$

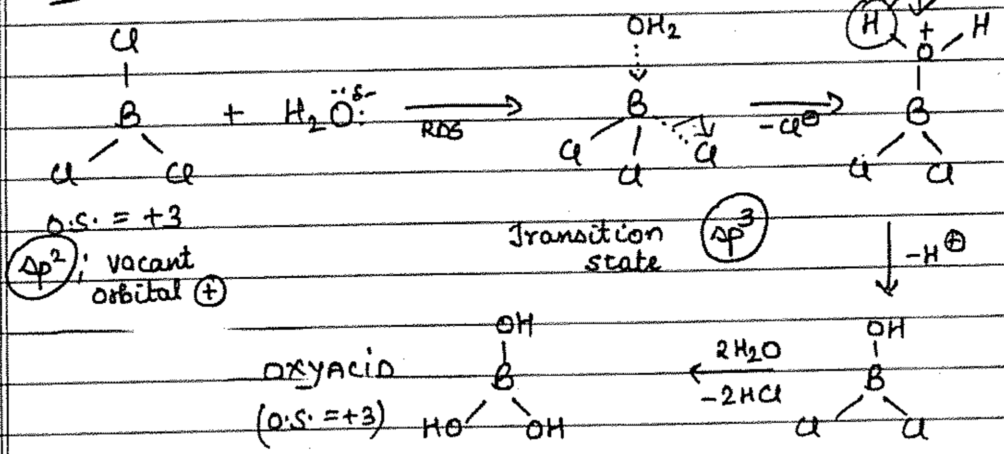
- $BF_3 < BCl_3 < BBr_3 < BI_3$ (size of anion ↑ Pol. ↑ Cov. ↑)
(Reality: Here, BF_3 has max. covalent character, as BB ✓ ionic ↓, cov. ↑)
- $NaCl < MgCl_2 < AlCl_3 < SiCl_4 < PCl_5$ (charge ↑ pol. ↑ cov. ↑)
- $NCl_3 > PCl_3 > AsCl_3 > SbCl_3 > BiCl_3$ (cation size ↑ pol. ↓)
- $SiCl_4 > GeCl_4 > SnCl_4 > PbCl_4 > \boxed{CCl_4}$ - Absence of vacant in C and -ve repulsion on Cl
NO HYDROLYSIS

* - $SF_6 < SeF_6 < TeF_6$ reason: In SF_6, smaller S is sterically protected by 6 F atoms. So, no hydrolysis.
inert with H_2O easily hydrolysed.

* Sub oxide ⇒ No. of CA > No. of TA (C_3O_2, N_2O)

* Sesque oxide ⇒ CA : TA ⇒ 2:3
(oxygen)

HYDROLYSIS OF HALIDES ⇒ S_N2 (bimolecular nucleophillic subs.)

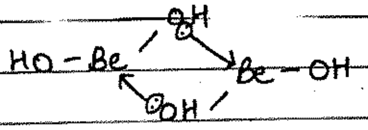


* → Hyb. steric no. increases by 1 from reactant to transition state.

* → C.A. converts to oxyacid / hydroxide on attack by H_2O (Same O.S.)
T.A. converts to HX.

– $BCl_3 + 3\,H{-}OH \longrightarrow H_3BO_3 + 3\,HCl$

* – $BeCl_2 + 2\,H{-}OH \longrightarrow Be(OH)_2 + 2\,HCl$



(dimer) OH can't release H^+ here, as already $[H^+]$↑ by HCl.

– $\overset{+3}{PCl_3} + 3\,HOH \longrightarrow \overset{+3}{H_3PO_3} + 3\,HCl$

– $AsCl_3 + 3\,HOH \longrightarrow H_3AsO_3 + 3\,HCl$

– $SiCl_4 + 4\,HOH \longrightarrow H_4SiO_4 + 4\,HCl$

* – $MgCl_2 + 2\,HOH \longrightarrow Mg(OH)_2\downarrow + 2\,HCl\uparrow$ (No effect on pH)
vapour — white fumes

*

- $AlCl_3 + 3\,HOH$ (vapour) $\longrightarrow Al(OH)_3\downarrow + 3\,HCl\uparrow$ (white fumes)
(No effect on pH)

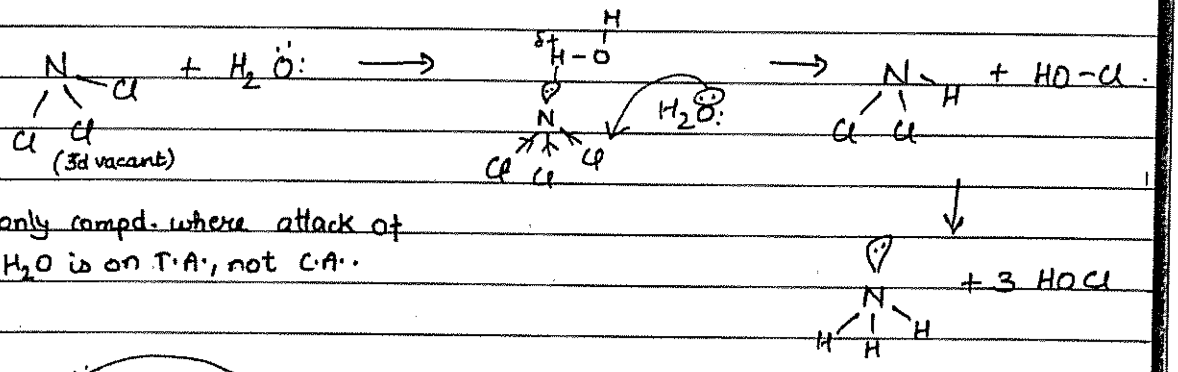
→ $AlCl_3$ and $MgCl_2$ become ionic in aq. sol^n
*

$$AlCl_3 \xrightarrow{\text{aq. sol}^n} [Al(H_2O)_6]^{3+} + 3Cl^-\,(aq.)\ \text{(Hydration)}$$

pH decreases ↓ slowly

$$[Al(H_2O)_5\,OH^-]^{+2} + H^+$$

- *



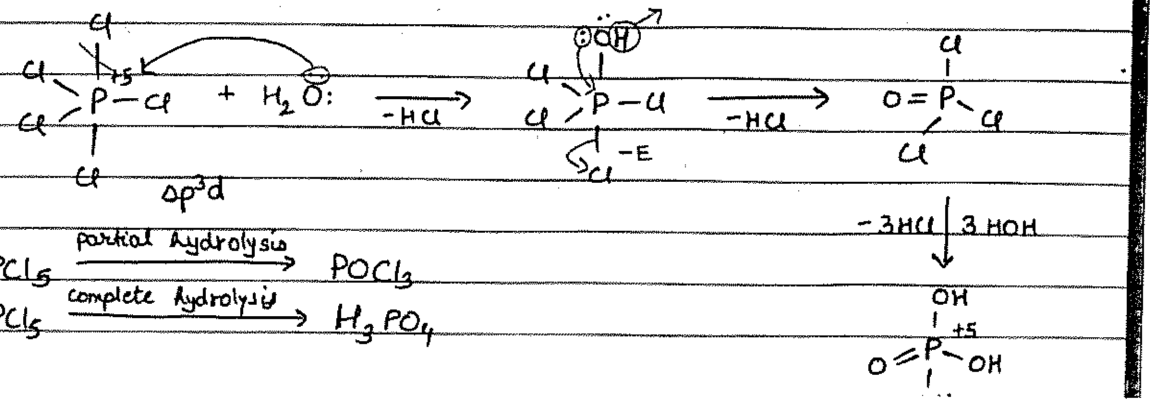
only compd. where attack of H_2O is on T.A., not C.A..

*

- $\overset{+1}{I}-Cl + H_2O \longrightarrow HO-\overset{+1}{I} + HCl$
- $\overset{+3}{Cl}F_3 + 2H_2O \longrightarrow H\overset{+3}{Cl}O_2 + 3\,HF$
- $\overset{+5}{Br}F_5 + 3H_2O \longrightarrow H\overset{+5}{Br}O_3 + 5\,HF$
- $\overset{+7}{I}F_7 + 4H_2O \longrightarrow H\overset{+7}{I}O_4 + 7\,HF$

$HOX = +1$
$HXO_2 = +3$
$HXO_3 = +5$
$HXO_4 = +7$

-



$$PCl_5 \xrightarrow{\text{partial hydrolysis}} POCl_3$$
$$PCl_5 \xrightarrow{\text{complete hydrolysis}} H_3PO_4$$

Jab tak C.A. की Hydrolysis में d participate कर रही हैं, उनको =O दे कर 2 HX निकालो।

- $SF_4 + H_2O \xrightarrow[-2HF]{} O=\ddot{S}\begin{smallmatrix}F\\F\end{smallmatrix} \xrightarrow[-2HF]{2HOH} O=\underset{\cdot\cdot}{\overset{OH}{S}}-OH$

sp^3d $\quad$ sp^3 product of partial hydrolysis $\quad$ product of complete hydrolysis

- $XeF_6 \xrightarrow[-2HF]{+H_2O} XeOF_4 \xrightarrow[-2HF]{+H_2O} XeO_2F_2 \xrightarrow[-2HF]{+H_2O} XeO_3$

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

products of partial hydrolysis $\quad$ complete hydrolysis

*

- $\overset{+2}{Xe}F_2 + H_2\overset{-2}{O} \longrightarrow \overset{0}{Xe} + \frac{1}{2}\overset{0}{O_2} + 2HF$ (REDOX)

sp^3d

Xe = O → not possible, as 2pπ–5pπ ✗ → $Xe + \frac{1}{2}O_2$

XeO, XeO_2 → not possible.

XeO_3 → possible, stable : O.S. of Xe = +6 ⇒ size ↓

XeO_4 → possible, not quite stable : Steric crowding of MB.

*

- $\overset{+4}{Xe}F_4 \xrightarrow[-2HF]{H_2O} XeOF_2 \xrightarrow[-2HF]{H_2O} XeO_2 \longrightarrow \overset{+6}{XeO_3} + \overset{0}{Xe} + \frac{1}{2}O_2$

sp^3d^2 $\quad$ sp^3d $\quad$ (REDOX)

*

- $BF_3 + 3HOH \longrightarrow B(OH)_3 + 3HF$ (sol^n)

$3BF_3$ (leftover) + $3H^+F^- \longrightarrow 3H^+BF_4^- \xrightarrow{HOH}$ ✗ : Partial hydrolysis

(LA) $\quad$ (LB) $\quad$ Tetrafluoro Boric Acid

3F$_3$ में से BF$_3$ का drolysis ी होता

$4BF_3 + 3HOH \longrightarrow B(OH)_3 + 3HBF_4$

*

- $SiF_4 + 4HOH \longrightarrow Si(OH)_4 + 4HF$

$2SiF_4 + 4HF \longrightarrow 2H_2SiF_6$ Hexafluoro Silicic acid

artial hydrolysis

$3SiF_4 + 4HOH \longrightarrow Si(OH)_4 + 2H_2SiF_6$

(steric repulsion)

* $BCl_3 + HCl \not\rightarrow HBCl_4$ $SiCl_4 + 2HCl \not\rightarrow H_2SiCl_6$

* $SbCl_3 + H_2O \longrightarrow SbOCl + 2HCl$

ANTIMONY OXYCHLORIDE

$BiCl_3 + H_2O \longrightarrow BiOCl\downarrow + 2HCl$

Partial Hydrolysis due to more ionic character (cation size ↑)

$\downarrow H_2O$ BISMUTH OXYCHLORIDE / WHITE TURBIDITY / WHITE PEARL

* $Bi^{+3} + 3Cl^-$

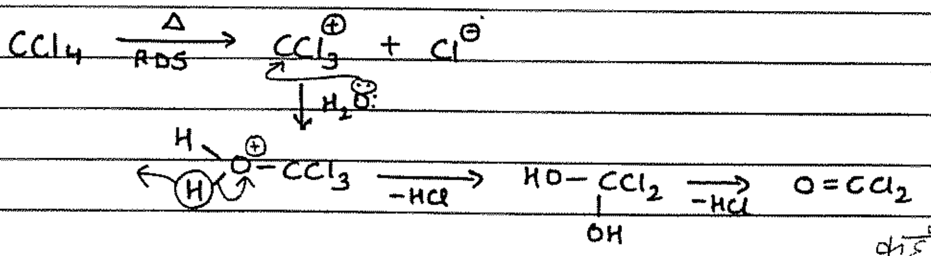
$Bi^{3+} \cdots O\begin{smallmatrix}H\\H\end{smallmatrix} \Rightarrow \overset{+3}{Bi}\overset{2-}{O} = \overset{+}{\boxed{BiO}}Cl^-\downarrow$

$CCl_4 + H_2O \xrightarrow{\text{ROOM TEMP.}} \times$ (steric crowding)

$CF_4 + H_2O \longrightarrow \times$ (B.E. of C−F is ↑↑ so E. of ABMO ↑↑)

* $CCl_4 + H_2O \xrightarrow{\text{TEMP. ↑↑}} COCl_2 + 2HCl$ $\boxed{S_N1}$

(phosgene)



$$CCl_4 \xrightarrow[\text{RDS}]{\Delta} CCl_3^{\oplus} + Cl^{\ominus}$$

$$\downarrow H_2\ddot{O}$$

$$H-\overset{\oplus}{O}(H)-CCl_3 \xrightarrow[-HCl]{} HO-\underset{OH}{\underset{|}{C}}Cl_2 \xrightarrow[-HCl]{} O=CCl_2$$

कहाँ थी ?

* $NF_3 + H_2O \xrightarrow{\text{ROOM TEMP.}} \times$ $NF_3 + H_2O \xrightarrow[(S_N)]{300°C} N_2O_3 + HF$

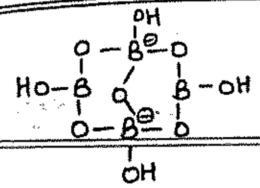
- <u></u>HYDROLYSIS OF CARBIDE, NITRIDE, PHOSPHIDE, HYDRIDE, etc.

→ $Mg_3N_2 + 6HOH \longrightarrow 3Mg(OH)_2 + 2NH_3$

→ $Ca_3P_2 + 6HOH \longrightarrow 3Ca(OH)_2 + 2PH_3$ (phosphene)

→ $Mg_3B_2 + 6HOH \longrightarrow 3Mg(OH)_2 + B_2H_6$ (excess H_2O leads to next rxn.)

- ## HYDROLYSIS OF BORAX

$2Na^+$ +


$Na_2B_4O_7 + 7H_2O \longrightarrow 2NaOH + 4H_3BO_3$

Salt　　S.B.　　W.A.

Aq. solⁿ Basic in nature

→ $B_2H_6 + 6HOH \longrightarrow 2B(OH)_3 + 6H_2$

→ $Li_3N + 3HOH \longrightarrow 3LiOH + NH_3$

→ $CaH_2 + 2HOH \longrightarrow Ca(OH)_2 + 2H_2$ $\boxed{MOP}$

[HYDROLITH]

→ $Be_2C + 4HOH \longrightarrow 2Be(OH)_2 + CH_4$

→ $Al_4C_3 + \overset{12}{\cancel{8}}HOH \longrightarrow 4Al(OH)_3 + 3CH_4$

→ $CaC_2 + 2HOH \longrightarrow Ca(OH)_2 + C_2H_2$

→ $Mg_2C_3 + 4HOH \longrightarrow 2Mg(OH)_2 + C_3H_4$

→ STRUCTURE OF Ionic CARBIDE ⇒

- $Be_2C \longrightarrow 2Be(OH)_2 + CH_4 \longrightarrow 2Be^{2+} + C^{4-}$
- $Al_4C_3 \longrightarrow 4Al^{3+} + C^{4-}$

METHANIDE

- $CaC_2 \longrightarrow Ca^{2+} + \bar{C}\equiv C^-$ Acetylide
- $Mg_2C_3 \longrightarrow 2Mg^{2+} + \overset{3-}{C}-C\equiv C^-$ Propynide (stability ↓ ; reactivity ↑ ⇒ major)

$\updownarrow$

$\overset{2-}{C}=C=C^{2-}$ Allylide (allene)

- ## HYDROLYSIS OF OXIDES ⇒

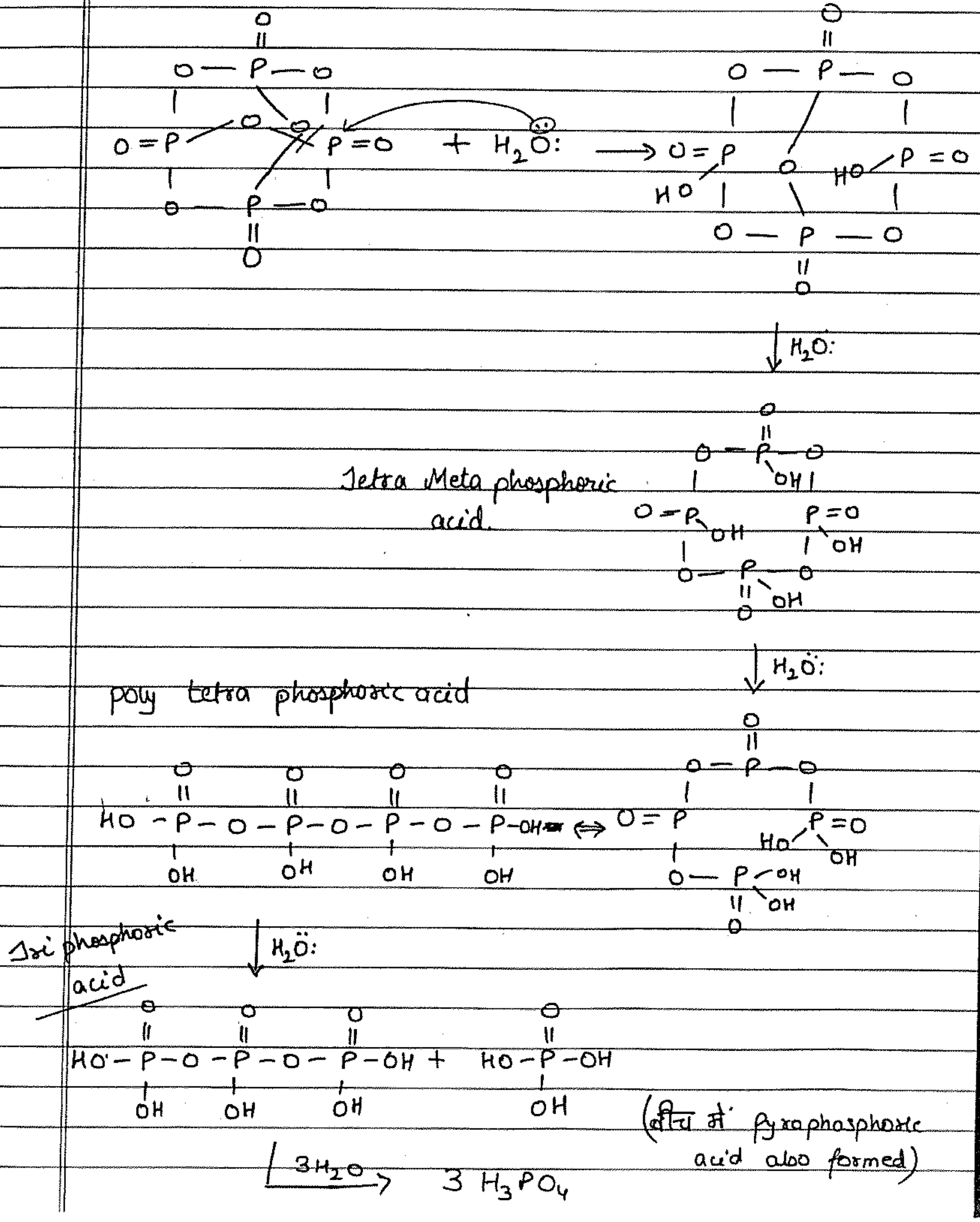
- $\overset{+5}{P_4O_{10}} + 6H_2O \longrightarrow 4\overset{+5}{H_3PO_4}$

Tetra Meta phosphoric
↓
Poly tetra phosphoric
↓
Tri phosphoric
Pyro phosphoric
↑

$$\underset{LA}{2\,B(OH)_3} + \underset{LB}{2\,Na^+OH^-} \longrightarrow 2\,Na^+B(OH)_4^-$$

$$\Rightarrow \underset{WA + SB \rightarrow salt}{2\,Na^+B(OH)_4^-} + \underset{WA}{2\,H_3BO_3}$$] Acidic Buffer Soln

- $P_4O_{10} + 6\,HOH \longrightarrow 4\,H_3PO_4$



Tetra Meta phosphoric acid.

poly ~~tetra phosphoric acid~~

Tri phosphoric acid

(बीच में Pyrophosphoric acid also formed)

IPE = Inert pair effect

- $\overset{+3}{P_4O_6} + 6H_2O \longrightarrow 4\ \overset{+3}{H_3PO_3}$

- $\overset{+5}{N_2O_5} + H_2O \longrightarrow 2\ \overset{+5}{HNO_3}$

- $2\underset{+4}{NO_2} + H_2O \longrightarrow \underset{+5}{HNO_3} + \underset{+3}{HNO_2}$

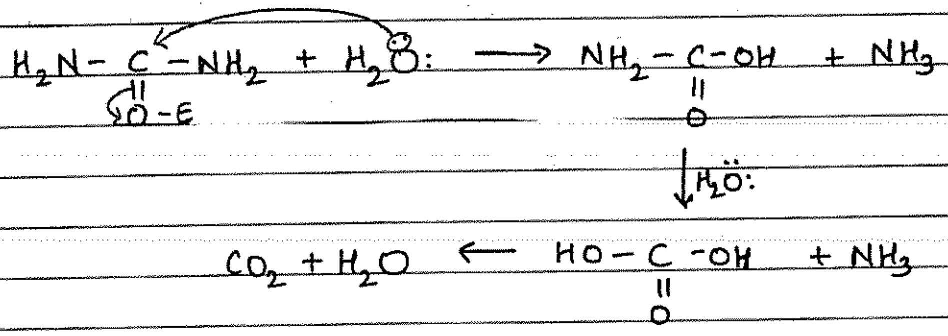
$+4 \to +3,\ +5$

(I.P.E.) $\downarrow H^+$ Disproportionation

$\overset{+5}{HNO_3} + \overset{+2}{NO}$ (final product)

→ N compounds having +1 to +4 O.S. give disproportionation reaction in acidic medium to convert to +5 O.S., which is more stable.

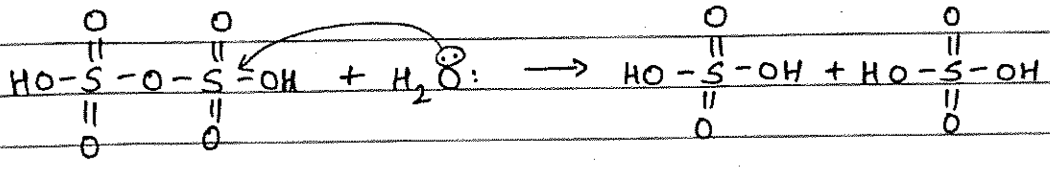
- HYDROLYSIS OF UREA ⟹ $NH_2(CO)NH_2 + H_2O \longrightarrow 2NH_3 + CO_2$



$$H_2N-\underset{\underset{O-E}{\|}}{C}-NH_2 + H_2\ddot{O}: \longrightarrow NH_2-\underset{\underset{O}{\|}}{C}-OH + NH_3 \xrightarrow{H_2\ddot{O}:} HO-\underset{\underset{O}{\|}}{C}-OH + NH_3 \longrightarrow CO_2 + H_2O$$

$NH_2(CO)NH_2 + 2H_2O \longrightarrow 2NH_3 + H_2O + CO_2$

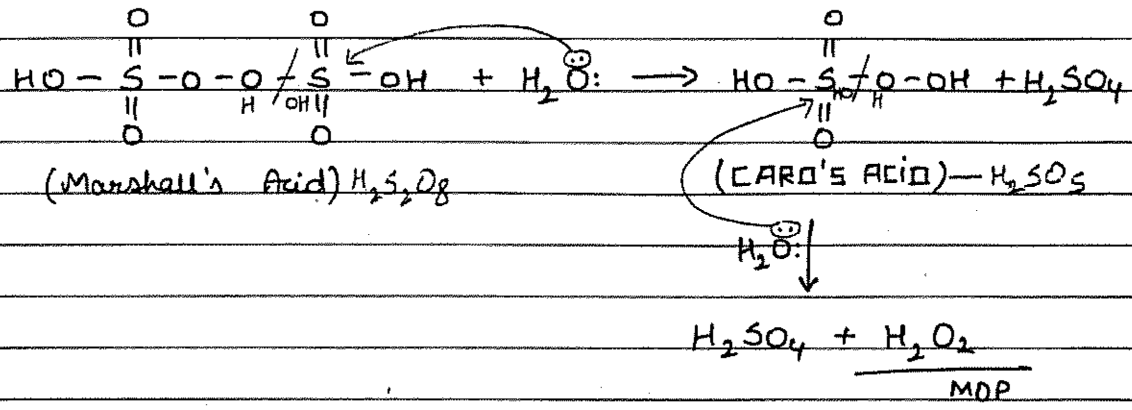
- HYDROLYSIS OF OLEUM & MARSHALL'S ACID ⟹



$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH + H_2\ddot{O}: \longrightarrow HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH + HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$$

oleum

$H_2S_2O_7 + 2H_2O \longrightarrow 2H_2SO_4$



$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-\underset{H}{O}/\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH + H_2\ddot{O}: \longrightarrow HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}/\underset{H}{O}-OH + H_2SO_4$

(Marshall's Acid) $H_2S_2O_8$

(CARO'S ACID)— H_2SO_5

$H_2\ddot{O}: \downarrow$

$H_2SO_4 + \underline{H_2O_2}$

MOP

- **Hydrolysis OF NM and Alkaline Hydrolysis** ⟹

– $\overset{0}{Cl_2} + H_2O \longrightarrow HO\overset{+1}{Cl} + H\overset{-1}{Cl}$ (Disproportionation)

– $Br_2 + H_2O \longrightarrow HOBr + HBr$ (—"—)

– $I_2 + H_2O \longrightarrow \times$ ($\Delta G = \oplus \Rightarrow$ non spontaneous)

$HOI + HI \longrightarrow I_2 + H_2O$

– $\overset{0}{F_2} + H_2\overset{-2}{O}(s) \longrightarrow H\overset{0}{O}\overset{-1}{F} + H\overset{-1}{F}$ (Redox)
(OA)

→ F_2 gives ozonide oxygen $[O_2 + O_3]$ when reacts with $H_2O(l)$

$H-\ddot{\underset{..}{O}}-\ddot{\underset{..}{F}}: \longrightarrow HF + [O]$

$[O] + [O] \rightarrow O_2$; $O_2 + [O] \longrightarrow O_3$.

– $P_4 + 6H_2O \longrightarrow 3H_3PO_2 + PH_3$ (structure wise attack)
(Disproportionation)

→ $NM + H_2O \longrightarrow$ oxyacid $+ NMH$ ~~(Disproportionation)~~
(lowest O.S.)

– $S_8 + H_2O \longrightarrow H_2\overset{(+2)_{av.}}{S_2}O_3 + H_2S$ (Disproportionation)
Thio Sulphuric Acid

$\overset{+}{[MO]}\overset{-}{Cl}$ oxychloride

$\overset{+}{M}[O-\overset{-}{Cl}]$ Hypochlorite

- $\overset{0}{S_8}$ + dil. NaOH $\longrightarrow$ $Na_2\overset{+2}{S_2}O_3$ + $Na_2\overset{-2}{S}$ (disproportionation)
  Sodium thiosulphate

- $\overset{0}{P_4}$ + 3NaOH + $3H_2O$ $\longrightarrow$ $3NaH_2\overset{+1}{P}O_2$ + $\overset{-3}{P}H_3$ (Disproportion)
  (white) Sodium Hypophosphite (weak L.B.)

- $\overset{0}{Cl_2}$ + cold, dil. NaOH $\longrightarrow$ $Na\overset{-1}{Cl}$ + $\overset{+1}{Na}\overset{-2}{O}\overset{+1}{Cl}$ + H_2O (—"—)
  Sodium hypochlorite/oxychloride?

  $\downarrow$ Hot, conc. NaOH

  $Na\overset{-1}{Cl}$ + $Na\overset{+5}{Cl}O_3$ + H_2O (disproportion) 1st upper rxn. occurs, then
  Sodium Chlorate as NaOH (conc. ⇒ N ↑) is still available, it reacts further with NaOCl ⇒ $[O-\underset{+1}{X}]^- \xrightarrow{[OH]^-} \underset{-1}{X^-} + \underset{+5}{XO_3^-}$

- Br_2 + cold, dil. NaOH $\longrightarrow$ NaBr + NaOBr + H_2O

  $\downarrow$ hot, conc. NaOH

  NaBr + $NaBrO_3$ + H_2O

- I_2 + cold, dil. NaOH $\longrightarrow$ NaI + NaOI + H_2O

  $\downarrow$ hot, conc. NaOH (OH⁻ is better Nu⊖ than H_2O)

  NaI + $NaIO_3$ + H_2O

→ F_2 gives OF_2 when reacts with cold, dil. NaOH, but gives O_2 (g) when reacts with hot, conc. NaOH.
(F_2 acts as good O.A.)

* SILICONES :-

- They are organo metallic polymer in which basic repeating unit is (R_2SiO).

- **PREPARATION** : Hydrolysis of alkyl chloro silane followed by condensation polymerisation.

$$SiCl_4 \xrightarrow[-MgCl_2]{RMgCl} \underset{Ⓒ}{\underline{R-SiCl_3}} \xrightarrow[-MgCl_2]{RMgCl} \underset{Ⓑ}{\underline{R_2-SiCl_2}} \xrightarrow[-MgCl_2]{RMgCl} \underset{Ⓐ}{\underline{R_3SiCl}}$$

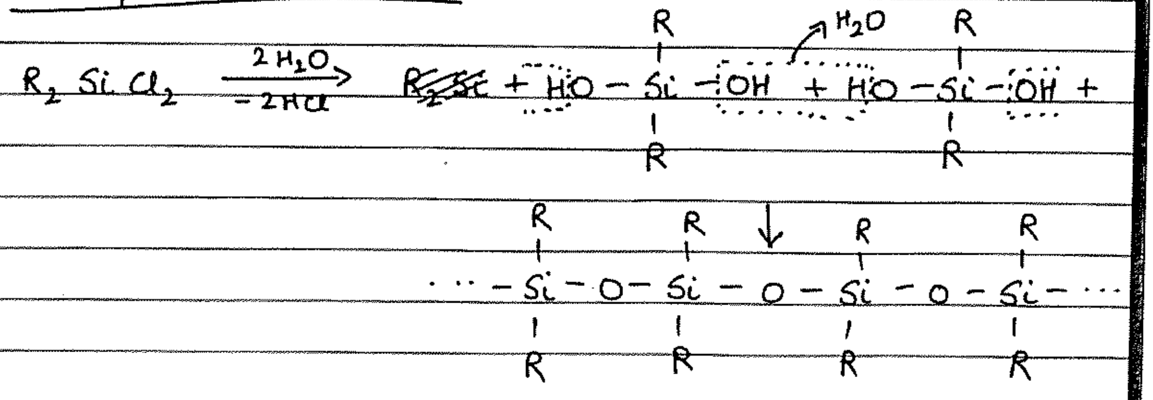
SiH_4 = Silane ⇒ A = Trialkyl mono chloro silane
B = Dialkyl dichloro silane
C = Alkyl trichloro silane

A) Disilicone (dimer)

$$2\,R_3SiCl \xrightarrow[-2HCl]{2\,H_2O} R_3Si-OH + HO-SiR_3 \xrightarrow{-H_2O} R_3Si-O-SiR_3$$

(not true silicone)

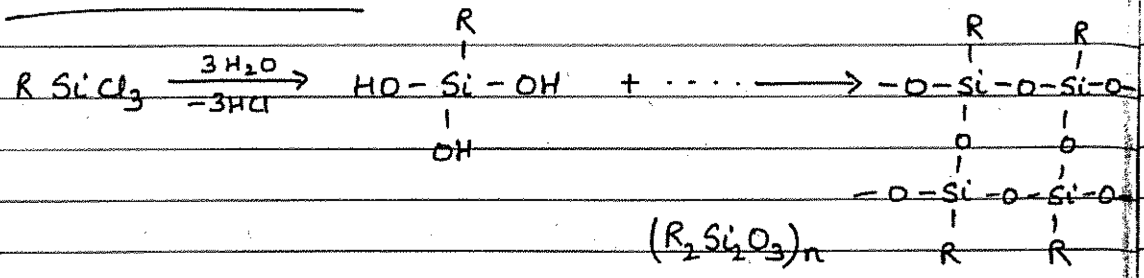
B) Linear / Chain Silicone



$$R_2SiCl_2 \xrightarrow[-2HCl]{2\,H_2O} \cancel{R_2Si} + HO-\overset{R}{\underset{R}{Si}}-OH + HO-\overset{R}{\underset{R}{Si}}-OH + \xrightarrow{-H_2O} \cdots-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-\cdots$$

$\underline{(R_2SiO)_n}$

c)• Cross linked Silicone



$RSiCl_3 \xrightarrow[-3HCl]{3H_2O} HO-\overset{R}{\underset{OH}{Si}}-OH + \cdots \longrightarrow$

$(R_2Si_2O_3)_n$

→ Chain controlling unit for silicones is R_3SiCl

• PROPERTIES :-

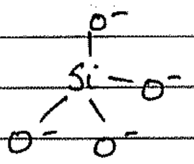
1\. Almost chemically inert due to high Bond Energy of Si–C and Si–O.

2\. Water repelling nature due to presence of hydrophobic R.

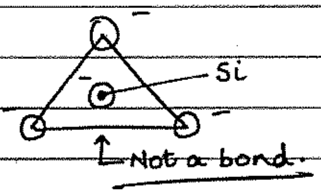
3\. Insulator (absence of free $e^{\ominus}$).

* SILICATES :-

• Metal salts in which basic structural unit is $(SiO_4)^{4-}$.

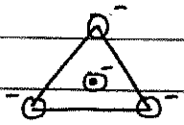
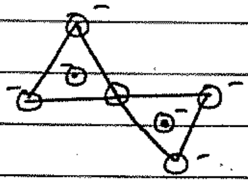
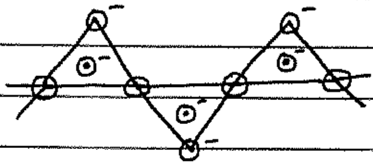
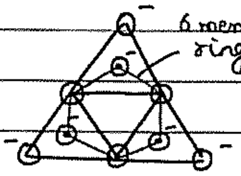
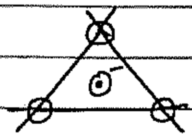
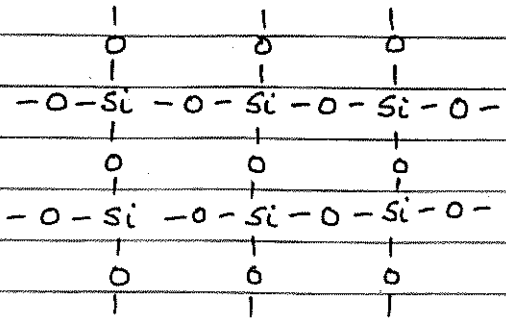


sp^3, tetrahedral
non planar



• No silicate is planar, all Si are sp^3

• Double Chain Silicate = Amphibole → $(Si_4O_{11}^{6-})_n$

	* SILICATE	NO. OF SHARED O per unit	GEN. FORMULA		
1. Zircon Willemite	ORTHO / MESO	0	SiO_4^{4-}		Zircon $ZnSiO_4$ Willemite Zn_2SiO_4
2. Hemimorphite	PYRO	1	$Si_2O_7^{6-}$ (OR) $(SiO_{3.5}^{3-})_2$ (unit)		Hemimorphite $Zn_4(OH)_2Si_2O_7$
3. Spodumene Diopsite	SINGLE CHAIN PYROXENE	2	$(SiO_3^{2-})_n$ (unit) $(Si_nO_{3n+1})^{-2n-2}$ (complete)		Spodumene $LiAl(SiO_3)_2$ Diopsite, ...
4. Beryl	Cyclic	2	$(SiO_3^{2-})_n$	 6 memb. ring	Beryl $Be_3Al_2Si_6O_{18}$
5. Talc Mica White asbestos	SHEET	3	$(SiO_{2.5}^{-})_n$ (unit) (OR) $(Si_2O_5^{2-})_n$		Talc $Mg_3(OH)_2(Si_2O_5)_2$ white asbestos, mica
6. Zeolite Feldspar	3-D	4	$(SiO_2)_n$		

Zeolite ; Feldspar ($KAlSi_3O_8$), Ultramarine

NAME	NO. OF O Shared/unit	General Formula
Ortho	0	SiO_4^{4-}
Pyro	1	$SiO_{3.5}^{3-}$
Chain/Cyclic	2	SiO_3^{2-}
Sheet	3	$SiO_{2.5}^{-}$
3 D	4	SiO_2

Q. Total no. of shared O in mineral $Be_3 Al_2 Si_6 O_{18}$.

Ans $Be_3\ Al_2\ Si_6 O_{18}$ 12 are unshared O. (monovalent)

$\underset{+6}{\downarrow}$ $\underset{+6}{\downarrow}$ $\Rightarrow (Si_6 O_{18})^{12-}$ $\Rightarrow$ 18 − 12 = 6 are shared O (bivalent)

Q. Amorphous form of silica is –

a) Quartz
b) Crestobelite
c) Trydemite

$\Rightarrow$ Crystalline

d) ✓ Keiselgur ⟶ Hydrated Silica; amorphous; used in cement industry and in making explosives.

- Sodium Zeolite (3-D) ($Na_2 Al_2 Si_2 O_8$) (porous structure) sp^3

→ For softening of hard water
→ For cracking and isomerisation of hydrocarbon.
→ ZSM-5 (a zeolite) is used to convert ethyl alcohol to petrol

- Generally silica is inert. But it can react with NaOH and HF.

→ $SiO_2 + 2\,NaOH \longrightarrow Na_2SiO_3 + H_2O$

Acidic S.B. WATER GLASS – only water soluble silicate.
used in silica garden

→ (Glass) $SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$

$SiF_4 + 2HF \longrightarrow H_2SiF_6$

Hexa fluoro silicic acid

itching of glass

HF can't be stored in glass container.

---

* **GLASS :-** Amorphous solid

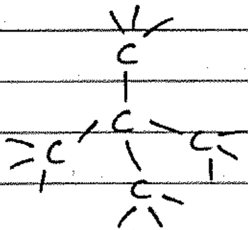
- Supercooled liquid, hard, transparent, brittle, no definite MP.
- SODA GLASS (soft) → Na Ca Silicate
- POTASH GLASS (hard) → K Ca Silicate
- PYREX GLASS → Contains B_2O_3 or Boro Silicate and used in laboratory apparatus due to very less thermal expansion.
- FLINT GLASS → Contains Pb Silicate and used in lenses formation due to high μ.
- CROOK'S GLASS → Contains CeO_2 which absorbs UV rays, so used in sunglasses.

* • ALLOTROPES :-

• CARBON ⇒

⇒ CRYSTALLINE –

1· Diamond



Giant Molecule
(Covalent Solid)
Hyb. = sp^3
B.A. = $109°28'$
B.L. = 1.54 Å
ρ = 3.35 g/cc
MP ≃ 4000 K.

→ Each C is bonded with 4 other C in tetrahedral geometry.

→ Hard; due to 3 D crystal structure and strong σ bonds.

→ Electric insulator due to absence of free $e^{\ominus}$.

→ Chemically inert due to strong σ bonds It can't react with conc. HNO_3.

→ Insoluble in H_2O and organic solvents'

→ Better conductor of heat than graphite. ($e^{\ominus}$ cloud surrounding C vibrates).

→ Used as abrasive.

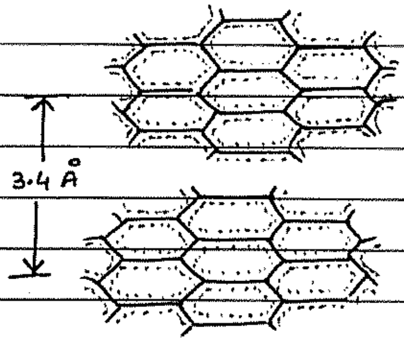
→ Anisotropic wrt mechanical strength. (different property when seen /checked from different direction).

→ Effective no. of C atom in unit cell = 8

2. Graphite

covalent
metallic
Bonding

(b/w 2 layer)



Hyb. = sp^2
B.A. = 120°
B.L. = 1.41 Å
ρ = 2.22 g/cc
MP ⇒ less than diamond.

→ Each C is bonded with 3 other C and forms hexagonal layer structure.

→ VWF present b/w 2 layers, so soft ; used as lubricant at high temperature

→ Good conductor of electricity due to presence of delocalized π $e^{\ominus}$ (pencil dotted), which are free $e^{\ominus}$.

→ Anisotropic wrt electric conductance. (no delocalization b/w layers → insulator ; deloc. only within layer → conductor).

→ Conductivity increases along ⊥ axis of layers and decreases on ∥ axis of layers on increasing temperature.

→ Thermodynamically more stable than diamond.

$$\Delta H_f = \text{Graphite} \xrightarrow{\Delta G = \oplus} \text{Diamond} \xrightarrow{\Delta G = \oplus} \text{Fullerene}$$

0 1.9 KJ/mol 38.1 KJ/mol

→• Graphite = Plumbago, used in lead pencil, contains 0% lead.

→ Diamond → Graphite is spontaneous ($\Delta G = \ominus$), but this doesn't take place as E_a of T.S. is v. high.

→ C−C B.S. Graphite > Diamond

→ Graphite is diamagnetic in nature.

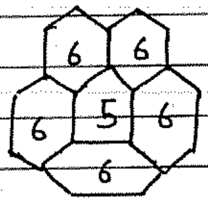
2. Fullerene

→ C_{60} (football like) and C_{70} (rugby ball like) are common fullerenes.

→ C_{60} is also k/a buckmeinster fullerene / bucky ball.

→ There are 32 hydrals (rings) in C_{60}

$$32 \begin{cases} \rightarrow 12 \text{ pentagonal} \\ \rightarrow 20 \text{ hexagonal} \end{cases}$$



Every C completes its 4 valencies.

→ A pentagonal ring is fused with only hexagonal rings. But a hexagonal ring is fused with both pentagonal and hexagonal.

→ Hyb. = sp^2 ; Aromatic

→ Total no. of σ bonds in C_{60} = $1 \times 3 \times \frac{1}{2} \times 60 = \underline{\underline{90}}$

→ Fullerene is a molecular solid.

→ Purest form of C due to dangling bond's absence.

→ DANGLING BOND – In diamond and graphite, surface C atoms have some free valencies. These C form new bonds with impurities which are k/a dangling bonds

- TIN ⇒

$$\alpha\text{-Tin} \xrightarrow{13.2^\circ C} \beta\text{-Tin}$$

Diamond like structure — Metallic structure

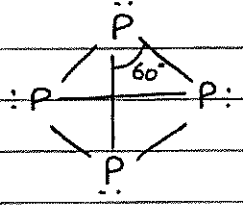
Grey Tin — White Tin (powdered form)

- Si, Ge also show diamond like structure, but Pb exists only as metallic crystal.

- Except Pb, all elements of C family show allotropy.

- PHOSPHOROUS ⇒

1. White P – Monomer of P_4



No hyb. (Drago's Rule)

No. of P–P bonds = 6

No. of 3 memb. ring = 4

No. of $P-\hat{P}-P$ B.A. = 12

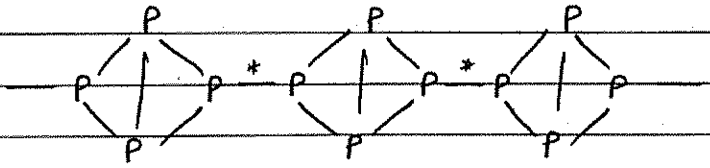
Non planar

Non polar

Highly reactive due to angle strain

→ All P atoms are present at corners of tetrahedral.

2. **Red P** – Polymer of P_4



3. **Black P** – Polymer of P_4
α β
some P form 6 memb ring, some others.

→ Thermodynamically most stable form of P allotrope.

→ Angle strains are reduced highly. (All B.A. ≃ 90°)

WHITE P	RED P
Waxy Solid	Brittle powder
Highly poisonous	Non poisonous
Highly reactive due to high angle strain. So, is kept underwater.	Comparatively more stable as some bonds have less angle strain (*)
Insoluble in H_2O (non polar) but soluble in CS_2.	Insoluble in both H_2O and CS_2 (is a polymer)
Less MP and less ρ. (intermolecular = VWA)	Comparatively high MP and ρ (intermolecular = covalent)
(CHEMILUMINESCENCE) Glows in dark due to	No Chemiluminescence.

	white P	Red P
⇒	Gives hypophosphite and PH_3 when reacts with NaOH	↳ $H_4P_2O_6$ (P-P) Gives hypophosphoric acid when reacts with NaOH.

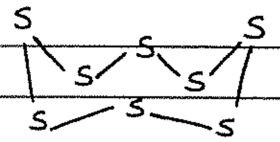
⇒
$$\begin{tikzcd}
\boxed{\text{Red P}} \arrow[r, "803\text{ K}", "\text{high pr.}"'] & \boxed{\alpha\text{-Black P}} \\
\boxed{\text{White P}} \arrow[u, "\text{inert medium}", "573\text{ K}"'] \arrow[r, "473\text{ K}", "\text{high pr.}"'] & \boxed{\beta\text{-Black P}}
\end{tikzcd}$$

- Except N, all elements of N family show allotropy.

- SULPHUR ⇒

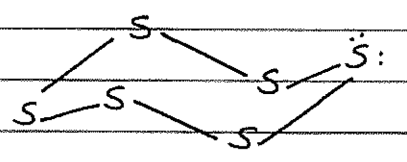
→ Has max. allotropic forms due to high catenation tendency.

a) S_8 = Crown shaped



sp^3 hyb.; B.A. = 107°

b) S_6 = ENGEL'S S = chair form



sp^3 hyb; B.A. = 102°

c) S_2 - exists in vapour state (600°C – 2200°C); paramag.

→ Stability : $S_8 > S_6 > S_2$

1. Rhombic S / Octahedral S / α S — S_8 units
VWA

→ Most stable form of S

→ MP = 114°C (sudden, not gradual heating) $\rightarrow \alpha \rightarrow \beta$

2. Monoclinic S / Prismatic S / β S — S_8 units (diff. crystal)
VWA

→ Less density than α S

→ MP = 119°C

⇒ Both α S and β S are crystalline, insoluble in H_2O, but soluble in CS_2

$$\alpha\, S \underset{<95.6^\circ C}{\overset{>95.6^\circ C}{\rightleftharpoons}} \beta\, S \xrightarrow[MP]{119^\circ C} liq.\, S \begin{pmatrix} 160^\circ C \rightarrow 200^\circ C \\ Viscosity \uparrow \end{pmatrix}$$

– 95.6°C = eq$^{\underline{m}}$ = transition temperature.

– Liq. S ⇒ zig zag chains form ⇒ S.A. ↑ ⇒ restriction to
viscosity ↑ ⇐ mobility ↑

– Max. viscosity of S @ 200°C. Beyond that, no. of S per chain ↓ and then mobility ↑ ⇒ viscosity ↓.

3. Plastic S / χ S — Liq. S + Cold. H_2O (amorphous)

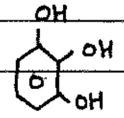
→ insoluble in CS_2 (only one in all allotropes of S).

4. Colloidal S / δ-S — $\underset{R.A.}{H_2S} \xrightarrow[]{\overset{(O.A.)}{conc.\ HNO_3}} S$
amorphous

*5. Milk of S

6. γ monoclinic S - Liq. S + CS_2

- OXYGEN -

⇒	O_2	O_3
→	Paramagnetic	Diamagnetic
→	Colorless gas	Pale blue gas, dark blue liquid, violet black solid
→	Acts as O.A.	Stronger O.A. than O_2.
→	Absorbed by pyrogallol sol^n  	Absorbed by cinnamon oil / turpentine oil

⇒ All O family members show allotropy

- Boron exists as → a) less reactive crystalline B
  b) more reactive amorphous B

* BLEACHING ACTION :-

- Colored Substance $\xrightarrow[\text{oxidation}]{[O]}$ Colorless substance] Permanent Bleaching
- Colored Substance $\xrightarrow[\text{reduction}]{[H]}$ Colorless substance] Temporary Bleaching
  ↑ atm. O_2

- Dry and permanent bleaching agent is –

~~a)~~ O_3 $O_3 \longrightarrow O_2 + [O]$
b) H_2O_2 $H_2O_2 \longrightarrow \underline{H_2O} + [O]$ (not dry)
c) Chlorine water $\underline{H_2O} + Cl_2 \longrightarrow HOCl + HCl$
$HOCl \hookrightarrow HCl + [O]$
d) moist SO_2 ⟶ $SO_2 + H_2O \rightarrow H_2SO_4 + 2[H]$

- Moist SO_2 is only temporary bleaching agent.

- BLEACHING POWDER ⇒ $CaOCl_2$

→ Composition : $\underbrace{Ca\overset{-1}{Cl_2} \cdot Ca(O\overset{+1}{Cl})_2}_{\text{major}} \cdot \underbrace{Ca(OH)_2 \cdot 2H_2O}_{\text{minor}}$

→ Preparation : $2\,Cl_2 + 2\,Ca(OH)_2 \xrightarrow[\text{dil.}]{\text{cold}} CaCl_2 + Ca(OCl)_2 + 2H_2O$

→ Active ingredient for bleaching action of bleaching powder is $Ca(OCl)_2$ (dissociates like HOCl; readily).

→ ~~Ca~~ ClO_2 is also used as bleaching agent in textile industry.

Q. Product formed by autooxidation of bleaching powder

a) $Ca(OCl)_2$ $\quad CaCl_2 \cdot Ca(\overset{+1}{O}Cl)_2$ $\quad OX^- \xrightarrow{OH^-} X^- + XO_3^-$

b) $Ca(ClO_2)_2$ $\quad \downarrow$

[✓ c)] $Ca(ClO_3)_2$ $\quad CaCl_2 + Ca(\overset{+5}{Cl}O_3)_2$

d) $Ca(ClO_4)_2$

* O.S. and their RELATIVE STABILITY ⇒

• Alkali metals show only +1 O.S.	Stable Inert Gas Configuration
• Alkaline Earth metals show only +2 O.S.	

- O.S. of p block elements are $(n-8)$ to $(+n)$, where n = outermost $e^{\ominus}$.

- INERT PAIR EFFECT :-

→ The inertness of ns $e^{\ominus}$ towards bonding is IPE.

→ Mainly applicable for group 13 to 16.

→ Increases on moving down a group.

→ Stability of higher O.S. ↓ and lower O.S. ↑ on moving down a group.

– $Al^+ < Ga^+ < In^+ < Tl^+$ (stability)

– $BX_3 > AlX_3 > GaX_3 > InX_3 > TlX_3$ (stability)

→ **13** $M = \underset{ns}{\boxed{1\downarrow}} \xrightarrow{E.E.} \underset{np}{\boxed{1 \mid \quad \mid \quad}}$ $G.S. = \textcircled{+1}$ L.O.S.

$M^* = \boxed{1}\ \boxed{1 \mid 1 \mid \quad}$ $E.S. = \textcircled{+3}$ H.O.S.

B
Al
Ga
In
Tl ↓

Z_{eff} ↑ ⇒ Attraction on ns $e^{\ominus}$ ↑ ⇒ E.E. ↑ ⇒ inertness ↑ ⇒ H.O.S tendency ↓ ⇒ L.O.S. ↑.

→ **14** $ns^2\ np^2$ L.O.S. = +2 H.O.S. = +4

→ **15** $ns^2\ np^3$ L.O.S. = +3 H.O.S. = +5

→ **16** $ns^2\ np^4$ L.O.S. = +4 H.O.S. = +6

– $CX_2 < SiX_2 < GeX_2 < SnX_2 < PbX_2$ (stability)

→ For last elements, L.O.S. > H.O.S.

$Tl^+ > Tl^{+3}$ $Pb^{2+} > Pb^{4+}$ $Bi^{3+} > Bi^{5+}$

→ For rest elements, H.O.S. > L.O.S.

$Al^+ < Al^{3+}$ $Ga^+ < Ga^{3+}$ $Sn^{2+} < Sn^{4+}$ $P^{+3} < P^{+5}$

→ Al^+ and Ga^+ give disproportionation ~~on~~ in aq. soln.

$$3\,Al^+ \xrightarrow{aq.\ sol^n} 2\,Al + Al^{3+}$$

Q. Assertion: Conc. HNO_3 oxidises S into H_2SO_4 but oxidises Se into H_2SeO_3

Reason: IPE ↑ on moving down a group.

Ans (A)

* Reducing Nature : $\underset{\text{never a R·A}}{F^-} < \underset{\text{weak R·A}}{Cl^-} < \underset{\text{stronger R·A·}}{Br^- < I^-}$

→ $SnCl_2$, $InCl$ act as R·A·

→ Pb (IV) compounds like $PbCl_4$, PbO_2, Pb_2O_3 ($PbO + PbO_2$) Pb_3O_4 ($2PbO + PbO_2$), Tl (III) compounds and Bi (V) (Red lead = सिंदूर) compounds act as O·A·

$$\underset{\text{O·A·}}{Pb^{+4}} + 2e^{\ominus} \longrightarrow Pb^{2+} \quad (\text{reduction})$$

→ $\underset{RA}{SnCl_2}$ and $\underset{OA}{HgCl_2}$ can't exist together· ($HgCl_2$ = OA = ⊕SRP)

$$SnCl_2 + HgCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$$

$$Hg_2Cl_2 \xrightarrow{SnCl_2} 2Hg + SnCl_4$$

Q. Identify species which don't exist–

~~a)~~ PbI_4 $Pb^{+4} + 4I^- \longrightarrow PbI_2 + I_2$
b) $PbCl_4$ $Pb^{+4} + 4Cl^- \xrightarrow{\text{ROOM °C}} X$
c) $\overset{+1}{Tl}I_3$ Tl^+ I_3^- No redox· O·S· of I = $-1/3$
~~d)~~ $\overset{+3}{Tl}I_3$ $Tl^{3+} + 3I^- \longrightarrow TlI + I_2$
~~e)~~ $BiBr_5$ $Bi^{+5} + 5Br^- \longrightarrow BiBr_3 + Br_2$
~~f)~~ $BiCl_5$ $Bi^{+5} + 5Cl^- \xrightarrow{\text{ROOM °C}} BiCl_3 + Cl_2$
~~g)~~ $\overset{+1}{Tl}F_3$ F_3^- doesn't exist·
h) $\overset{+3}{Tl}Cl_3$ $Tl^{3+} + 3Cl^- \longrightarrow$ No reaction
~~i)~~ $AlCl$ $Al^+ + Cl^- \longrightarrow Al^{+3}$ $3\overset{+1}{Al}Cl \longrightarrow \overset{+3}{Al}Cl_3 + 2\overset{0}{Al}$

→ $\overset{+1}{Tl}F_3 < \overset{+1}{Tl}Cl_3 < \overset{+1}{Tl}Br_3 < \overset{+1}{Tl}I_3$ (stability)

chance of existence
=0 ~~=0~~ ≃0

→ $\overset{+3}{Tl}F_3 > \overset{+3}{Tl}Cl_3 > \overset{+3}{Tl}Br_3 > \overset{+3}{Tl}I_3$ (stability)

O.S. of d-block elements ⇒

→ Transition metals show variable O.S. due to less energy difference b/w ns and (n-1)d subshells.

→ Min. O.S. = ns $e^\ominus$
Max. O.S. = ns $e^\ominus$ + (n-1)d unpaired $e^\ominus$

→

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$3d^1$	$3d^2$	$3d^3$	$3d^5$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^{10}$	$3d^{10}$
$4s^2$	$4s^2$	$4s^2$	$4s^1$	$4s^2$	$4s^2$	$4s^2$	$4s^2$	$4s^1$	$4s^2$
~~+2~~	+2	$+2^*$	+1	$+2^*$	$+2^*$	$+2^*$	$+2^*$	+1	+2
+3	$+3^*$	↓	$+3^*$	↓	$+3^*$	$+3^*$	+3	$+2^*$	
	$+4^*$	↓	↓	↓	↓	↓	+4		
		$+5^*$	↓	↓	↓	+5			
			$+6^*$	↓	+6				
				$+7^*$					

→ Max. O.S. in d-block = +8 (Ru, Os)

⇒ RELATIVE STABILITY OF O.S. ⇒

table inert gas config. $Sc^{+2} < Sc^{+3}$ $Ti^{3+} < Ti^{4+}$

$V^{+4} < V^{+5}$ $Mn^{6+} < Mn^{7+}$

^{5}stable ⇐ $Fe^{+2} < Fe^{3+}$ $Mn^{3+} < Mn^{2+}$

→ $Cr^{+2}(aq.) < Cr^{3+}(aq.)$ (t_{2g}^3 config.)

→ In aq. sol^n, or in (s), $Cu^{2+} < Cu^+$

$$\underset{\text{less stable (ionic compd)}}{2\,Cu^+} \xrightarrow[\text{solid state}]{\text{aq. sol}^n} \underset{\text{more stable}}{Cu^{2+}} + Cu$$

* Sm can show +2 O.S., but is very less stable

→ II I.E. of Cu is compensated by extra L.E. or extra H.E. of Cu^{2+}.

→ $\underset{\text{less stable}}{3Au^{+}} \rightleftharpoons \underset{\text{more stable}}{Au^{+3}} + 2Au$ $\quad Au^{+3}(aq)/(s) > Au^{+}(aq)/(s)$

→ On moving down a group in d-block, stability of H.OS ↑. (opposite of I.P.E.)

- $CrO_3 < MO_3 < WO_3$ +6 H.OS
- $MnO_4^- < TcO_4^- < ReO_4^-$ +7 HOS
- $Ni^{+4} < Pt^{+4}$
- $Pt^{+2} < Pt^{+4}$ On the basis of IP values.
  $Ni^{+2} > Pt^{+2}$
- $Ni^{+2} > Ni^{+4}$

→ d block metals can show 0 O.S. also. eg. $[Ni(CO)_4]$, $[Fe(CO)_5]$.

• O.S. of f-block elements →

→ Most stable and general O.S. of Lanthanides is +3.

→ Ce and Tb show +3 as well as +4 O.S.

→ Eu and Yb show +3 as well as +2 O.S.

→ $Ce^{+4} = [Xe]\,4f^{0}$ $\quad Tb^{+4} = [Xe]\,4f^{7}$
$Eu^{+2} = [Xe]\,4f^{7}$ $\quad Yb^{2+} = [Xe]\,4f^{14}$ due to stable config.

Q. Assertion: Actinides show H·OS than lanthanides
Reason: Energy difference b/w 5f and 6d is less than that of 4f and 5d.

Ans (A)

→ Th = +3, +4 (mainly)
Pa = +3 —— +5
U = +3 —— +6
* Np = +3 —— +7 } ⟹ max. O.S.
* Pu = +3 —— +7
Am = +3 —— +5
⋮

Last elements only +3. (Z_{eff} ↑↑)

→ Study of actinides is more complicated than lanthanides due to radioactive nature and variable O.S.

→ H·OS of an element is more stable with more EN atom like F, O, etc. due to smaller size and high B.E.

- $PF_5 > PCl_5 > PBr_5 > PI_5$ ⇒ doubtful existence
- $BiF_5 > \cancel{BiCl_5}$ $\cancel{BiBr_5}$ $\cancel{BiI_5}$
- $PbF_4 > PbCl_5 > PbBr_5$ $\cancel{PbI_5}$
  doubtful existence
- $FeF_3 > FeCl_3 > FeBr_3$ $\cancel{FeI_3}$
- $CuF_2 > CuCl_2 > CuBr_2$ $\cancel{CuI_2}$

Q. Pair of Cu halides which don't exist :-

a) $CuCl_2$, Cu_2Cl_2
b) CuF_2, Cu_2I_2
✓ c) CuF, CuI_2
d) $CuCl_2$, Cu_2Br_2

$\overset{\therefore\ \times}{2\,Cu^+F^-} \longrightarrow \overset{\therefore\ +2\ \checkmark}{CuF_2} + Cu$

(ionic) HOS with more EN

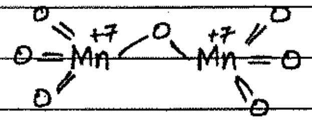
$Cu^{2+} + 2I^- \longrightarrow Cu^+I^- + \frac{1}{2}I_2$

⊕ SRP (RA)
(OA) CHAPA

Q. Highest fluoride and Highest oxide of Mn are -

a) MnF_7 and Mn_2O_7
b) MnF_6 and Mn_2O_3
✓ c) MnF_4 and Mn_2O_7
d) MnF_7 and MnO_3

Mn^{+7} is quite small ⇒ 7 F ⇒ steric crowd↑



Explosive nature.

→ O has strong tendency to stabilize H.OS in comparison to F as it can form multiple bond and thereby it causes less steric hinderance for higher rise in O.S.

→ MnO_3F exists.

→ Highest fluoride for V and Cr are VF_5 and CrF_6.

* OA ∝ RA :- (A) REDUCING NATURE OF METALS →

• $M(g) \longrightarrow M^+ + e^\ominus$ oxidation Metal = R.A.

→ Reducing strength in (g) $\propto \frac{1}{I.E.}$

Li < Na < K < Rb < Cs (IP ↓)

→• <u>Reducing Strength (aq.)</u> $\propto \frac{1}{SRP}$

→ $\underset{RA}{M(s)} \xrightarrow{S.E.} M(g) \xrightarrow{I.E._1} \underset{\text{oxidation}}{M^+(g)} \xrightarrow[H_2O]{H.E.} M^+(aq.)$

→ <u>Favourable conditions for stronger R.A. :-</u>

① Low SE
② Low IE
③ High HE

→ $\underset{\text{more } \ominus}{\underline{SRP}} = \underset{\downarrow}{SE} + \underset{\downarrow}{IE} - \overset{\uparrow}{HE}$ (theoretically)

• <u>Reducing Strength</u> :

→ $\underset{\underline{-3.05}}{Li} \geq \underline{Cs \geq \underset{-2.92}{Rb} \cong K} > \underset{-2.71}{Na}$ (SRP)

due to highest HE

→ Be < Mg < Ca < Sr < Ba

Q. Assertion : $E^\circ_{M^{+2}/M}$ is ⊕ for Cu and ⊖ for rest 3d.
Reason : Sum of SE and IE of Cu > HE of Cu^{2+}.

Ans (A)

• SRP = ⊖ ⇒ oxidation is favourable ⇒ good R.A.

SRP = ⊕ ⇒ reduction is favourable ⇒ good O.A.

Q. Which is the strongest O.A. →

✓a) $Cu^{2+} \longrightarrow Cu$ Reduction favourable

b) $Zn^{2+} \longleftarrow Zn$

c) $Mn^{2+} \longleftarrow Mn$

d) $V^{2+} \longleftarrow V$

e) $Ni^{2+} \longleftarrow Ni$

$\rightarrow$ oxidation favourable
SRP = more ⊖ than expected.

↓ highest HE in 3d (smallest cation)

$Zn^{2+} \rightarrow 3d^{10}$ $Mn^{2+} \rightarrow 3d^5$

$V^{2+} \rightarrow 3d^3 \rightarrow t_{2g}^3$ in aq.

• $\underline{\overset{(SRP)}{E^\circ_{M^{+3}/M^{+2}}}}$ for 3d ⇒

ion → ion

$\underbrace{SRP}_{\text{irregular}} = \underbrace{IE - HE}_{\text{irregular}}$

Sc = $-\infty$

Zn = $+\infty$

Co > Mn > Fe ⊕

rest ⇒ ⊖

→ $Sc^{3+} \longrightarrow Sc^{2+}$ ⇒ reduction ∞ not favourable ⇒ SRP = $-\infty$.

↓ नहीं बनता

oxidation ∞ favourable

→ Same for Zn ⇒ Zn^{3+} doesn't exist.

Q. Which has strong tendency to convert into M^{+2} :-

✓a) Co^{+3}

b) Fe^{3+}

c) V^{3+}

d) Cr^{+3}

$M^{+3} \longrightarrow M^{2+}$ ⇒ reduction favourable ⇒ SRP ⊕

Co has max SRP in given.

→ Fe^{2+} is more stable than Fe^{3+} in (aq.). Otherwise,

$Fe^{3+} \longrightarrow Fe^{2+}$ SRP = ⊕

⇒ reduction favourable ⇒ Fe^{2+} more stable

$Fe^{2+} < Fe^{3+}$

$(d^5) \rightarrow t_{2g}^3$

Q. • Trihalide of Co which can exist :-

✓ a) CoF_3 | Co has ⊕ SRP ⇒ $Co^{+3} \longrightarrow Co^{2+}$ favourable
b) $CaCl_3$ | ⇒ good O.A. ⇒ can't exist with R.A
c) $CoBr_3$
d) CoI_3 | $Co^{+3} + 3X^- \longrightarrow CoX_2 + \frac{1}{2}X_2$.

(Cl^-, Br^-, I^-)

Q. Trihalide of Fe which does not exist :-

a) FeF_3 | Fe^{3+} / is weaker O.A. than Co^{+3}. So no
b) $FeCl_3$ | redox with F^-, Cl^-, Br^-. Only with max. strong
c) $FeBr_3$ | R.A, I^-.
✓ d) FeI_3

Q. • Classify species acc. to oxidising nature and reducing nature.

a) CeO_2 OA $Ce^{+4} \longrightarrow Ce^{+3}$ more stable ⇒ red^n fav.
b) $SnCl_2$ RA $Sn^{2+} \longrightarrow Sn^{4+}$ more stable
c) H_3PO_3 RA $P^{+3} \longrightarrow P^{+5}$ IPE
d) $YbSO_4$ RA $Yb^{+2} \longrightarrow Yb^{+3}$ more stable
e) Mn_2O_3 OA $Mn^{3+} \longrightarrow Mn^{2+}$ SRP ⊕
f) Pb_3O_4 OA $Pb_3O_4 = PbO_2 + 2PbO$ ⇒ $\overset{+4}{Pb}O_2 \longrightarrow Pb^{2+}$
g) $CrSO_4$ RA $Cr^{2+} \longrightarrow Cr^{3+}$ t_{2g}^3 ; SRP ⊖
h) $InCl$ RA $In^+ \longrightarrow In^{3+}$ more stable

• Cr^{2+} is stronger R.A. than Fe^{2+}

$Fe^{3+} \longrightarrow Fe^{2+}$ SRP = ⊕ reduction fav. ⇒ oxidation less fav.
⇒ Fe^{2+} weak R.A.

$Cr^{3+} \longrightarrow Cr^{2+}$ ⇒ SRP = ⊖ oxidation fav. ⇒ Cr^{2+} strong RA

- $E^\circ_{M^{+3}/M^{+2}} = \oplus \Rightarrow$ Higher → OA
- $E^\circ_{M^{+3}/M^{+2}} = \ominus \Rightarrow$ lower → RA

Q. Which of the following can be reduced by $H_2(g)$?

a) $AuCl_3$
b) $PbCl_4$
c) $FeCl_3$
✓d) All

SRP of $H_2 = 0 \Rightarrow$ If with $\oplus$ SRP metal,
metal = OA $\Rightarrow$ H = RA = <u>reduces</u>

$$AuCl_3 \xrightarrow{H_2(RA)} Au + HCl \quad E^\circ_{Au^{+3}/Au} = \oplus$$

$$\underset{+4}{Pb}Cl_4 \xrightarrow{H_2(RA)} PbCl_2 + HCl \quad E^\circ_{Pb^{4+}/Pb^{2+}} = \oplus \text{ (stability)}$$

$$FeCl_3 \xrightarrow{H_2(RA)} \overset{+2}{Fe}Cl_2 + HCl \quad E^\circ_{Fe^{3+}/Fe^{2+}} = \oplus \text{ (stability)}$$

$\ominus$ SRP

- $$Fe \xrightarrow{\text{dil}\cdot 2HCl} FeCl_2 + H_2$$

more stable (aq.)

$$Fe \xrightarrow{\text{dil } 3HCl} \downarrow$$

$$\underset{\boxed{OA}}{FeCl_3} + \underset{\boxed{RA}}{\tfrac{3}{2}H_2} \longrightarrow \underline{\underline{FeCl_2}}.$$

Fe + dil. HCl
↓
$FeCl_2 + H_2$
$\boxed{\text{NO } FeCl_3}$

B) <u>OXIDISING NATURE OF NON METALS</u> ⇒

<u>Reduction</u>

- $$\underset{\boxed{OA}}{\tfrac{1}{2}X_2(g)} \xrightarrow[\downarrow]{BDE} X(g) \xrightarrow[+e^\ominus]{\uparrow EA} X^-(g) \xrightarrow[+H_2O]{\uparrow HE} X^-\underline{(aq.)}$$

- Favourable condition for stronger OA

① low BDE
② High EA
③ High HE

• • For halogen :-

① BDE = $Cl_2 > Br_2 > \overset{\text{due to lp-lp}}{F_2} \geq I_2$

② EA = $Cl > F > Br > I$

③ HE = $F^- > Cl^- > Br^- > I^-$

④ Oxidising Nature : $F_2 > Cl_2 > Br_2 > I_2$ (HE dominates)

⑤ Reducing Nature : $\underset{\text{never R.A.}}{F^-} < Cl^- < Br^- < I^-$

• F_2 among halogens is best OA because of :-

a) lowest BDE	a) low BDE
b) highest EA	b) high EA
[✓ c) highest HE]	c) highest / high HE
d) all	[✓ d) all]

⑥ Reactivity : $F_2 > Cl_2 > Br_2 > I_2$

⑦ density : $F_2 < Cl_2 < Br_2 < I_2$ (mass)

⑧ Reactivity wrt oxidising nature : $F_2 > Cl_2 > O_2 > N_2$

O_2 and N_2 ⇒ high BDE, and $\oplus\ \Delta H_{eg}$ (formation of poly $\ominus$ anion is always endo)

- $MgBr_2 (aq.) + \underset{\text{more reactive}}{Cl_2} \longrightarrow MgCl_2 (aq) + Br_2$ MOP

- $2\,NaI (aq) + \underset{\text{greenish yellow (upper layer in apparatus)}}{Cl_2} \longrightarrow 2\,NaCl + \underset{\text{violet (lower layer)}}{I_2}$] Halide layer test

- $2\,KBr (aq) + \underset{\text{less reactive}}{I_2} \longrightarrow$ X

C) OXIDISING NATURE OF OXIDES & REDUCING NATURE OF HYDRIDE

• OXIDISING NATURE OF OXIDES $\propto \frac{1}{T.S.}$

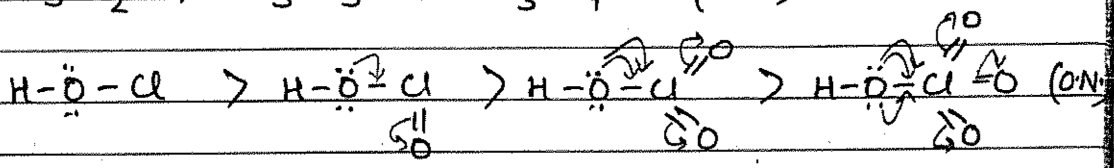
• REDUCING NATURE OF HYDRIDES $\propto \frac{1}{T.S.}$

- $SO_2 < SeO_2 < TeO_2$ (O.N.)
- $CO_2 < SiO_2 < GeO_2 < SnO_2 < PbO_2$ (O.N.)
- $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$ (R.N.)
- $H_2O < H_2S < H_2Se < H_2Te$ (R.N.)

size ↑
B.L. ↑
B.S. ↓
T.S. ↓
O.N. ↑
R.N. ↑

- $CrO_3 > MoO_3 > WO_3$ (O.N.) $(d \rightarrow \downarrow \rightarrow Z_{eff} \uparrow \Rightarrow T.S. \uparrow)$
- $MnO_4^- > TcO_4^- > ReO_4^-$

- $H_3PO_2 > H_3PO_3 > H_3PO_4$ (R·N·)

- 

(O·N·)

Reso ↑ ⇒ multiple bond character in breakable O–Cl bond ↑
B·S· ↑ ⇒ T·S· ↑ ⇒ O·N· ↓

⊕ charge on Cl ↑ ⇒ attraction with δ– ↑ ⇒ B·S· ↑
(B·L ↓) ⇒ T·S· ↑ ⇒ O·N· ↓

- $MnO_4^- > Cr_2O_7^{2-} > VO_2^+$ (O·N·) On the basis of stability of product (SRP)

- $HNO_3 > H_2SO_4 > H_3PO_4$ (O·N·)
any conc. v.v. bad.

- Species having highest O·S· can act as O·A· only.
eg. $KMnO_4$, $K_2Cr_2O_7$, HNO_3, etc.

- Species having lowest O·S· can act as R·A· only.
eg. H_2S, $Cl^{\ominus}$, $Br^{\ominus}$, HI, $I^{\ominus}$, etc.

- Species having intermediate O·S· can act as both O·A and R·A.
eg SO_2, H_2O_2, O_3, NO_2, HNO_2, etc.

→ acidified $\underset{\text{only O·A·}}{\overset{+7}{KMnO_4}} + \underset{\text{both} \Rightarrow \text{R·A}}{\overset{+4}{SO_2}} \longrightarrow Mn^{2+} + \underset{+6}{SO_4^{2-}}$

→ $2\underset{\text{only R·A·}}{H_2\overset{-2}{S}} + \underset{\text{both} \Rightarrow \text{O·A·}}{\overset{+4}{SO_2}} \longrightarrow 3\overset{0}{S} + 2H_2O$ (Comproportionation)

- SOME IMPORTANT R.A. :-

→ $H_2S \longrightarrow S$

→ $SO_2 \longrightarrow SO_4^{2-}$ / SO_3 (rare)

→ —ite ⟶ —ate (NO_2^-, $SO_3^{2-} \longrightarrow NO_3^-$, SO_4^{2-})

→ L.O.S. of metal ion ⟶ H.O.S. of metal ion
(Sn^{2+}, $Fe^{+2} \longrightarrow Sn^{4+}$, Fe^{3+})

→ Halide ⟶ Halogen (Cl^-, Br^-, $I^- \longrightarrow Cl_2$, Br_2, I_2)

→ Metal ⟶ Metal Salt

→ NM or metalloid ⟶ —ic acid

→ HCOOH or $H_2C_2O_4 \longrightarrow CO_2 + H_2O$

- SOME IMPORTANT O.A. :-

→ $KMnO_4$ (purple)
- $\xrightarrow{\text{acidified}}$ Mn^{2+} or $MnSO_4$ (colorless sol^n)
- $\xrightarrow{\text{natural or weak alkaline}}$ MnO_2 (black solid)
- $\xrightarrow{\text{alkaline}}$ MnO_4^{2-} (green)

→ acidified $K_2Cr_2O_7$ (orange) $\longrightarrow Cr^{3+}$ or $Cr_2(SO_4)_3$ (green)

→ conc. $H_2SO_4 \longrightarrow SO_2$

→ Conc. $HNO_3 \longrightarrow NO_2$

(CHAPA)

→ dil. HNO_3 $\xrightarrow{\oplus \text{ SRP metal}}$ NO

$\xrightarrow{\ominus \text{ SRP metal}}$ N_2O

$\overset{\text{lewis base}}{NH_3} + \text{rest } \overset{\text{Acid}}{HNO_3} \rightarrow NH_4NO_3$ (finally)

→ v. dil. HNO_3 $\xrightarrow{\ominus \text{ SRP metal}}$ NH_3 or NH_4NO_3

$\xrightarrow{\oplus \text{ SRP metal}}$ X

→ $H_2O_2 \longrightarrow H_2O$

→ $O_3 \longrightarrow O_2$

→ Cl_2 water $\longrightarrow$ HCl

→ PbO_2 or Pb_3O_4 or $Pb_2O_3 \longrightarrow PbO$ (Pb^{2+} salt)

BORON FAMILY

* B_2H_6 :- DIBORANE

• PREPARATION :-

1. INDUSTRIAL : $BF_3 + LiAlH_4 \xrightarrow{Ether} B_2H_6 + \underbrace{LiF + AlF_3}_{LiAlF_4}$

2. LAB : $I_2 + 2\,NaBH_4 \longrightarrow 2NaI + B_2H_6 + H_2$

— $LiAlH_4$ and $NaBH_4$ acts as R.A.

3. $2\,BF_3 + 6\,NaH \xrightarrow{Ether} B_2H_6 + 6\,NaF$

⇒ BF_3 or I_2 + Metal Hydride $\longrightarrow B_2H_6$

• B_2H_6 and LEWIS BASE :-

a) In presence of smaller L.B. like H^-, $\underbrace{NH_3,\ CH_3-NH_2,\ (CH_3)_2-NH}_{\text{presence of H-bonding}}$

2 units of same L.B. molecule get bonded ⇒ have to attack on 1 B only ⇒ asymmetric

→ $B_2H_6 \longrightarrow BH_2^+ + BH_4^-$ (asymmetric cleavage)

→ $$2\,\overset{+}{Na}\underset{LB}{\overset{-}{H}} + B_2H_6 \longrightarrow \underbrace{Na^{+}\left[\begin{matrix}H^{-}\searrow \\ H^{-}\nearrow\end{matrix}\overset{+}{B}H_2\right] + \overset{+}{Na}BH_4^{-}}_{2\,NaBH_4}$$

b) In presence of larger L.B. like $(CH_3)_3-N$, pyridene, THF, etc.

→ $B_2H_6 \longrightarrow BH_3 + BH_3$ No intermolecular association ⇒ 2 units of same attack on 2 B ⇒ symmetric cleavage

* $(BN)_x$ = Borazone ; diamond like structure

→ $2\ (CH_3)_3-\ddot{N} + B_2H_6 \longrightarrow 2\left[(CH_3)_3N \rightarrow BH_3\right]$ adduct

→ $2\ CO + B_2H_6 \longrightarrow 2\ (OC \rightarrow BH_3)$

- CO is gaseous, so no intermolecular association ⇒ attack on 2 B ⇒ symmetric cleavage.

- $:C \overset{\leftarrow}{\equiv} O: \;=\; :\overset{-}{C} \equiv \overset{+}{O}:$ C is donor atom

• B_2H_6 and NH_3 -

$\boxed{B_2H_6}$

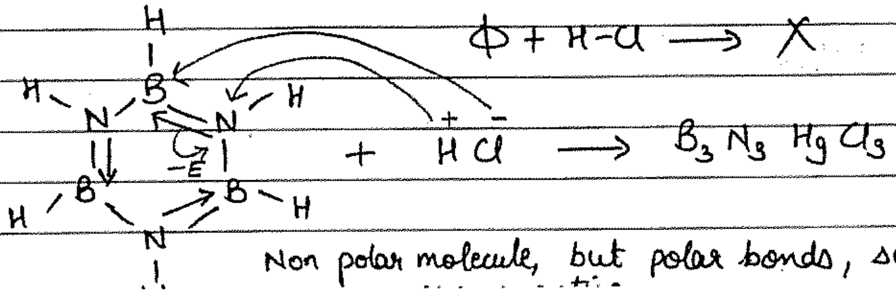
$\xrightarrow[\text{low temp}]{NH_3 \text{ excess}} \left[\begin{matrix} H_3N \searrow \\ H_3N \nearrow \end{matrix} \overset{+}{B}H_2\right] \overset{-}{B}H_4$

$\xrightarrow[T \simeq 200^\circ C]{B_2H_6 : NH_3 :: 1:2}$ —— 11 —— $\xrightarrow{H_2(g)\uparrow} B_3N_3H_6$
= inorganic benzene
= borazine = borazol

$\xrightarrow[T > 200^\circ C]{NH_3 \text{ excess}} (BN)_x$ inorganic graphite
≠ borazone ; graphite like structure.

Q. Assertion : Inorg. ϕ is more reactive than ϕ.
Reason : Inorg. ϕ is a polar molecule but ϕ is not.

try (C)



ϕ + H-Cl → X

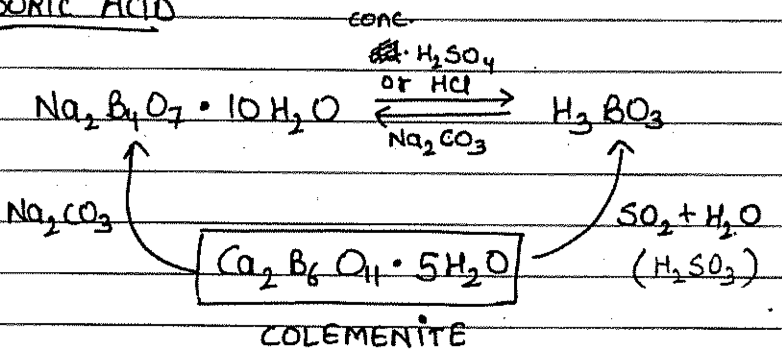
+ HCl → $B_3N_3H_9Cl_3$

Non polar molecule, but polar bonds, so

→ B_2H_6 is used as rocket ~~f~~ fuel due to high heat of combustion.

* H_3BO_3 :- BORIC ACID

- PREPARATION :-



$$Na_2B_4O_7 \cdot 10H_2O \underset{Na_2CO_3}{\overset{\text{conc. } H_2SO_4 \text{ or } HCl}{\rightleftharpoons}} H_3BO_3$$

$Na_2B_4O_7 \cdot 4H_2O$
KERNITE

- H_3BO_3 and ALCOHOL :-

$$\underset{\text{OH जाएगा}}{H_3BO_3} + 3\ \underset{\text{H जाएगा}}{C_2H_5-OH} \xrightarrow[-3H_2O]{} (C_2H_5)_3BO_3$$

triethyl borate (green flame)
(test of borate ion →)

- Acidic NATURE :-

→ H_3BO_3 is a weak monobasic Lewis Acid.

$$\underset{L.A.}{B(OH)_3} + H_2\ddot{O}: \rightleftharpoons B(OH)_4^- + H^+$$

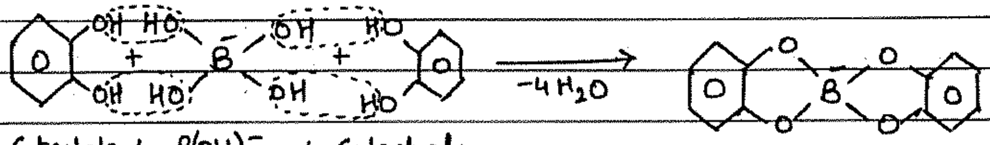
→ H_3BO_3 becomes tribasic when reacts with fused NaOH / KOH.

$$\underset{\text{BRONSTED ACID}}{H_3BO_3} + 3\,NaOH \xrightarrow{\Delta} Na_3BO_3 + 3H_2O$$

→ Due to weak acidic nature of Boric acid, it can't be titrated with NaOH soln. But in presence of cis-1,2-diol, glycerol, mannitol or catechole it behaves as strong acid due to

- shifting of rxn. in forward direction by eliminating $B(OH)_4^-$ from rxn. mixture

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$$



Catechole + $B(OH)_4^-$ + Catechole

stable chelate compound.

- BORAX BEAD TEST :- Test of transition metal ions.

$$Na_2B_4O_7\cdot 10H_2O \xrightarrow[-10H_2O]{100^\circ C} Na_2B_4O_7 \xrightarrow{740^\circ C} 2NaBO_2 + B_2O_3$$

crystal changes → vol. ↑ → swells up

$$\underset{\text{Sodium metaborate}}{2NaBO_2} + \underset{\text{Boron sesque oxide}}{B_2O_3} \longrightarrow \text{transparent mixture} = \text{Borax bead}$$

→ Co^{2+} = dark blue Cr^{2+} = green
Cu^{2+} = blue Fe^{3+} = yellow
Ni^{2+} = reddish brown
Mn^{2+} = pink

* EN :- $B > \underbrace{Al < Ga < In < Tl}_{Z_{eff}\uparrow}$

- Tl is less electropositive than Al due to high I.P.

- ^{10}B isotope is used as controller in nuclear reactor, absorbs neutrons.

- Boric acid and Borax are used to make pyrex glass.
- Ga is used in thermometers for measuring high temperature due to less MP and high BP.

CARBON-FAMILY

* **CO** :-

- **PREPARATION** :-

1. $\underset{\text{COKE}}{C} + \underbrace{\frac{1}{2}O_2 + N_2}_{\text{air}} \xrightarrow{\Delta} \underbrace{CO + N_2}_{\text{producer gas}}$

2. $CO_2 + C \longrightarrow 2CO$

3. Coal gasification :- $C + H_2O \xrightarrow{473-1273\ K} \underbrace{CO + H_2}_{\text{water gas}}$

$\underbrace{CO + H_2}_{\text{water gas}} + \underbrace{H_2O}_{\text{water}} \longrightarrow CO_2 + \underset{\text{MOP}}{\underline{\underline{2H_2}}}$ "water gas shift rxn."

→ Natural Gas = CH_4
→ Coal Gas = $CO_2 + CO + H_2 + CH_4$
→ Semi-Water gas = $CO + H_2 + N_2$

4. $HCOOH \xrightarrow{\text{conc. } H_2SO_4} H_2O + CO$

- Colorless gas, neutral oxide, v. less soluble in water, burns with blue flame.

- CO is absorbed by ammonical Cu_2Cl_2 sol^n.
  CO_2 is absorbed by KOH sol^n

- CO acts as Lewis Base. $Ni + 4\overset{\cdot\cdot}{C}O \longrightarrow [\overset{0}{Ni}(CO)_4]$

- CO acts as R.A. $\underset{\text{Haematite}}{Fe_2O_3} + 3C \xrightarrow{\text{high temp.}} 2Fe + 3CO\uparrow$

$Fe_2O_3 + 3CO \xrightarrow{\text{low temp.}} 2Fe + 3CO_2\uparrow$

- ~~ACTIVATION~~ ESTIMATION OF CO :-

$$\underset{O.A.}{\overset{+5}{I_2O_5}} + \underset{R.A.}{5\overset{+2}{C}O} \longrightarrow 5\overset{+4}{C}O_2 + \underset{\text{(violet)}}{\overset{0}{I_2}}$$

$+ 2Na_2S_2O_3$ Redox $\downarrow$ TITRATION WITH HYPO SOL^n ($Na_2S_2O_3 \cdot 5H_2O$)

$$\underset{\text{colorless}}{\underline{2NaI}} + \underset{\text{Sodium tetra thionate}}{Na_2S_4O_6}$$

- ESTIMATION OF O_3 :-

$$2\underset{R.A.}{KI} + H_2O + \underset{O.A.}{O_3} \longrightarrow 2KOH + O_2 + I_2 \text{ (violet)}$$

$+ 2Na_2S_2O_3$ $\downarrow$ Titration with Hypo sol^n ($Na_2S_2O_3 \cdot 5H_2O$)

$$\underset{\text{colorless}}{\underline{2NaI}} + Na_2S_4O_6$$

TEST OF CO :-

$PdCl_2 + H_2O + CO \longrightarrow CO_2 + 2HCl + Pd$ (Black)

- CO is a poisonous gas. $Hb + CO \longrightarrow$ Carboxy Hb
- Antidote of CO = Carbogen (90–95% O_2 + 5–10% CO_2)
- Carbogen is also used for artificial respiration of pneumonia patients.

* REACTION OF dil. HCl with CARBONATE & SULPHITE SALTS ⇒

- $CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$
  $CaCO_3$ insoluble in H_2O; $CaCl_2$ soluble in H_2O
- $CaSO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + SO_2$
  $CaSO_3$ insoluble in H_2O; $CaCl_2$ soluble in H_2O
- II A carbonates are insoluble / sparingly soluble in water, but soluble in dil. HCl.

* PLUMBOSOLVANCY ⇒

Dissolution of Pb in H_2O.

→ $Pb + H_2O + \frac{1}{2}O_2 \longrightarrow Pb(OH)_2$ (poisonous)

→ ∴ Pb pipes are not used for transportation of drinking water.

* In C family, amorphous C and Sn react with H_2O only.

Q. Which of these can react with water –

a) Diamond
b) silicon
c) Ge
✓ d) Sn

$$Sn + 2\,H_2O \xrightarrow{\Delta} SnO_2 + 2\,H_2$$

$$Sn + 4\,HOH \rightarrow Sn(OH)_4 + 2H_2$$

$$\downarrow \Delta$$

$$SnO_2 + 2H_2O$$

Q. Incorrect statement for CO_2 is:

a) used in soft drinks
b) used as fire extinguisher
c) cause of green house effect
✓ d) doesn't show resonance

$$^{-}O-C\equiv O^{+} \quad \text{B.L. slightly}$$

$$\updownarrow$$

$$:\ddot{O}=C=\ddot{O}:$$

$$\updownarrow$$

$$^{+}O\equiv C-O^{-}$$

C=O B.L. is slightly less than expected B.L. in sp^2 C=O, as charge induces so attraction ↑.

- Si and Ge are used in SC and transitor

- Lamp black is softest form of C.

- Carbon black is obtained by heating hydrocarbons in limited supply of air.

- Charcoal and coke are obtained by heating wood and coal respectively, in absence of air

- $H_2CO_3 + HCO_3^-$ buffer sol^n helps to maintain blood pH.

NITROGEN-FAMILY

* **HNO_3** :- NITRIC ACID

- PREPARATION ⇒

1. LAB : $NaNO_3 + \text{conc. } H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$

2. OSTWALD METHOD :-

a) By catalytic oxidation of ammonia

$$\overset{-3}{N}H_3 + \overset{0}{O_2} \xrightarrow[500\,K]{Pt,\ 9\,bar} \overset{+2}{N}O + H_2\overset{-2}{O}$$

b) $2NO + O_2 \longrightarrow 2NO_2$

c) $2\overset{+4}{N}O_2 + H_2O \longrightarrow H\overset{+5}{N}O_3 + H\overset{+3}{N}O_2$

$$\downarrow H^+$$

$$H\overset{+5}{N}O_3 + \overset{+2}{N}O$$

3. BERKLAND EYDE PROCESS :- NO is obtained by reaction of N_2 and O_2.

$N_2 + O_2 \xrightarrow{\text{Electric Arc}} 2NO$

Rest same as Ostwald's process.

Q. Assertion : 68% HNO_3 is converted to 98% HNO_3 by using conc. H_2SO_4

Reason : conc. H_2SO_4 acts as dehydrating agent

Ans (A)

→ On standing / pure form, 100% / conc. HNO_3 decomposes to form $H_2O + NO_2 + [O]$. As a result, solⁿ becomes brown initially. Then [O] fades NO_2 to become yellow.

- $Cu + \text{dil. } HNO_3 \xrightarrow{} Cu(NO_3)_2 + NO + H_2O$ ($\simeq$ 20% HNO_3)

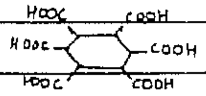
- $Zn + \text{dil. } HNO_3 \longrightarrow Zn(NO_3)_2 + N_2O + H_2O$

- $Sn + \text{dil. } HNO_3 \longrightarrow Sn(NO_3)_2 + NH_4NO_3$

- ~~($\simeq$ 6% HNO_3)~~
  $Zn + \text{v. dil. } HNO_3 \longrightarrow Zn(NO_3)_2 + NH_4NO_3$

→ मन मोंगो H_2
Mg and Mn give H_2 gas with v. dil. HNO_3.
Mg/Mn + v. dil. HNO_3 ⟶ Mg/Mn nitrate + H_2 (RA) but v. dil. HNO_3 is a quite weak O.A., so no further redox.

→ Pb is a ~~negative~~ ⊖ SRP metal but behaves as ⊕ SRP metal with dilute HNO_3 or v. dil. HNO_3

R.A. ↓	conc. HNO_3 (O.A.)
Zn	$Zn(NO_3)_2$
Cu	$Cu(NO_3)_2$
H_2S	S
SO_2	SO_4^{2-}
SO_3^{2-}	SO_4^{2-}
X^-	X_2 (except F)
Fe^{2+}	Fe^{3+}
B	H_3BO_3
P_4	H_3PO_4
As	H_3AsO_4
S	H_2SO_4
I_2	HIO_3
C (charcoal)	$H_2CO_3 \longrightarrow H_2O + CO_2$
* C (graphite)	$C_6(COOH)_6$ **MELLITIC ACID** 

* Au^{3+} C.N = 4
Pt^{4+} C.N = 6

conc. HNO_3

* Sn ↓ H_2SnO_3 Meta Stannic Acid
HCOOH ↓ $CO_2 + H_2O$
~~HNO_3~~ ↓ ~~NO_2~~
NO_2

→ Skin becomes yellow in presence of conc. HNO_3 as it gets oxidised; HNO_3 oxidises proteins to xanthoproteins.

→ Be, Al, Cr, Fe do not dissolve ~~ka~~ (become inert) in Conc. HNO_3 due to formation of oxide layer.

→ Au and Pt (noble metals) react only with AQUA REGIA.
Aqua Regia = (3 part conc. HCl + 1 part conc. HNO_3)

$$\Downarrow$$

$$NOCl + 2H_2O + 2[Cl]$$

– $Au + 3Cl \rightarrow AuCl_3 \xrightarrow[HCl]{} H^+[Au(Cl_4)]^-$
Tetra Chloro Auric Acid.

– $Pt + 4Cl \rightarrow PtCl_4 \xrightarrow{2HCl} H_2[PtCl_6]$
Hexa Chloro Platinic Acid

→ Ag doesn't react with aqua regia.

Q. Conc. HNO_3 is used in/as

① fertiliser and explosive formation [TNT; (2,4,6 – TNT)]
② as oxidiser for rocket fuel.
③ for itching of metals.
④ for pickling of stainless steel.
✓⑤ all

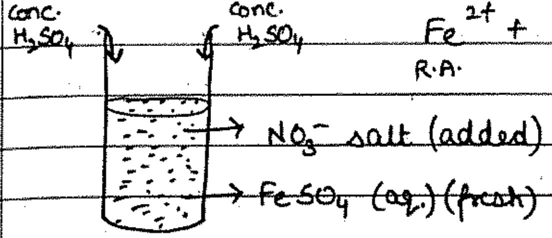
* Ag_2SO_4 is insoluble in water.

Q. • Which of these is an explosive substance –

a) TNT (tri nitro toluene)
b) nitroglycerine
c) Mn_2O_7
d) NCl_3
e) XeO_3
f) all

• **BROWN RING TEST** :– NO_3^- and NO_2^-

$$\underset{R.A.}{Fe^{2+}} + \underset{O.A.}{NO_3^-} + 4H^+ \longrightarrow Fe^{3+} + NO + 2H_2O$$



$FeSO_4(aq) = FeSO_4 \cdot 7H_2O$.
$6H_2O$ coordinate with Fe, in [ ]
1 with H bond → टंगा here

$$[Fe(H_2O)_6]SO_4 + \overset{\cdot\cdot}{N}O \longrightarrow [Fe(H_2O)_5(NO)]SO_4$$

$:N \equiv O$

(Brown Ring complex)

$$NO_2^- + H^+ \longrightarrow HNO_2 \xrightarrow{H^+} \underline{HNO_3} + \underline{NO}$$

• Identification of NO_3^- by brown ring test in presence of NO_2^- is not a confirmatory test.

• It is not a confirmatory test of NO_3^- in presence of metal ions which form insoluble metal sulphate like Pb^{2+}, Sr^{2+}, Ba^{2+}, Ca^{2+}, Ag^+

- NO is isolated / purified ~~by~~ from a mixture of nitrogen oxides by using aq. $FeSO_4$ sol^n followed by warming or shaking.

$$NO + N_2O, NO_2, N_2O_5, \cdots \xrightarrow[FeSO_4\,(aq)]{[Fe(H_2O)_6]SO_4} [Fe(H_2O)_5(NO)]SO_4$$

$$\Delta \downarrow \text{warming / shaking}$$

$$\underline{NO} + \cdots$$

- PREPARATION OF NO ⇒

$$FeSO_4\,(aq) + NaNO_2\,(aq) + \text{conc. } H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + NO + NaHSO_4 + H_2O$$

Q: $A + B \xrightarrow{250\,K} C$ A, B, C are nitrogen oxides

Neutral NO   Dimer N_2O_4 N_2O_3 blue solid @ low temp <0°C

Incorrect statement is –

a) C can exist in both symmetric and asymmetric structure.
b) monomer of B is paramagnetic and colored
✓ c) B has all identical B.L
d) B.O. of A is 2.5.

* NH_3 :-

- PREPARATION :-

1. HABER'S PROCESS :- $N_2 + 3H_2 \xrightleftharpoons{Fe_2O_3,\ K_2O,\ Al_2O_3} 2NH_3$ $(\Delta H = \ominus)$

Favourable conditions : 700 K (low temp), 200 atm (high pr)

2. Reaction of NaOH ~~NH_4OH~~ with ammonium ~~metal~~ salt:

$$(NH_4)_2SO_4 + NaOH \longrightarrow Na_2SO_4 + 2NH_4OH$$

$$\downarrow$$

$$2NH_3 + 2H_2O$$

3. By hydrolysis of urea.

$$(NH_2)CO(NH)_2 + H_2O \longrightarrow 2NH_3 + CO_2$$

4. All N containing acid radicals (anions, like NO_2^-, NO_3^-, CN^-, SCN^-, etc.) give NH_3 gas when reacts with Zn or Al and NaOH.

$$\underset{(O.A)}{NO_2^-} \text{ or } NO_3^- + Al/Zn + OH^- + H_2O \longrightarrow NH_3 + [Al(OH)_4]^-$$

Q. Incorrect statement for NH_3 is –

a) highly soluble in water but weak base
b) liq. NH_3 is used as a refrigerant
c) gives brown ppt with Nessler's Reagent ($K_2HgI_4 + KOH$)
✓d) if excess amt. of NH_3 reacts with Cl_2 then NCl_3 forms

4 a) highly soluble due to H bonding; $NH_3 + H_2O \rightleftharpoons \underset{W.B.}{NH_4OH}$

b) high pressure NH_3 gives liq. @ v. low temp

c) NH_3 or NH_4^+ salt $\xrightarrow{\text{Nessler's Reagent}}$ $HgO \cdot Hg(NH_2)I \downarrow$

BROWN; iodide of Millon's Base

* d block ⇒ d^0 / d^{10} = colorless
$d^1 - d^9$ = mostly colored

d) $\underset{R.A.}{\overset{-3}{NH_3}} + \underset{(excess)}{3\overset{\overset{O.A.}{0}}{Cl_2}} \longrightarrow 3H\overset{-1}{Cl} + \underset{explosive}{\overset{+3}{N}\overset{-1}{Cl_3}}$

$\underset{(excess)}{2\overset{-3}{NH_3}} + 3\overset{0}{Cl_2} \longrightarrow 6H\overset{-1}{Cl} + \overset{0}{N_2}$

$6\overset{-3}{NH_3} + 6HCl \longrightarrow 6\overset{-3}{N}H_4Cl$

$\underset{excess}{8NH_3} + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$

- REACTION WITH METAL SALT ⇒

→ $\underset{(salt)}{FeCl_3\,(aq.)} + 3NH_4OH \longrightarrow 3NH_4Cl + \underset{(BROWN)}{Fe(OH)_3} \downarrow / Fe_2O_3 \cdot xH_2O$

→ $ZnSO_4\,(aq.) + 2NH_4OH \longrightarrow (NH_4)_2SO_4 + \underset{(WHITE)}{Zn(OH)_2} \downarrow$

→ $\overset{+}{Ag}\overset{-}{Cl}\,(ppt.) + 2NH_3 \longrightarrow [Ag(NH_3)_2]^+Cl^-$ colorless sol^n (d^{10})

$CuSO_4 \cdot 5H_2O$, blue (s)

→ $CuSO_4\,(aq.) + \underset{L.B.}{4NH_3} \longrightarrow \underset{Dark\ Blue\ sol^n}{[Cu(NH_3)_4]SO_4}$

- s-block metal and liq. NH_3 sol^n ⇒

→ $M(s) + \underset{(polar)}{(x+y)NH_3} \longrightarrow \underset{ammoniated\ cation}{M^+(NH_3)_x} + \underset{ammoniated\ e^\ominus}{e^\ominus(NH_3)_y}$

→ Be, Mg do not form this kind of sol^n due to high I.P.

* Amide = $NH_2^{\ominus}$
Imide = NH^{-2}

→ PROPERTIES :- $M^+(NH_3)_x + e^-(NH_3)_y$ sol^n

1. Paramagnetic in nature
2. Acts as R.A
3. Blue in color (bond break + form)
4. Best conductor in sol^n form

→ due to presence of ammoniated $e^{\ominus}$.

→ If concentration of Metal ion ↑, then blue color of sol^n turns into bronze color and its paramagnetism also decreases due to formation of 'metal cluster.'

→ In presence of impurities or on standing, metal reacts with NH_3 and forms metal amide.

$$Na + NH_3(l) \xrightarrow[\text{Fe as impurity}]{\text{standing}} \underset{\text{Sodamide}}{\overset{+}{Na}\overset{-}{NH_2}} + \frac{1}{2}H_2$$

$$2Li + NH_3 \longrightarrow \underset{\text{Lithium Imide}}{Li_2(NH)} + H_2$$

Q. Product formed when $Na_2[\overset{+2}{N}i(CN)_4]$ reacts with $\overset{\text{reducing agent}}{Na + NH_3(l)}$ sol^n

a) ✓ $Na_4[Ni(CN)_4]$ b) $Na_2[Ni(CN)_4(NH_3)_2]$

c) $[Ni(NH_3)_4]^{2+}$ d) $NaNH_2$

Ans $Na_2[Ni(CN)_4] \xrightarrow{2e^{\ominus}} Na_4[\overset{0}{Ni}(CN)_4]^{-4}$

* **N_2 :-**

Q. Purest N_2 can be obtained by heating of

a) $NH_4NO_3 \xrightarrow{\Delta} N_2O + H_2O$
b) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$ (green residue)
c) $Ba(N_3)_2 \xrightarrow{\Delta} Ba + N_2$
d) $NaNO_2\,(aq) + NH_4Cl\,(aq) \longrightarrow NaCl + \overset{R.A.}{\overset{-3}{N}}H_4\overset{O.A.}{\overset{+3}{N}}O_2$
(Lab Method for preparation of N_2)

$$\overset{-3}{N}H_4\overset{+3}{N}O_2 \xrightarrow{\Delta} N_2 + 2H_2O$$

Q. • Impure N_2 is purified by passing through acidified $K_2Cr_2O_7$ solⁿ.

• Li, all IIA metals, Al and amorphous B form metal nitride when heated with N_2.

- $6Al + 3N_2 \xrightarrow{\Delta} 6AlN$
- $3Mg + N_2 \xrightarrow{\Delta} Mg_3N_2$

• Li, Be, Mg, Al, and amorphous B form metal oxide and metal nitride when heated with air.

$$\begin{tikzcd} B\ (\text{amorphous}) \arrow[r, "\Delta", "O_2+N_2"'] & {[B_2O_3 + BN]} \arrow[l, bend left, "\Delta", "Mg\ \text{or}\ Al"'] \end{tikzcd}$$

$([B_2O_3] > [BN]$ as reactivity $O_2 > N_2)$

• Except Li, other IA metals don't form metal nitride due to less L.E.

$$M(s) + N_2\,(g) \longrightarrow Mg_3N\,(s)$$

gas → solid ⇒ $\Delta S = \ominus$
$|-T\Delta S| = \oplus$

$$SE + IE + BDE + EA - \underline{LE} = \Delta H$$

low ⇒ $\Delta H = \oplus$

$$\Delta G = \underset{\oplus}{\Delta H} - \underset{\oplus}{T\Delta S}$$

↳ $\oplus$ = non spontaneous.

• • Metal nitride give NH_3 (g) on hydrolysis which produce white fumes in presence of HCl.

$$\underset{}{Li_3N} + 3HOH \rightarrow 3LiOH + \underline{NH_3} \xrightarrow{HCl} \underline{NH_4Cl}$$

produces white fumes

• N_2 (l) is used as refrigerant.

• N_2 is used for inert atmosphere (high BDE)

* $\underline{\underline{PH_3}}$:- phosphine

• **PREPARATION** :-

1. $\overset{0}{P_4} + 3NaOH + 3H_2O \longrightarrow 3NaH_2\overset{+1}{P}O_2 + \overset{-3}{P}H_3$ (disp.)
(white) Sodium Hypophosphite

2. $Ca_3P_2 + 6HOH \longrightarrow 3Ca(OH)_2 + 2PH_3$

3. $H_3\overset{+3}{P}O_3 \xrightarrow{\Delta} H_3\overset{+5}{P}O_4 + \overset{-3}{P}H_3$ (disproportionation)
1 P-H

Q. Incorrect statement for PH_3 is :-

a) Non inflammable in pure form
b) Becomes inflammable in presence of ~~B_2~~ $\overset{-2}{P_2}H_4$ + P_4 (vapour)
c) Purified by HI
d) Rotten fish smell
e) Decomposes in presence of light to red P and H_2
f) Used in smoky screen
g) Weaker L.B. than NH_3
~~h)~~ Non poisonous.

→ $:PH_3(\text{impure}) + HI \xrightarrow{\text{impurities}} PH_4^+ I^- \xrightarrow{KOH} KI + \underset{\text{pure}}{\underline{PH_3}} + H_2O$

→ white smoke produced after combustion of impure PH_3 is called 'Vortex Ring', used for smoky effect in theatres.

- **HOLME'S SIGNAL** ⇒

$$CaC_2 + Ca_3P_2 \xrightarrow{H_2O} \underset{\text{colored smoke}}{C_2H_2 + PH_3}$$

- **REACTION WITH METAL SALT** :-

- $3CuSO_4 + 2PH_3 \longrightarrow 3H_2SO_4 + \underset{\text{(Black)}}{Cu_3P_2} \downarrow$
- $3HgCl_2 + 2PH_3 \longrightarrow 6HCl + \underset{\text{(Black)}}{Hg_3P_2} \downarrow$

Q. Which of the following is not correctly matched?

a) $P_4O_{10} + H_2O \longrightarrow H_3PO_4$
b) $Br_2 + H_3PO_3 \longrightarrow (HPO_3)_n$ (Redox)
c) $PCl_3 + H_3PO_3 \longrightarrow$ pyrophosphorous acid (condensation later)
✓d) white P + NaOH ⟶ hypophosphoric acid

Q. Which of these is incorrect?

a) Bismuth has least tendency to exhibit −3 O.S.
b) Bi^{+3} is most stable wrt disproportionation reaction.
c) NF_3 is most stable halide of N
d) Pentahalides are more covalent than trihalides.
e) P and As can form dπ-dπ bond with transition metals

F). • BiF_5 is most ionic halide of N family

⇒ BiF_3 is most ionic halide of N family.

Q.
$$\begin{tikzcd}
P + Cl_2 \text{ (excess)} \arrow[r] \arrow[drrr, "\text{excess } O_2"'] & A \arrow[r, "\text{partial}", "\text{Hydrolysis}"'] & B \arrow[r, "H_2O"] & C \arrow[r, "200\,C"] & D \arrow[d, "600^\circ c"] \\
 & & & F & E \arrow[l, "\Delta"']
\end{tikzcd}$$

Ans. $A = PCl_5$ $B = POCl_3$ $C = H_3PO_4$ $D = H_4P_2O_7$
$E = (HPO_3)_n$ $F = P_4O_{10}$

Q. PCl_3 can't be obtained by :-

a) $PCl_5 \xrightarrow{\Delta} PCl_3 + Cl_2$
b) $PCl_5 + 2Ag \longrightarrow 2AgCl + PCl_3$
c) $P_4 + SOCl_2$ (thionyl chloride) $\longrightarrow PCl_3$
d) $P_4 + SO_2Cl_2$ (sulphuryl chloride) $\longrightarrow PCl_5$

OXYGEN FAMILY

* H_2SO_4 :- oil of Vitriol; King of Chemicals

• PREPARATION :-

1. CONTACT PROCESS – (i) $S + O_2 \longrightarrow SO_2$

or $\overset{+2}{Fe}S_2 + O_2 \longrightarrow Fe_2O_3 + SO_2$
iron pyrite

* Metal Sulphide + O_2 → Metal Oxide + SO_2

2) LEAD CHAMBER METHOD :- $SO_2 + \frac{1}{2}O_2 \xrightleftharpoons{NO_2} SO_3$

Rest same as Contact Process

- (ii) $SO_2 + \frac{1}{2} O_2 \xrightleftharpoons[\text{or } Pt/Fe_2O_3]{*\ V_2O_5} SO_3$ $(\Delta H = \ominus)$

Favourable conditions :- low temp. (700K), high pressure (2 bar)

(iii) $SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7 \xrightarrow{H_2O} 2\ H_2SO_4$

Q. In contact process, impurity of As_2O_3 is absorbed by —

a) H_2O ⇒ to remove dust particles
b) conc. H_2SO_4 ⇒ to remove moisture
[✓ c)] $Fe_2O_3 \cdot x\,H_2O$
d) Al_2O_3

Q. Conc. H_2SO_4 is —

corrosive; on skin, as dehydrates then exo ↑↑ when dissolves in H_2O.

a) an O.A.
b) a dehydrating agent
c) strong acid $(Ka_1 > Ka_2)$ (I.C. on O ∝ 1/stability of anion)
d) less volatile due to H - bonding
[✓ e)] all

- OXIDISING NATURE -

→ Conc. H_2SO_4 acts as mild O.A. and reduces to SO_2.

→ dil. H_2SO_4 doesn't act as O.A., only as acid.

R.A. conc. H_2SO_4 (O.A.)

Zn	$ZnSO_4$
Cu	$CuSO_4$
P_4	H_3PO_4
C	$H_2CO_3 \rightarrow CO_2 + H_2O$
S	SO_2
HBr / Br^-	Br_2
HI / I^-	I_2
F^- and Cl^-	NO REDOX

$\downarrow$

SO_2

Q. Assertion: conc. H_2SO_4 is used for preparation of acids from their corresponding salts.

Reason: conc. H_2SO_4 is a strong acid and less volatile ↓ *

Ans (A) $CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF\uparrow$ *

$HF < H_2O < H_2SO_4$ (B.P.), based on extent of H-bonding

mass ↑ ⇒ vw ↑ ⇒ volatility ↓ ⇒ HF can be separated pure

$NaCl + \text{conc. } H_2SO_4 \longrightarrow NaHSO_4 + HCl$

$NaNO_3 + \text{conc. } H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$

Q. which of the following acids can't be obtained by reaction of its corresponding salt and H_2SO_4 –

a) HF

b) HCl

c) HNO_3

[✓ d)] HBr / HI

$2NaI + H_2SO_4 \longrightarrow Na_2SO_4 + 2HI$ (RA)

$\downarrow H_2SO_4$ (OA)

$SO_2 + I_2 + H_2O$

Redox occurs more readily than double displacement

Q.• which of the following acids is used to obtain HI from NaI?

a) conc. HNO_3 b) conc. H_2SO_4 c) dil. H_2SO_4 ✓d) conc. H_3PO_4

$HI \rightarrow H^+ + I^-$

$3\,NaI + H_3PO_4 \longrightarrow Na_3PO_4 + 3HI$

(v.weak O.A.) $H_3PO_4 \hookrightarrow \times$

Q. which of the following acids doesn't form more than one series of salts -

HS^-, S^{2-} $F^-, [HF_2^-]$

a) H_2SO_4 b) H_3PO_4 * c) H_2S * d) HF

✓e) H_3PO_2

Q. conc. H_2SO_4 is used -

a) in petroleum refining
b) in fertiliser formation
c) as drying agent for gases like HCl, Cl_2
d) in storage batteries
✓e) all

* H_2S :-

• PREPARATION :- By KIPP'S APPARATUS

1. $FeS + \text{dil. } H_2SO_4 \longrightarrow FeSO_4 + H_2S$

• TEST OF H_2S :- ① Rotten egg smell.
② Gives black ppt with lead acetate solⁿ.

$(CH_3COO)_2Pb + H_2S \longrightarrow \underset{\text{Black}}{\underline{PbS}}\downarrow + 2\,CH_3COOH$

③ • Turns yellow solⁿ of $FeCl_3$ into green solⁿ of $FeCl_2$.

$$\underset{\text{Yellow}}{FeCl_3\,(aq.)} + H_2S \longrightarrow \underset{\text{Green}}{FeCl_2(aq)^{*}} + S + HCl$$

---

* **O_3 :-**

• PREPARATION :- $3\,O_2 \xrightarrow[\text{to prevent decomp of } O_3]{\text{silent elec. discharge}} 2\,O_3$ $(\Delta H = ⊕)$

$(10\%\ O_3 + 90\%\ O_2)$ max.

Q. Assertion: High conc. of O_3 is explosive in nature.
Reason: Decomposition of O_3 to O_2 is exothermic and
(A) entropy changes are also ⊕.

• OXIDISING NATURE :-

	O_3 (O·A)
H_2S	S
SO_2	SO_3
NO	NO_2
SO_3^{2-}	SO_4^{2-}
$Cl^-/Br^-/I^-$	$Cl_2/Br_2/I_2$
Fe^{+2}	Fe^{3+}
MnO_4^{2-}	MnO_4^-
$[Fe(CN)_6]^{-4}$	$[Fe(CN)_6]^{-3}$
moist I_2	HIO_3
moist S	H_2SO_4
moist P	H_3PO_4
* dry I_2	I_4O_9 (ionic solid) $(I^{3+} + 3\,IO_3^-)$

*	KOH	$\overset{+}{K}\overset{-}{O_3}$ O_3^- = paramagnetic
*	PbS (black)	$PbSO_4$ (colorless)
*	Hg	Hg_2O 'Tailing of Mercury' + Test of O_3

$\downarrow O_2$

→ Hg doesn't adhere to glass container surface as ST ↑↑.
O_3 is passed ⇀ Hg_2O forms ⇒ Hg separates and goes towards borders of container (away from Hg_2O). 'Tails' like appear. So, 'tailing' of mercury. Also is a confirmatory test of O_3.

→ O_2 and H_2O_2 are used to remove black stains of old paintings (Pb in paint + H_2S air → PbS black).

→ Iodine shows some metallic character due to less I.P.

→ Supersonic jets are also responsible for O_3 layer depletion as they release NO gas. ($NO + O_3 \rightarrow O_2 + NO_2$)

Q. Which of the following can act as R.A. with $\overset{+4}{SO_2}$:-

a) Acidified $KMnO_4$
b) O_3 O.A.
c) $Fe_2(SO_4)_3$
✓d) H_2S → only R.A.

Q. Which of the following salts give a gas with dil. HCl which turns lime water milky ?

a) $NaHCO_3$
b) $CaCO_3$
c) Na_2SO_3
✓d) all

Q.• CO_2 and SO_2 gas can't be distinguished by :-

$SO_2 \longrightarrow SO_4^{2-}$

a)	Acidified $KMnO_4$ (purple)	$MnSO_4$ (colorless)
b)	Acidified $K_2Cr_2O_7$ (orange)	Cr^{3+} or $Cr_2(SO_4)_3$ (green)
c)	$FeCl_3$ (aq.) (yellow)	$FeCl_2$ (green)

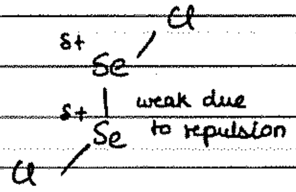
d) Beryta water ($Ba(OH)_2$ aq.) ⇒ basic, so both give white turbidity.

→ CO_2 never acts as R.A, O.S = +4; highest.

→ SO_2 is used as 'antichlor agent' ⇒ $SO_2 + Cl_2 \longrightarrow SO_2Cl_2$

→ Monohalides of O_2 family exist in dimer form and give disproportionation reaction easily.

- O_2F_2, S_2F_2, S_2Cl_2, Se_2Cl_2, etc. [Half open book like]



$\overset{+1}{Se_2Cl_2} \longrightarrow \overset{+4}{SeCl_4} + \overset{0}{Se}$

→ O_2F_2 and OF_2 are good fluorinating agents.

- $XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$

- $\underset{\text{(impure)}}{Pu} + 3\,O_2F_2 \longrightarrow \underset{\downarrow \text{ pure Pu}}{PuF_6} + 3\,O_2$ ENRICHMENT OF Pu (in nuclear reactor)

Q. which of these doesn't give $O_2(g)$ on decomposition?

a) $KClO_3$
b) $KMnO_4$
c) $K_2Cr_2O_7$
d) PbO_2
e) H_2O_2
f) Ag_2O
[✓ g)] $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2$ Ammonium salts strong O.A. anion $\xrightarrow{\Delta}$ N_2
—〃— weak OA anion $\xrightarrow{\Delta}$ NH_3

Q. Which of these doesn't react with O_2 :-

a) Na [✓ b)] Pt c) Ti d) Al

Q. Which of these isn't correct :-

a) Po is a radioactive element
b) S_2Cl_2 is used for vulcanisation of rubber
[✓ c)] Reducing nature increases from SO_2 to TeO_2
d) Stability of −2 O.S. decreases from O_2 to Po

→ Natural rubber has (elasticity + strength) ↓↓. So, it is melted with a compound having S–S bond. On cooling, it mixes and rubber gets S–S bonds too. So, strength ↑ and elasticity ↑ too. This is 'Vulcanisation of Rubber'.

HALOGEN-FAMILY

* • Cl_2

• PREPARATION :-

1. DECON'S PROCESS → $\underset{\text{(weak R.A.)}}{4\,HCl} + O_2 \xrightarrow[CuCl_2]{\Delta} 2\,Cl_2 + 2\,H_2O$

2. LABORATORY → $\underset{\underset{NaCl\ +\ conc.\ H_2SO_4}{\uparrow}}{4\,HCl} + MnO_2 \xrightarrow{\Delta} Cl_2 + 2H_2O + MnCl_2$

3. $\left.\begin{array}{l} \text{Acidified } KMnO_4 \\ \quad -{''}-\quad K_2Cr_2O_7 \\ CaOCl_2 \\ PbO_2 \\ O_3 \end{array}\right]$ OA $+ \underset{(RA)}{HCl} \longrightarrow Cl_2$

• OXIDISING NATURE :-

→ Chlorine water acts as a good OA and permanent bleaching agent.

$$Cl_2 + H_2O \longrightarrow HCl + \underline{HOCl} \longrightarrow HCl + [O]$$

→ $\boxed{Cl_2 \text{ water}}$ → (O.A.)

H_2S	S
SO_2	SO_4^{2-}
NO_2^-	NO_3^-
Fe^{2+}	Fe^{3+}
Br^- / I^-	Br_2 / I_2
I_2	HIO_3

↓

$\boxed{HCl}$

* $\underline{T.S.}$ $Cl-F < Br-F < I-F$ (ΔEN)

PSEUDOHALIDE	PSEUDOHALOGEN	POLYHALIDE	INTERHALOGEN COMPOUNDS
CN^-, OCN^-,	$(CN)_2$ = Cyanogen	Br_3^-	$\boxed{XX'}$ = ClF, BrF,
SCN^-, $SeCN^-$,	$(OCN)_2$ = Oxy -"-	I_3^-	IF, ICl, $BrCl$, ...
N_3^- (azide)	$(SCN)_2$ = Thio -"-	ICl_2^-	$\boxed{XX'_3}$ = ClF_3, good fluorinating agents
	$(SeCN)_2$ = Seleno -"-	$[IClBr]^-$	BrF_3, IF_3,
			ICl_3 (dimer)
			$\boxed{XX'_5}$ = BrF_5,
			ClF_5, IF_5
			$\boxed{XX'_7}$ = IF_7

- CN^- is a pseudohalide, and it shows similarity in properties with halides.

→ It also forms acids.

→ Salts with Ag^+, Pb^{2+} and Hg^{2+} are insoluble in water.

→ Act as R.A., like Br^- and I^-.

\- CuI_2 and $Cu(CN)_2$ do not exist

$$\underset{\text{O.A.}}{Cu^{2+}} + \underset{\text{R.A.}}{2I^-} \longrightarrow CuI + \frac{1}{2}I_2$$

$$Cu^{2+} + 2CN^- \longrightarrow CuCN + \frac{1}{2}(CN)_2$$

Q. Assertion: Interhalogen compounds are more reactive than halogens except F_2.

Reason: Interhalogen compounds have less BDE and also have bond polarity.

Ans (A)

→ • ClF_3, BrF_3, etc are good fluorinating agents.
All interhalogens after XX' are.

— $U + 3\,ClF_3 \longrightarrow UF_6 + 3\,ClF$ Enrichment of U.
(impure)

- <u>Stability of oxides</u> :- $I > Cl > \underbrace{Br}_{\text{middle row anomaly}}$
(on basis of both thermodynamic and kinetic stability)

- <u>Test of Halide ions.</u> :-

→ F^- → itching of glass

→ Cl^- salts
→ Br^- salts
→ I^- salts
$\xrightarrow{AgNO_3(sol^n)}$
→ $AgCl$ white ↓
→ $AgBr$ pale yellow ↓
→ AgI yellow ↓

- I_2 gives blue color with starch solⁿ.
- I_2 is also obtained from sea weeds ($0.5\%\ I_2$)
- $3\,Ca_3(PO_4)_2 \cdot CaF_2$ = fluorapatite.
- $(KI + KIO_3)$ = iodised salt

Q. Which of these is a poisonous gas –

a) Phosgene ($COCl_2$)
b) Tear Gas (CCl_3-NO_2)
c) Mustard Gas ($S(CH_2CH_2Cl)_2$)
✓ d) All

INERT GASES

* PREPARATION OF XENON FLUORIDE ⇒

- $Xe + F_2 \xrightarrow[1\ bar]{673\ K} XeF_2$
  2 : 1

- $Xe + F_2 \xrightarrow[6-7\ bar]{473\ K} XeF_4$
  1 : 5

- $Xe + F_2 \xrightarrow[60-70\ bar]{673\ K} XeF_6$
  1 : 20

- Xenon fluorides can act as both F^- donor and acceptors.

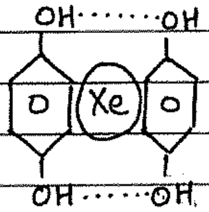
→ $XeF_4 + SbF_5 \longrightarrow [XeF_3^+][SbF_6^-]$ ($LE\uparrow$; $\Delta G = \ominus$)
F^- donor covalent F

→ $XeF_6 + \overset{+}{Cs}\overset{-}{F} \longrightarrow Cs^+[XeF_7^-]$
F^- acceptor ionic F

* • CLATHERATE COMPOUNDS :-

- Larger inert gas atoms like Kr, Xe, etc. are packed into crystal structure of some organic compounds. e.g.:

Xenon diquinol



→ He, Ne don't form clatherate compounds due to smaller size.

Q. Which of these shows sublimation :-

a) XeF_2
b) XeF_4
c) XeF_6
d) Al_2Cl_6
[✓ e)] All

Q. Which of these doesn't exist :-

[✓ a)] NeF_2
b) XeF_4
c) XeO_3
d) KrF_2

He, Ne, Ar don't form compounds due to high IP.

→ Noble gases are inert due to stable configuration, high IP and p $\Delta H_{eg} = \oplus$

* $\underline{^{286}_{88}Ra} \xrightarrow{-\alpha} \underline{^{282}_{86}Rn}$

→ 1st inert gas compound was prepared by Neil Bartlette
↳ $Xe^+[PtF_6]^-$, similar to $O_2^+[PtF_6^-]$

— IP of Xe ≃ O_2, so it all happened.

- Main constituent of inert gases is Argon.
- Main source of He is natural gas (CH_4).
- He is also present in U ore pitch blende (U_3O_8) and Th ore monazite (ThO_2)

Q. Assertion : He is used for dilution of oxygen in modern diving apparatus
Reason : He is less soluble in blood in comparison to N_2

Ans (A)

* USES OF INERT GASES :-

- **HELIUM** : Non inflammable light gas.

1. Filling balloons for meteorological observations.
2. Used in gas-cooled nuclear reactors.
3. Liquid He (BP = 4.2 K) is used as cryogenic agent for carrying out various experiments @ low temp.
4. Used to produce and sustain powerful superconducting magnets which form an essential part of modern NMR spectrometers and MRI systems.
5. Used as diluent for O_2 in modern diving apparatus as it has very low solubility in blood.

- **NEON :-**

1. Used in discharge tubes and fluorescent bulbs for ads.
2. Ne bulbs are used in botanical gardens and green houses.

- **ARGON :-**

1. Mainly used to provide an inert atmosphere in high temperature metallurgical processes, like arc welding of metals or alloys, and for filling electric bulbs
2. Used in laboratory for handling substances that are air-sensitive.

- **Xe and Kr** – used in light bulbs designed for special purposes.

COORDINATION CHEMISTRY

* ADDITION COMPOUNDS :-

- When two or more ~~normal~~ simple salts are allowed to chemically combine in a fixed ratio, addition compounds form.
- On the basis of behaviour in aq. sol^n, they are :-

(A) DOUBLE SALTS :-

- Addition compounds in which the simple salts don't lose their identity and its aq. sol^n gives test of all constituent ions.
- Double salts lose their identity in aq. sol^n.
- $$KCl + MgCl_2 + 6H_2O \longrightarrow \boxed{KCl \cdot MgCl_2 \cdot 6H_2O} \text{ (CARNELITE)}$$

$$\downarrow \text{aq. sol}^n$$

$$K^+ + Mg^{2+} + \underline{3Cl^-} + 6H_2O$$

$$\downarrow AgNO_3 \text{ sol}^n$$

$$AgCl \text{ (white ppt)}$$

No. of ions/mol = 5 mol.
Type of ions = 3

- $$(NH_4)_2SO_4 + FeSO_4 + 6H_2O \longrightarrow \boxed{(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O} \text{ [MOHR'S SALT]}$$

$$\downarrow \text{aq. sol}^n$$

$$\underline{2NH_4^+} + Fe^{2+} + 2SO_4^{2-} + 6H_2O$$

NH_4^+ $\downarrow$ Nessler's Reagent $\downarrow$ Brown ppt.

SO_4^{2-} $\downarrow$ $BaCl_2$ sol^n → $\underline{BaSO_4}$ (white ppt)

- All alums are double salts.

B) COMPLEX COMPOUND :-

- Addition compounds in which simple salts lose their identity and its aq. solⁿ doesn't give test of its all constituent ions (complex ions give their resp. test, as whole).

- Complex compounds retain their identity in aq. solⁿ.

- $4\,KCN + Fe(CN)_2 \longrightarrow 4\,KCN \cdot Fe(CN)_2$ (OR) $K_4[Fe(CN)_6]$ (non-poisonous)

poisonous

$\downarrow$ aq. solⁿ

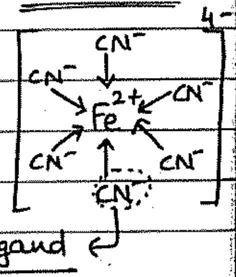
$4\,K^+ + [Fe(CN)_6]^{4-}$

test ✓ complex ion

CMA

Central Metal Atom

No. of ions = 5



CMA

$K_4[Fe(CN)_6]$ = Potassium Ferro cyanide

- CLASSIFICATION OF COMPLEX COMPOUNDS ⇒

a) on the basis of type of ligands -

1. HOMOLEPTIC COMPLEX - Same type of ligands.

$[Cu(NH_3)_4]SO_4$ = Switzer's Salt

CMA

2. HETEROLEPTIC COMPLEX – Different types of ligands

$$[\underset{\substack{\uparrow \\ \text{CMA}}}{Co}\underbrace{(NH_3)_3\,(H_2O)_2\,Br}_{\text{Ligands}}]Cl_2$$

b) on the basis of degree of dissociation –

1. PERFECT COMPLEX COMPOUNDS – Relatively more stable.
aq. solⁿ doesn't give test of all ions.

→ $3\,KCN + CuCN \longrightarrow 3KCN\cdot CuCN \xrightarrow[\text{sol}^n]{\text{aq.}} \underset{\text{test}\checkmark}{3K^+} + \underset{\text{test of complex}\checkmark}{[Cu(CN)_4]^{-3}}$

$[Cu(CN)_4]^{-3} \xrightleftharpoons{\text{v. less dissociation}} Cu^+ + 4CN^-$ (conc. of product ↓↓)

Hydration ↑↑
⇒ more stable complex ion
⇓
perfect complex compd.

$Cu^+ \xrightarrow{H_2S(g)}$ No black ppt ⇒ $[Cu^+][S^{2-}] < K_{sp}$.

2. IMPERFECT COMPLEX COMPOUNDS – Relatively less stable, and aq. solⁿ gives test of all of its ions.

→ $2\,KCN + Cd(CN)_2 \longrightarrow 2KCN\cdot Cd(CN)_2$ OR $K_2[Cd(CN)_4]$

⇑ complex compd.

$\downarrow$ aq. solⁿ

$\underset{\text{test}\checkmark}{2K^+} + \underset{\text{test of complex ion}\checkmark}{[Cd(CN)_4]^{2-}}$

$[Cd(CN)_4]^{2-} \xrightleftharpoons{\text{more ionisation}} Cd^{2+} + 4\,CN^-$ (|charge| ↑, so H.E. ↑ Product Stability ↑)

Hydration ↓
⇒ less stable
⇓
imperfect complex compd.

$Cd^{2+} \xrightarrow{H_2S(g)} \underset{\text{(yellow)}}{CdS\downarrow}$ $[Cd^{2+}][S^{2-}] > K_{sp}$

→• Imperfect complex compounds which undergo 100% ionisation are double salts (no test of complex ion).

→ $FeCl_3 + 3K^+SCN^- \longrightarrow \overset{+3}{\underline{Fe}}(SCN)_3 + 3KCl$
(Blood Red sol^n)

$[\overset{+3}{Fe}F_6]^{3-} \xrightarrow{3\,KSCN}$ No color ⇒ $\underset{[FeF_6]^{3-}}{\underline{Fe^{3+}}}$ is perfect wrt (SCN^-)

$\downarrow NaOH$

$Fe(OH)_3\downarrow$ ⇒ $[FeF_6]^{3-}$ is imperfect wrt NaOH.
(reddish brown)

→ $[Ag(NH_3)_2]^+$

$\rightleftharpoons$

$Ag^+ + 2NH_3$

less KBr → No ppt, $[Ag^+][Br^-] < K_{sp}$

excess KBr → $AgBr\downarrow$ (pale yellow)

KI → AgI (yellow) (K_{sp} is less)

⇒• There is no sharpline b/w perfect and imperfect complex ions or compounds.

⇒ It also depends on testing reagent used.

- REPRESENTATION OF COMPLEX COMPOUNDS —

→ [ ] = coordination sphere

→ out of [ ] = ionisation sphere = free ion = counter ion

→ $[ML_x]^{\pm n}$

↓ CMA ↑ Ligands (acc. to alphabetic order)

a) $K_3[Fe(CN)_6] \Rightarrow 3K^+ + [\overset{+3}{Fe}(CN)_6]^{3-}$ = 4 ions

(potassium ferricyanide) ↓ simple cation ↳ complex anion

b) $[Cu(NH_3)_4]SO_4 \Rightarrow [\overset{+2}{Cu}(NH_3)_4]^{2+} + SO_4^{2-}$ = 2 ions

(Swittzer's Salt) complex cation simple anion

c) $[Pt(NH_3)_4Cl_2][ZnCl_4] \Rightarrow [\overset{+4}{Pt}(NH_3)_4Cl_2]^{+2} + [ZnCl_4]^{-2}$ = 2 ions

complex cation complex anion

d) $[\overset{0}{Fe}(CO)_5]$ = neutral complex compound

* LIGANDS :- Species which donate lp to CMA. Naming:-

→ —o suffix is provided to name of anionic ligands

→ —ium suffix is provided to name of cationic ligands.

→ anion $\xrightarrow[+o]{-e}$ ligand

—ate → —ato

—ite → —ito

—ide → —ido

↳ —o [Exception: N^{3-}, N_3^-, H^-, ..]

• • CLASSIFICATION OF LIGANDS –

A) On the basis of denticity (no. of donor atoms) –

1. MONODENTATE LIGAND :- Only 1 donor atom.

a) NEUTRAL ⇒ * H_2O aqua
* NH_3 ammine
* CO carbonyl
CS thio carbonyl
* NO nitrosyl
* PH_3 phosphine
* $P(Ph)_3$ triphenyl phosphine


pyridene (Py)

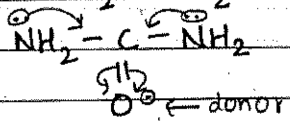
N_2 = dinitrogen

* O_2 = dioxygen

CH_3-NH_2 Methylamine

CH_3-OH Methyl alcohol

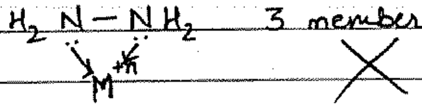
NH_2-NH_2 Hydrazine



$NH_2-\overset{\parallel}{C}-NH_2$ Urea.

O ← donor

→ Hydrazine never acts as bidentate ligand.


H_2N-NH_2 3 membered ring

b) CATIONIC ⇒ * O_2^+ oxygenium
* NO^+ nitrosylium = nitrosonium
NO_2^+ nitronium
$NH_2-\overset{\oplus}{N}H_3$ Hydrazinium

c) * **ANIONIC** ⇒

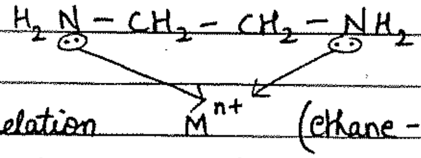
F^-	fluorido / fluoro	
Cl^-	chlorido / chloro	
Br^-	bromido / bromo	
I^-	iodido / iodo	
O^{2-}	oxido / oxo	
OH^-	hydroxido / hydroxo	
S^{2-}	sulphido / sulpho	
$CH_3-O^{\ominus}$	methoxido / methoxo	
O_2^-	superoxido / superoxo	
O_2^{2-}	peroxido / peroxo	
N_3^-	azido	(azo = $-N=N-$)
N^{3-}	nitrido	(nitro = NO_2^-)
NH_2^-	amido	
NH^{2-}	imido	
H^-	hydrido	(hydro = H_2O)

(N_3) = azido $(N)_3$ = trinitrido

(NH_2) = amido $(NH)_2$ = diimido

2\. **BIDENTATE LIGANDS** :- 2 donor atoms

* a) **ethylene diamine (en)**



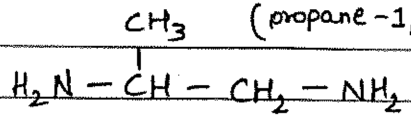
$H_2N-CH_2-CH_2-NH_2 \rightarrow M^{n+}$

(ethane-1,2-diamine)

5 memb. ring; stable due to chelation

neutral and symmetric bidentate ligand.

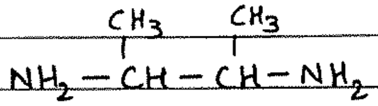
b) **propylene diamine (pn)** (propane-1,2-diamine)



$H_2N-CH(CH_3)-CH_2-NH_2$

5 memb. ring; neutral, asymmetric.

c) **butylenediamine** (bn)

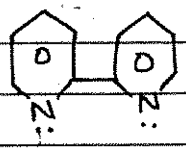


$NH_2-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-NH_2$

(butane-2,3-diamine)

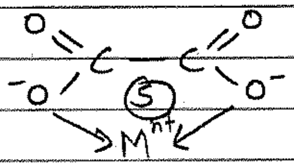
neutral, symmetric

d) **dipyridyl** (dipy)



neutral, symmetric

e) **oxalato** $(ox)^{-2}$

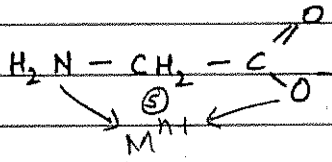


(O^- are donors)

Not 4 memb ring

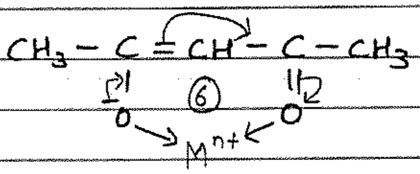
anionic, symmetric

f) **glycenato** $(gly)^{-1}$



anionic, asymmetric

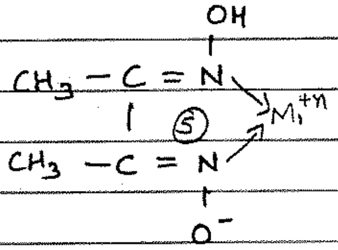
g) **acetyl acetonato** $(acac)^{-1}$

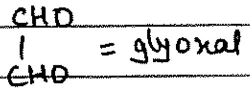


anion, symmetric

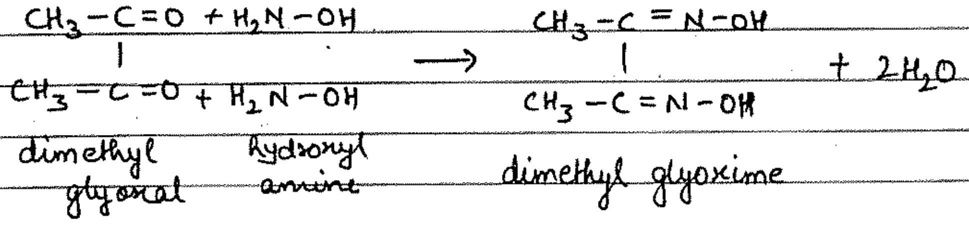
h) **dimethyl glyoxinato** $(dmg)^{-1}$

asymmetric





$\begin{array}{l} CHO \\ | \\ CHO \end{array}$ = glyoxal

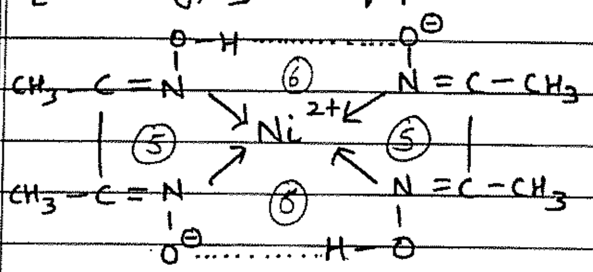


$$\begin{array}{l} CH_3-C=O + H_2N-OH \\ \quad\ | \\ CH_3-C=O + H_2N-OH \end{array} \longrightarrow \begin{array}{l} CH_3-C=N-OH \\ \quad\ | \\ CH_3-C=N-OH \end{array} + 2H_2O$$

dimethyl glyoxal　hydroxyl amine　dimethyl glyoxime

जिनका नाम Amine में end हो,
वो Neutral (0 charge, so 0 O.S) होते हैं।

- ~~[Ni(dmg)$_2$]~~ sq. planar



↳ symmetric H-bonding

Had O$^\ominus$ been a donor, H bonding wouldn't have been possible.

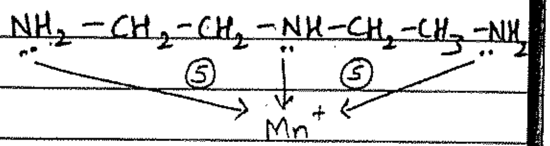
(dmg)$_2$ = symmetric

3. POLYDENTATE LIGANDS :- More than 2 donor atoms.

→ All bidentate and polydentate ligands are chelating ligands.

→ No. of chelate rings = (denticity − 1)

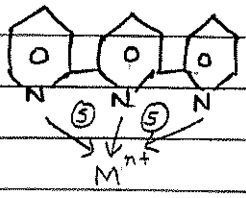
* a) diethylene triamine (dien)



denticity = 3
(every amine → 1 denticity)
neutral ; chelate rings = 2

* b) (trien) trimethyl tetramine
(neutral)
denticity = 4 ; rings = 3

c) tripyridyl (tripy)



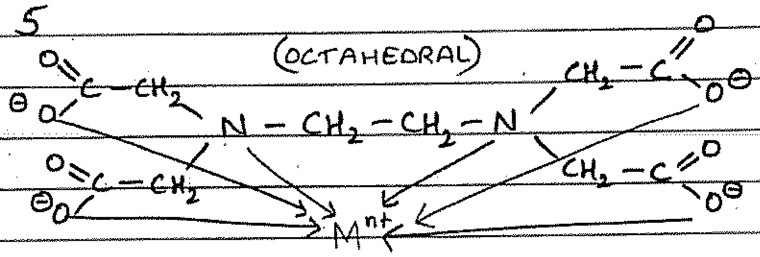
neutral ; denticity = 3
no. of chelate rings = 2

d) • ethylene diamine tetra acetato $(EDTA)^{-4}$

(anionic)

denticity $= 2N + 4O^{\ominus} = \underline{\underline{6}}$

chelate rings = 5

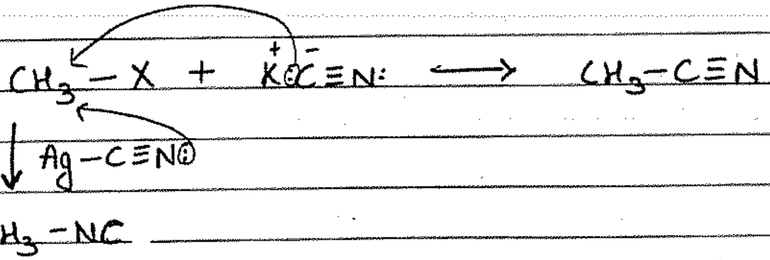


e) $(EDTA)^{-3}$ ethylene diamine tri acetato

denticity = 2 + 3 = 5

chelate rings = 4.

4. **AMBIDENTATE LIGANDS** :- which have 2 different donor atoms, but at the time of coordination, such ligand can be coordinated with CMA by either of 2 donor atoms.



a) $M^{n+} \leftarrow \overset{\ominus}{C} \equiv N$ $\qquad$ $M^{n+} \longleftarrow N \equiv \overset{\ominus}{C}$

cyanido $\qquad$ isocyanido

(cyanido − C) (CN) $\qquad$ (cyanido − N) (NC)

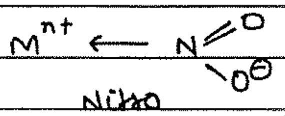
b) $M^{n+} \leftarrow \overset{\ominus}{O} - C \equiv N$ cyanato (cyanato − O) (OCN)

$M^{n+} \leftarrow N \equiv C - O^{\ominus}$ isocyanato (cyanato − N) (NCO)

c) $M^{n+} \leftarrow \overset{\ominus}{S} - C \equiv N$ Thiocyanato (thiocyanato − S) (SCN)

$M^{n+} \leftarrow N \equiv C - S^{\ominus}$ isothiocyanato (thiocyanato − N) (NCS)

d) $M^{n+} \leftarrow \overset{\ominus}{O} - N = O$ Nitrito (Nitrito − O) (ONO)

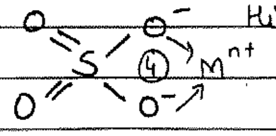


$M^{n+} \leftarrow N(=O)O^{\ominus}$

Nitro (Nitrito − N) NO_2

→ Thiosulphato ($S_2O_3^{2-}$) also acts as ambidentate ligand.

5. **FLEXIDENTATE LIGANDS** :- Ligands capable of changing denticity e.g. SO_4^{2-}, NO_3^-, NO_2^-, CO_3^{2-}, CH_3COO^-, generally behave as monodentate ligands, but in some compounds acts as bidentate ligands.



a) $[Co(NH_3)_4 SO_4]Cl$ $Co \Rightarrow O.S. = +3$

$C.N = 6$

4 by NH_3, 2 by SO_4^{2-} ⇒ SO_4 = bidentate

or $[Co(en)_2 SO_4]Cl$ ⇒ 4 by en, 2 by SO_4^{2-} = bidentate.

b) $[Co(NH_3)_5 SO_4]Cl$ $Co \Rightarrow O.S. = +3$

$CN = 6$

5 by NH_3, 1 by SO_4^{2-} ⇒ SO_4^{2-} = monodentate

Q. Find no. of chelate rings

~~trien → denticity = 4 rings = 4-1 = 3~~

a) $[Pt(trien)]Cl_2$

b) $Na_2[\overset{+3}{Fe}(OH)(EDTA)^{-4}]$

~~c)~~ ~~2 + 2+4 = 6 = 8 rings = 7~~

+3 → CN = 6 1 OH^-, 5 by $EDTA^{-4}$ → Denticity = 5 ~~CMA~~ (Not 6)

Chelate rings = 4

⇒ $EDTA^{-4}$ can be a FLEXIDENTATE LIGAND

B) On the basis of $e^\ominus$ donating and accepting nature –

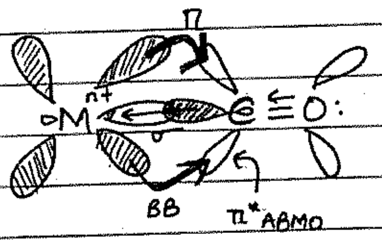
1. NORMAL / CLASSICAL LIGANDS – which only donate lp to CMA and form coordinate σ bond.

e.g. NH_2^-, OH^-, F^-, O^{2-}, NH_3, N^{-3}, etc.

2. NON CLASSICAL / π-acid / π-acceptor LIGANDS – which donate $e^\ominus$ pair to CMA and form coordinate bond, but simultaneously accept $e^\ominus$ pair from CMA through BB.

$14e^\ominus$, so π^* ABMO empty | π bond, so $e^\ominus$ in $\pi > \pi^*$ ⇒ π^* empty | d empty

e.g. CO, NO^+, CN^-, $C_6H_6^\phi$, $CH_2=CH_2$, $C_5H_5^-$, R_3P, R_3As, PH_3, PF_3, etc.



$$[M \underset{\pi}{\overset{\sigma}{\rightleftarrows}} L]$$

Synergic Bonding

→ Extent of BB ↑es with

*a) ↑ O.S. of CMA

b) decreasing no. of CO

c) ↑ no. of CMA (bridging CO > terminal CO)

↳ दो-दो $M^\oplus$ ABMO में $e^\ominus$ देंगे ⇒ BB ↑

→ Due to BB,

a) M—C B.O. ↑ b) C—O B.O. ↓
M—C B.S. ↑ C—O B.S. ↓
M—C B.L. ↓ C—O B.L. ↑ (no. of ABMO $e^{\ominus}$ ↑)

c). Stretching ν for C—O bond ↓ as required energy is ↓ as B.S. is ↓.

d) μ of M—C bond is v. less

Q. Which of the following orbitals can participate in synergic bonding?

a) s-orbital (lp of $:PH_3$ is in pure s, as Drago's Rule, no hyb.)
b) π BMO (ϕ)
c) π* ABMO ($C\overset{\leftarrow}{\equiv}O:$)
d) d_{xy} / d_{yz} / d_{xz} (R_3P)
e) NBMO (CO)
✓ f) all

Q. The strongest C—O bond is present in :-

a) $[V(CO)_6]^-$ ~~[Max. M—C B.O. (⊖ O.S ↑)]~~
b) $[Fe(CO)_5]$
c) $[Cr(CO)_6]$
✓ d) $[Mn(CO)_6]^+$ O.S. = +1 ⇒ O.S. = ⊕ ⇒ extent of BB ↓

B.S. of C-O. ↑
⇑
~~impact of B.B ↓~~
⇑

Max. stretching ν of C-O bond. ⟹ (d)
—— " —— of M—C bond ⟹ (a) ~~(doubtful)~~

Q. Which of the following complex has max. M–C B.O. and min. stretching ν for C–O bond?

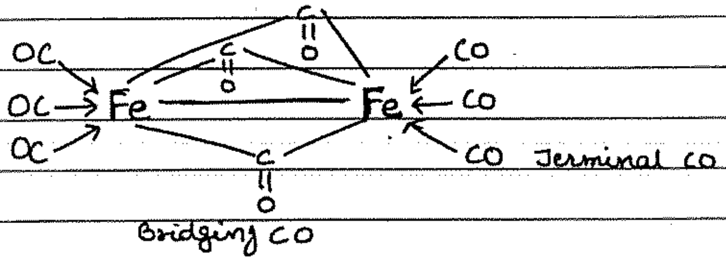
a) $[Cr(CO)_6]$
b) $[Cr(en)(CO)_4]$
c) $[Cr(dien)(CO)_3]$
~~d)~~ $[Cr(trien)(CO)_2]$

no. of CO ↓ ⇒ impact/extent ↑

Q. $C\equiv O$ B.L. is 1.128 Å. Then, C–O B.L. in $Fe(CO)_5$:-

a) 1.128 Å   ✓~~b)~~ 1.158 Å   c) 1.78 Å   d) 1.118 Å

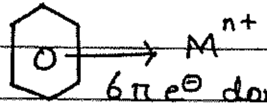
Q. Which of these is incorrect order for



a) Bridging CO > Terminal CO B.L.
b) " CO > " CO Extent of BB
~~c)~~ " CO > " CO Stretching frequency
d) M – bridge CO > M – terminal CO B.O.

• π donor and π acceptor ligand ⇒

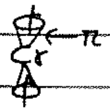
→ ligands which donate π $e^{\ominus}$ to CMA and also accept $e^{\ominus}$ density from CMA through BB.

- 

$6\pi e^{\ominus}$ donor

e.g. Cromocene $[Cr(\Phi)_2]$

Sandwich comp~~lex~~ound



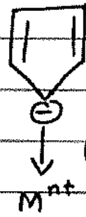
Aromatic

Hepaticity

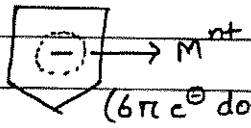
$(\eta^6$-benzene$)$

No. of π bond = 6
No. of σ bond = 24

η = whenever $\pi e^{\ominus}$ cloud of 2 or more atoms is donated
6 = no. of atoms whose $\pi e^{\ominus}$ cloud got donated (here, 6C).

- 

$(\sigma - C_5H_5)$



$(6\pi e^{\ominus}$ donor$)$

$(\pi - C_5H_5)$ η^5– cyclopentadienyl

e.g. Ferrocene $[Fe(\pi - C_5H_5)_2]$

- $\overset{\ominus}{C}H_2 - CH = CH_2$
$\downarrow$
M^{n+} $(\sigma - C_3H_5^-)$

$CH_2 \cdots CH \cdots CH_2$
$\searrow \swarrow$
M^{n+}
$(4\pi e^{\ominus}$ donor$)$

$(\pi - C_3H_5^-)$

$(\eta^3$- Allyl$)$

- $CH_2 = CH_2$
$\downarrow$
M^{n+} $(2\pi e^{\ominus}$ donor$)$

$(\eta^2$-ethylene$)$ Forms 1 coordinate bond with CMA

e.g. $K[PtCl_3(C_2H_4)]$ ZEISEL'S SALT

- cyclobutadiene, $CH_2 = CH - CH = CH_2$

- COORDINATION NUMBER :-

→ Total no. of $e^{\ominus}$ pair accepted by CMA

- $[Ni(dmg)_2] = 4$

- $[Cr(ox)(en)_2]Cl$ = $2 + 2(2) = 6$
- $[Fe(EDTA)]^-$ = $(2+4)1 = 6$
- $[Pt(trien)]Cl_2$ = 4 (tetramine)
- $[Pt(NH_3)_4Cl_2][Pt(SCN)_4]$ = $4+2; 4$ = 6, 4

- SOME CONCLUSIONS :-

1. Generally C.N. of monovalent Metal ion is 2 or 4.
EXCEPT :- Ag^+ = only 2 , Cr^+ = only 6.

$$\underset{C.N. = 2}{[Cu(CN)_2]^-} \xrightarrow[\text{excess}]{2CN^-} \underset{C.N. = 4}{[Cu(CN)_4]^{-3}} \quad (\text{O.S. of } Cu = +1)$$

2. Generally C.N. of bivalent metal ion is 4 or 6.
EXCEPT :- Pt^{+2}, Pd^{+2} $\rightleftharpoons$ only 4

3. Ni^{+2}, Cu^{2+}, Mn^{+2} also show C.N. = 5.

4. Generally C.N. of trivalent metal ions is 6.
EXCEPT :- Al^{+3} = 4 and 6
Au^{+3} = 4 and 6

5. C.N. of tetravalent metal ions is 6.

$Xe^+[PtF_6]^-$ ⇒ C.N. of Pt = 6, but OS = +5

Otherwise whenever C.N. of Pt = 6, OS = +4.

- **EAN :- EFFECTIVE ATOMIC NUMBER**

→ Total no. of $e^\ominus$ of CMA after accepting $e^\ominus$ pair from ligands.

→ EAN = Z − (O.S.) + 2 × C.N.

– $K_4[Fe(CN)_6] \Rightarrow 26 - (2) + (2 \times 6) = 36.$ (O.S. = 2, CN = 6)

– $K_3[Fe(CN)_6] \Rightarrow 26 - 3 + 12 = 35$

– $[\overset{2}{Fe}(\eta^5\text{-}C_5H_5)_2] \Rightarrow 26 - (+2) + 2 \times 6 = 36$ $C.N. = \frac{12}{2} = 6\,e^\ominus$ pair

– $[\overset{-2}{Fe}(CO)_2(\overset{+2}{NO})_2] \Rightarrow 26 - (-2) + 2(4) = 36.$ $\boxed{OR}$ $26 - 0 + 2(2+3) = 36$

→ NO acts as $3\,e^\ominus$ donor $\boxed{OR}$ $\underset{\substack{15e^\ominus \\ B.O. = 2.5}}{NO} \xrightarrow{-e^\ominus \,\to\, CMA.} \underset{\substack{14\,e^\ominus \\ B.O. = +3}}{\overset{+}{NO}}$

→ If in a complex compound, EAN of CMA = Z of Noble gas for that period, it follows 'EAN Rule'.

Q. Which of these ~~does not~~ follows EAN Rule?

a) $[\overset{+4}{Pt}(NH_3)_4Cl_2]Cl_2$ EAN = 78 − 4 + 2(6) = 86 ✓

b) $[Cr(\eta^6\text{-}C_6H_6)_2]$ 24 − 0 + 6 (2) = 36 ✓

✓ c) $[Ag(NH_3)_2]Cl$ 47 − 1 + 2(2) = 50 ✗

d) $H[Mn(CO)_5]$ 25 − (−1) + 10 = 36 ✓

Q. If max. no. of CO are replaced by NO, in $[Fe(CO)_5]$ then ~~pos~~ correct formula will be -

a) $[Fe(NO)_5]$ b) $[Fe(CO)_2(NO)_2]$

c) $[Fe(CO)(NO_3)]$ ✓d) $[Fe(CO)(NO)_3]^+$

Ans CO CO CO = 6 $e^{\ominus}$ donor
NO NO = 6 $e^{\ominus}$ donor ⇒ $-3CO + 2NO$
⇒ $[Fe(CO)_2(NO)_2]$

Then CO = NO^+ = 2 $e^{\ominus}$ donor ⇒ $[Fe(CO)(NO)_3]^+$
Further possibility = $[Fe(NO)_4]^{2+}$ doesn't exist practically

- SIDGWICK RULE ⇒ Applicable only for metal carbonyl

→ If EAN of Metal atom in metal carbonyl is equal to at. no. of nearest inert gas, then stability of metal carbonyl is high.

- $[Mn(CO)_5] < [Mn(CO)_5]^-$ (stability)
EAN = 35   EAN = 36

- $[Mn(CO)_6] \xrightarrow[\text{oxidation}]{-e^{\ominus}} [Mn(CO)_6]^+$ more stable
EAN = 37   EAN = 36
$\boxed{RA}$

- $[V(CO)_6] \xrightarrow[\text{reduction}]{+e^{\ominus}} [V(CO)_6]^-$ more stable
EAN = ~~36~~ 35   EAN = 36
$\boxed{OA}$

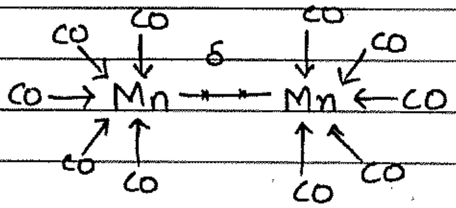
- $[Fe(CO)_5]$ → neither OA nor RA

  EAN = 36

- **EAN OF POLYNUCLEAR METAL CARBONYL ⇒**

- $2[Mn(CO)_5] \xrightarrow[\text{(low temp)}]{\text{dimerisation}} [Mn_2(CO)_{10}]$

  EAN = 35 EAN = 36



EAN = 24 + 12 = 36

Non bonding e⊖ pair

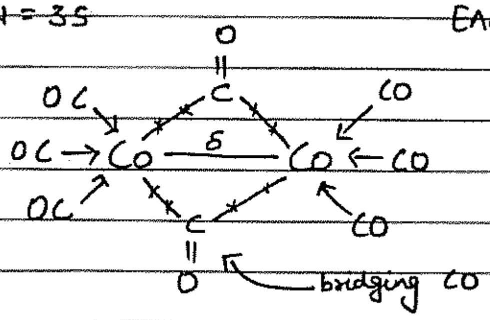
EAN = $[Mn(CO)_5]$ + 1 of δ = 35+1=36

$$EAN = \frac{25\times2 + 1\times2\,(\delta) + 10\times2}{2} = 36.$$

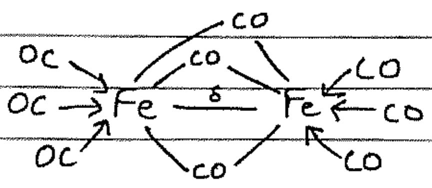
→ EAN of CMA in polynuclear metal carbonyl is always equal to at. no. of inert gas of that period.

- $2[Co(CO)_4] \xrightarrow{\text{dimerisation}} [Co_2(CO)_8]$ (bridging CO = 2)

  EAN = 35 EAN = 36



- $[Fe_2(CO)_9]$



* Hg → mercurate, not hydragyr~~ate~~ -umate

* Cation, Anion के Total no. को represent नहीं करना।

Q. Get x –

a) $[Cr(CO)_x] \Rightarrow 36 = 24 - 0 + 2x \Rightarrow \underline{x = 6}$

b) $[Co_2(CO)_x] \Rightarrow 36 = \dfrac{27 \times 2 + 1 \times 2\,(\delta) + 2x}{2}$

$\Rightarrow 36 = 27 + 1 + x \rightarrow \underline{x = 8}$

c) $H_x[Mn(CO)_5] \Rightarrow 36 = 25 - x + 10 \Rightarrow \underline{x = -1}$

* **IUPAC NAMING** ⇒

Rules → ① Cation Anion separation
② O.S. = ?
③ Naming = Cation → Anion.

– $K_4[Fe(CN)_6]$ = ~~tetra~~potassium hexacyanido ferrate(II)

④ [ligand → CMA (O.S. in Roman)]
↳ acc to alphabetical order

⑤ If anionic complex, CMA — (–ate) suffix

– **PRUSSION BLUE** ⇒ $Fe_4[Fe(CN)_6]_3$

~~Iron hexacyanido ferrate (III)~~

Iron (III) hexacyanido ferrate (II)

classmate
Date
Page

NH_2^- = amido
NH^{2-} = imido

- $\overset{+3}{[Cr(NH_2)_2(NH_3)_4]}\overset{+}{}ClO_4$

Diamido tetrammine ~~chromate~~ chromium (III) perchlorate

- $[\overset{+4}{Pt}(NH_3)_4(SCN)_2]^{(+2)}[\overset{+2}{Pt}(NO_2)_4]^{(-2)}$

~~Tetra ammine dithiocyanido platinum (II) tetra~~

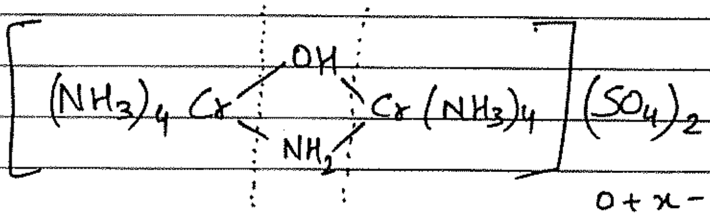
Tetra ammine ~~dithiocyanido~~ dithiocyanato platinum (IV) tetra nitro platinate (II)

- $\overset{+1}{[Co(ox)(en)_2]}Cl \cdot 2H_2O$ $(x-2+0-1=0 \rightarrow x=+3)$

bis (ethylenediamine) oxalato cobalt (III) chloride -2- water (dihydrate)

- $[Cr(\pi-C_6H_6)_2]$ O.S.=0

bis (or di) (η^6-benzene) chromium (0)

- 

$$\left[(NH_3)_4Cr\overset{OH}{\underset{NH_2}{\rightleftharpoons}}Cr(NH_3)_4\right](SO_4)_2$$

$0+x-1-1+x-0-4=0$
$\rightarrow x=3$

Bridging ligand $\Longrightarrow$ μ-preffix.

⇒ Tetraammine chromium (III) -μ-amido-μ-hydroxido tetraammine chromium (III) ~~di~~ sulphate.

⇒ μ-amido-μ-hydroxido bis (tetraammine chromium (III)) sulphate

⇒ μ-amido-μ-hydroxido octaammine dichromium (III) sulphate

$2 + x - 4 = 0 \Rightarrow x = +2$

- $2KI + HgI_2 \longrightarrow K_2[HgI_4]$ Nesseler's Reagent·

  Potassium tetraiodo mercurate (II)

- TURN BULL BLUE = $Fe_3[Fe(CN)_6]_2$

  Iron (II) Hexacyanido ferrate (III)

- Brown Ring Complex = $[Fe(H_2O)_5(NO)]SO_4$

  Pentaqua nitrosyl iron (II) sulphate

- Sodium nitroprusside = $Na_2[Fe(CN)_5(NO)]$

  Sodium pentacyanido nitrosyl ferrate (III)

- Ferrocene = $[\overset{+2}{Fe}(\pi - \overset{-2}{C_5H_5})_2]$

  ~~Iron (II~~) bis (η^5 - cyclopentadienyl) Iron (II)

- Zeisel's Salt = $\overset{+1}{K}[\overset{+2}{Pt}\overset{-3}{Cl_3}(\eta^2 - C_2H_4)]$

  Potassium trichlorido η^2 ethylene plantinate (II)

- $\overset{2+}{[Fe(NH_3)_6]}_3\overset{3-}{[Co(ONO)_6]}_2$ ~~Iron (II~~) Iron(II) hexaammine, hexanitrito-O Cobaltate (III)

- $\underset{+1}{K}[\underset{+3}{Cr}(\overset{\text{ammine}}{NH_3})_3(\overset{\text{dioxygen}}{O_2})\underset{-4}{(\overset{\text{oxido}}{O})_2}]$ Potassium triammine dioxygen dioxido Chromate (III)

O_2 dioxygen
O^{2-} oxido
O_2^{2-} peroxo
O_2^- superoxo

- $[\overset{+4}{Pt}(NH_3)_4(\overset{-2}{NCS})_2][\overset{+2}{Zn}\overset{-4}{Cl_4}]$ ~~Platinum~~ tetraammine di Thiocyanato - N, tetrachlorido Platnium IV) Zincate (II)

- $\overset{+2}{H_2}[\overset{+4}{Pt}\overset{-6}{Cl_6}]$ = acid ⇒ no name for H.
  = Hexachlorido platinic (IV) acid

* BONDING IN COMPLEX COMPOUNDS ⇒

1. WERNER'S THEORY –

CMA has 2 type of valencies –

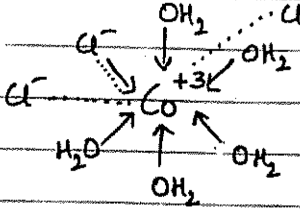
	1° VALENCY	2° VALENCY
a)	= O.S.	= C.N.
b)	Satisfied by anions	Satisfied by ligands
c)	Ionisable and non directional	Non ionisable but directional
d)	Not helpful in geometry prediction.	Helpful in geometry prediction.
e)	Represented by -----	Represented by ——

- All 2° valencies have specific arrangement acc. to C.N.

C.N. = 2 Linear
= 3 Trigonal planar
= 4 Tetrahedral or square planar
= 5 TBP or square pyramidal
= 6 Octahedral (SBP)

- Ionic bond → 1° valency
  Coordinate bond → 2° valency.

- $[Co(H_2O)_5 Cl] Cl_2$



non directional so placed anywhere

O.S. = +3	C.N. = 6
1° Valency = 3	2° Valency = 6
Satisfied by = $3Cl^-$	Satisfied by = $5H_2O + Cl^-$

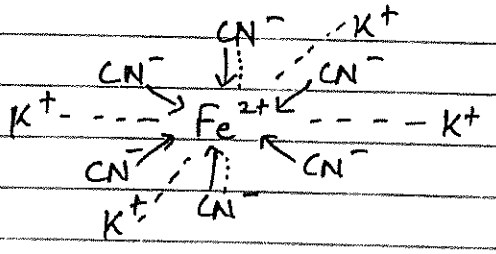
1 Cl^- shows dual nature, all properties are acc. to 2° valency.

% of non ionisable Cl^- = $33.\overline{33}$ %.

- $K_4[Fe(CN)_6]$

O.S. = +2	C.N. = 6
1° val. = 2	2° val. = 6
Satisfied by = $2CN^-$ + $4K^+$	Satisfied by = $6CN^-$

2 CN^- show dual nature.



- $CrCl_3 \cdot 6H_2O \longrightarrow$ all possibilities = ?

O.S. = +3, CN = 6.

Ⓐ → $[Cr(H_2O)_6] Cl_3$ → 4 ~~3~~ ions

Ⓑ ~~→ $[Cr(H_2O)_5] Cl_2 \cdot H_2O$~~ $\underbrace{[\overset{+3}{Cr}(H_2O)_5 \overset{-1}{Cl}]}_{\oplus}\underbrace{Cl_2}_{\ominus} \cdot H_2O$ → 3 ions

polar = ion-dipole

Ⓒ $\underbrace{[\overset{+3}{Cr}(H_2O)_4 \overset{-2}{Cl_2}]}_{\oplus}\underbrace{Cl}_{\ominus} \cdot 2H_2O$ → 2 ions

polar = ion-dipole

Ⓓ → $[Cr(H_2O)_3Cl_3]\cdot 3H_2O$ Not possible

neutral polar ⇒ no strong attraction

→ No. of moles of AgCl ppt. on adding excess $AgNO_3$ solⁿ:

Ⓐ > Ⓑ > Ⓒ (3mol > 2mol > 1mol Cl)

→ Conductivity order :- A > B > C

Conductivity ∝ no. of ions ∝ charge of ions
(if no. of ions same)

→ Weight loss on heating with conc. H_2SO_4 (water molecules not in complex ↑)

No wt. loss A < B < C

→ % of non ionisable Cl^- = A < B < C
0% 33% 67%

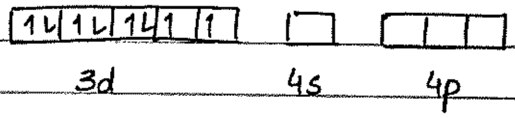
- $PtCl_4\cdot 4NH_3 \xrightarrow{AgNO_3}$ 2 mol AgCl ↓
  O.S. = +4 CN = 6 ⇒ $[Pt(NH_3)_4Cl_2]Cl_2$
- $PtCl_4\cdot 2HCl \xrightarrow{AgNO_3}$ No ppt
  O.S. = +4 CN = 6 $H_2[Pt(Cl)_6]$ $(= 2H^+ + [PtCl_6]^{2-})$
- $PdCl_2\cdot 4NH_3 \xrightarrow{AgNO_3}$ 2 mol AgCl ↓
  O.S. = +2 CN = +4 ⇒ $[Pd(NH_3)_4]Cl_2$

→ NH_3 act as WFL with Fe^{2+}, Mn^{2+} (CN = 6)

→ H_2O acts as SFL for Cu^{2+} (CN = 4)

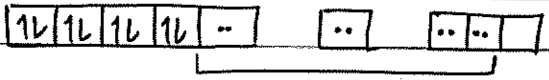
- $[Ni(CN)_4]^{2-}$ O.S. = +2 CN = 4 ligand = SFL

Ni = $3d^8\ 4s^2$

Ni^{2+} =


pairing possible

↓

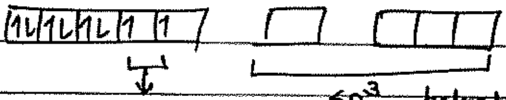
Ni^{2+} =


$dsp^2 \Rightarrow$ sq. planar ; diamagnetic

- Spin Magnetic moment $\mu = \sqrt{n(n+2)}$ B.M.

n = 1	$\mu = 1.73$	$\sqrt{3}$
n = 2	$\mu = 2.83$	$\sqrt{8}$
n = 3	$\mu = 3.87$	$\sqrt{15}$
n = 4	$\mu = 4.90$	$\sqrt{24}$
n = 5	$\mu = 5.92$	$\sqrt{35}$

- $[NiCl_4]^{2-}$ or $[Ni(SCN)_4]^{2-}$ O.S. = +2 CN = 4 ligand = WFL

Ni^{2+} =

No pairing

paramagnetic sp^3 = tetrahedral

μ = 2·something

* If pairing / s $e^{\ominus}$ shifting is possible, then low spin complex is formed. Otherwise it's high spin complex, where spin Q.N. remains same. spin paired complex ✗

- $[Ni(CO)_4]$ OR $[Ni(CN)_4]^{4-}$ O.S. = 0 CN = 4 ligand = SFL

Ni = [↑↓|↑↓|↑↓|↑|↑] [↑↓] [| |]

s $e^{\ominus}$ shifting = compulsory for s to be there in hyb.

CN = 4 → sp^3 / → dsp^2

↓

Ni = [↑↓|↑↓|↑↓|↑↓|↑↓] $\underbrace{[\ ]\ [\ |\ |\ ]}$

sp^3 → tetrahedral; diamagnetic

- $[Fe(CO)_5]$; $\mu = 0$ (Dipole) O.S. = 0 CN = 5 ligand = SFL

Fe = [↑↓|↑|↑|↑|↑] [↑↓] [| |] Spin Q.N. = 2.

↓ s shifting + d pairing ↓ Spin Q.N. ↓ ⇒ Low spin complex

Fe = [↑↓|↑↓|↑↓|↑↓|] [ ] [| |] Spin Q.N. = 0 $[Fe(CO)_5]$

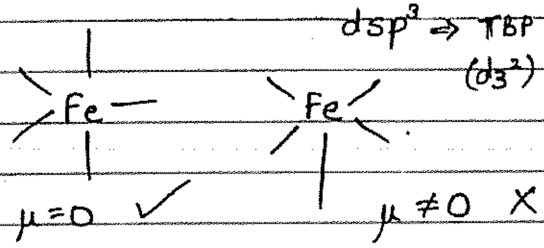
dsp^3 ⇒ TBP ; diamagnetic ; IOC

(d_{z^2})

Inner d participates in hyb.

⇓

Inner orbital Complex (IOC)



- $[Cu(NH_3)_4]SO_4$ O.S. = +2 CN = 4 lig. = SFL

Cu = $3d^{10}4s^1$ ⇒ Cu^{2+} = [↑↓|↑↓|↑↓|↑↓|↑] $\underbrace{[\ ]\ [\ |\ |\ ]}$

(pairing not possible) ~~sp^3 Tetrahedral; paramagnetic~~

Cu^{2+} = [↑↓|↑↓|↑↓|↑↓|↑] [ ] [| |]

d $e^{\ominus}$ transference (only in SFL)

= [↑↓|↑↓|↑↓|↑↓|] [ ] [| |↑]

dsp^2 = square planar, paramagnetic, ~~$\mu=\sqrt{3}$~~ $\mu = \sqrt{3}$

	WERNER COMPLEX	MODERN COMPLEX	NO. OF IONS	TOTAL ELECTRIC CHARGE
1.	$CoCl_3 \cdot 6NH_3$	$[Co(NH_3)_6]Cl_3$	4	6
2.	$CoCl_3 \cdot 5NH_3$	$[Co(NH_3)_5Cl]Cl_2$	3	4
3.	$CoCl_3 \cdot 4NH_3$	$[Co(NH_3)_4Cl_2]Cl$	2	2
4.	$CoCl_3 \cdot 3NH_3$	$[Co(NH_3)_3Cl_3]$	0	0 (Neutral)

Which can't act as electrolyte = ④
Which exhibits max. conductivity = ①
Which has max. % of non ionisable Cl = ④ (100%)

---

2. **VBT :-**

① CMA releases $e^{\ominus}$ acc. to O.S.

② CMA will provide vacant orbitals acc. to C.N.

③ These vacant orbitals undergo hybridisation and form coordinate bond with donor atoms by axial overlapping.

④ Hyb. state of CMA depends on C.N. and nature of ligands.

Dipole moment, Magnetic moment, isomerism, etc. are also helpful in geometry prediction.

C.N. = 2	sp	linear
C.N. = 3	sp^2	trigonal planar

- $C.N. = 4 \begin{cases} \rightarrow sp^3 = \text{Tetrahedral} \\ \rightarrow dsp^2 = \text{Square Planar} \end{cases}$

$C.N. = 5 \begin{cases} \rightarrow sp^3d \rightarrow \text{TBP} \\ \rightarrow dsp^3 \begin{cases} \rightarrow \text{TBP } (d_{z^2}) \\ \rightarrow \text{square pyramidal } (d_{x^2-y^2}) \end{cases} \end{cases}$

$C.N. = 6 \begin{cases} \rightarrow sp^3d^2 \\ \rightarrow d^2sp^3 \end{cases} \Big] = \text{octahedral (SBP)}$

⑤ In presence of strong field ligand (SFL), pairing of $(n-1)d$ $e^{\ominus}$ of CMA is possible before hybridisation, but this pairing is not possible in presence of weak field ligands (WFL).

→ Ligand Strength order :- (spectrochemical series)

$$\underbrace{I^- < Br^- < SCN^- < Cl^- < S^{2-} < \boxed{N_3^-} < F^-}_{X^- \text{ or } S \text{ donor}} < \underbrace{OH^- < C_2O_4^{2-} < H_2O}_{O \text{ donor}} <$$

$$\underbrace{NCS^- < EDTA < NH_3 < en < NO_2^-}_{N \text{ donor}} < \underset{\substack{\downarrow \\ P \text{ donor}}}{PR_3} < \underbrace{CN^- < CO}_{C \text{ donor}}$$

$$\underbrace{X \text{ or } S \text{ donor} < O \text{ donor}}_{} < \underbrace{N\text{-donor} < P \text{ donor} < C \text{ donor}}_{}$$

WFL ⇒ for 3d series CMA ⇐ SFL

→ All ligands act as SFL for 4d or 5d series CMAs.

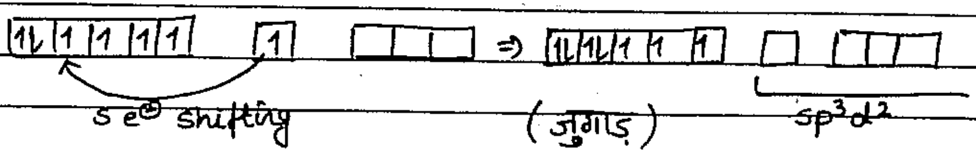
→ F^- acts as SFL for Ni^{4+} (CN = 6)

→ H_2O and $C_2O_4^{2-}$ (ox) act as SFL for Co^{3+} (CN = 6)

- $[Fe(H_2O)_5(\overset{+}{N}O)]SO_4$ (Brown Ring Complex)

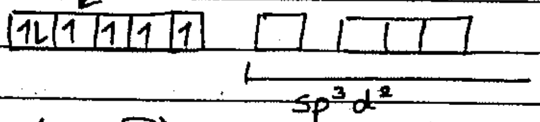
O.S. = +1 CN = 6 ligand = 5 WFL + 1 SFL = WFL

Fe^{+} =



$Fe^{2+} \xrightarrow[\overset{\uparrow}{e^\ominus}]{} Fe^{+}$ $NO \longrightarrow NO^{+}$

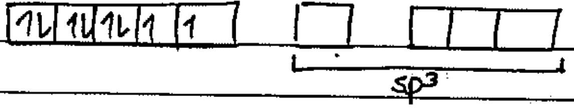
$NO \xrightarrow{e^\ominus} NO^{+}$ Fe^{2+} =



octahedral, paramagnetic ($\mu = \sqrt{15}$), outer orbital complex, low spin complex.

- $[NiCl_2(PPh_3)_2]$ O.S. = +2 CN = 4 ligand = 2 WFL, 2 SFL
  ↳ paramagnetic

Ni^{2+} =



(high spin complex ~~outer orbital complex~~)

If sp^3 ⇒ paramagnetic If dsp^2 ⇒ diamagnetic

- $[Ni(Cl_2)(PMe_3)_2]$ O.S. = +2, CN = 4 ligand = 2WFL, 2SFL.
  diamagnetic

Ni^{2+} =

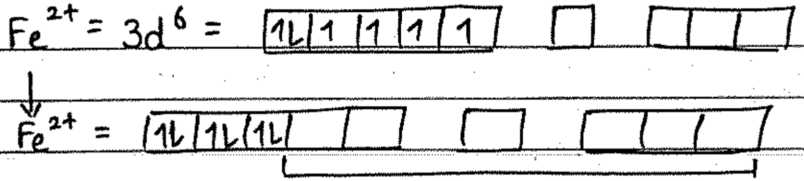
dsp^2 = square planar, diamagnetic,
IOC, low spin complex, G.I. ✓

- $[RhCl(PPh_3)_3]$, $[PdCl_2(NH_3)_2]$, $[AgF_4]^-$
WILKINSON'S CATALYST

Rh^{+}, Pd^{2+}, Ag^{3+} ⇒ $4d^8$
Ir^{+}, Pt^{2+}, Au^{3+} ⇒ $5d^8$

CN=4 ↘ dsp^2 (sq. pl.)
(any ligand),
diamagnetic

- $[Fe(CN)_5(O_2^-)]^{4-}$ O.S. = +2 CN = 6
  lig. = 5 SFL + 1 WFL = SFL

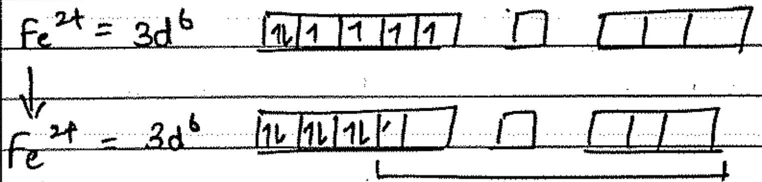


d^2sp^3 = octahedral, low spin complex, ~~diamagnetic~~, IOC

paramagnetic due to presence of O_2^-, an odd $e^\ominus$ species.

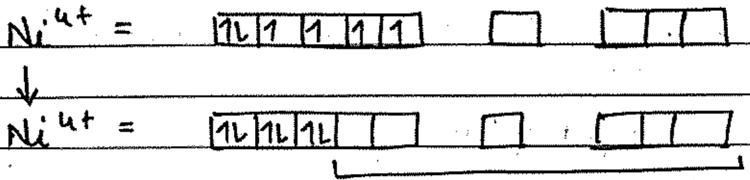
Complex will be paramagnetic with ligands
O_2, O_2^+, O_2^-, NO ⇒ odd $e^\ominus$ / paramag. (MOT; O_2)

- $[Fe(NH_3)_6]^{2+}$ OS = +2 CN = 6 lig. = ~~SFL~~ WFL



d^2sp^3 = octahedral, diamagnetic, IOC, low spin complex.

- $[NiF_6]^{2-}$ OS = +4 CN = 6 lig = ~~WFL~~ SFL



d^2sp^3 = octahedral, diamagnetic, IOC, low spin complex.

- $[Cr(NH_3)_6]^{2+}$ O.S. = +2 CN = 6 lig. = SFL

$Cr^{+2} = 3d^4$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\ }\quad\boxed{\ }\quad\boxed{\ }\boxed{\ }\boxed{\ }$

↓

$Cr^{2+} =$ $\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\underbrace{\boxed{\ }\boxed{\ }\quad\boxed{\ }\quad\boxed{\ }\boxed{\ }\boxed{\ }}$

d^2sp^3 = octahedral, paramagnetic, $\mu = \sqrt{8}$, IOC, low spin complex

- $[FeF_6]^{3-}$ O.S. = +3 CN = 6 lig. = WFL

$Fe^{3+} = d^5$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\quad\boxed{\ }\quad\boxed{\ }\boxed{\ }\boxed{\ }$

↓

$Fe^{3+} =$ $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\underbrace{\boxed{\ }\boxed{\ }\quad\boxed{\ }\quad\boxed{\ }\boxed{\ }\boxed{\ }}$

d^2sp^3 = octahedral, paramagnetic, $\mu = \sqrt{3}$, IOC, low spin complex.

- $[Ni(CN)_5]^{3-}$ 4 Ni – C bonds identical

O.S. = +2 CN = 5 lig. = SFL

$Ni^{2+} = d^8$ $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\quad\boxed{\ }\quad\boxed{\ }\boxed{\ }\boxed{\ }$

4 Ni – C bonds same ⇒ TBP ✗ ⇒ sq. pyramidal ✓
⇒ dsp^3

↓

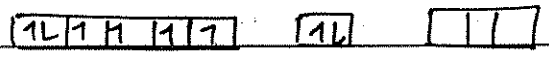
$Ni^{2+} =$ $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\underbrace{\boxed{\ }\quad\boxed{\ }\quad\boxed{\ }\boxed{\ }\boxed{\ }}$

dsp^3 = sq. pyramidal, diamagnetic, IOC, low spin complex

- $[Mn(CO)_5]^-$ (dipole moment = 0)

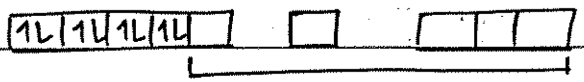
O.S. = −1 CN = 5 lig. = SFL

$Mn^{-1} = s^2d^6$

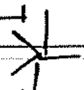


↓

$Mn^{-1} =$



dsp^3 = TBP =



$\vec{P} = 0$

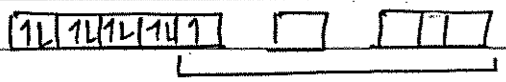
diamagnetic, lowspin complex, IOC

- $[CuCl_5]^{3-}$ O.S. = +2 CN = 5 lig. = WFL

$Cu^{2+} = d^9$

↓

$Cu^{2+} =$



dsp^3d = TBP, paramagnetic, $\mu = \sqrt{3}$,
low spin complex, IOC

- $[MnCl_4]^{2-}$ O.S. = +2 CN = 4 lig. = WFL

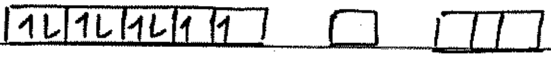
$Mn^{2+} = d^5$

sp^3 = Tetrahedral,
paramagnetic, $\mu = \sqrt{35}$; high spin complex

5d

- $[PtCl_4]^{2-}$ O.S. = +2 CN = 4 lig. = ~~WFL~~ SFL

$Pt^{2+} = d^8$



↓

Pt^{2+} =

sq. planar

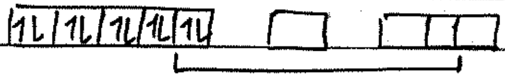
dsp^2 = ~~Tetrahedral~~, diamagnetic, low spin complex, IOC

- $[Fe(CO)_2(\overset{+}{N}O)_2]$ O.S. = −2 CN = 4 lig = SFL

$Fe^{2-} = d^8 s^2$

↓

Fe^{2-} =

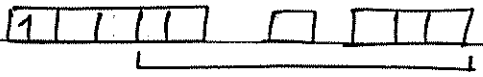


~~sq. planar~~

dsp^3 = Tetrahedral; diamagnetic, low spin complex, IOC

- $[Ti(H_2O)_6]^{3+}$ O.S. = +3 CN = 6 lig. = WFL

$Ti^{3+} = d^1$



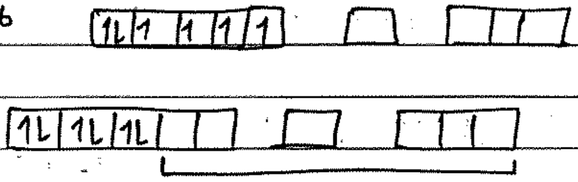
d^2sp^3 = octahedral, paramagnetic, $\mu = \sqrt{3}$, high spin complex, IOC

- $Na_2[Fe(CN)_5(\overset{+}{N}O)]$ O.S. = +2 CN = 6 lig. = SFL

$Fe^{2+} = d^6$

↓

Fe^{2+} =



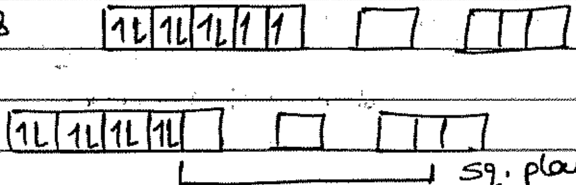
d^2sp^3 = sq. bipyramidal /octahedral, diamagnetic, low spin complex, IOC

- $[AuCl_4]^-$ O.S. = +3 CN = 4 lig. = SFL (5d)

$Au^{3+} = d^8$

↓

Au^{3+} =



sq. planar

dsp^2 = ~~Tetrahedral~~, diamagnetic, low spin complex, IOC

- $[Ag(CN)_2]^-$ O.S. = +1 CN = 2 lig. = SFL

$Ag^+ = d^{10} \Rightarrow sp$, ~~octahedral~~ linear, diamagnetic, high spin complex.

- $[\overset{2+}{Hg}\ \overset{-}{I_3}]^-$ $[Hg^{2+} + (3) I_3^-]$ ⇒ O.S = +2 CN = 3 lig. = SFL

$Hg^{2+} = d^{10} = sp^2$, trigonal planar, diamagnetic, high spin complex.

- $[Zn(NH_3)_6]^{2+}$ O.S. = +2 CN = 6 lig. = SFL

$Zn^{2+} = d^{10} = sp^3d^2$ = octahedral, diamagnetic, high spin complex.

- DRAWBACKS OF VBT :-

1. It can't explain stability of complex compound
2. —— " —— color —— " ——
3. It can't explain d $e^\ominus$ transference.
4. It doesn't give any criteria for classification of SFL, WFL.
5. It doesn't give successful explaination of pairing of d $e^\ominus$.

3. CRYSTAL FIELD THEORY :-

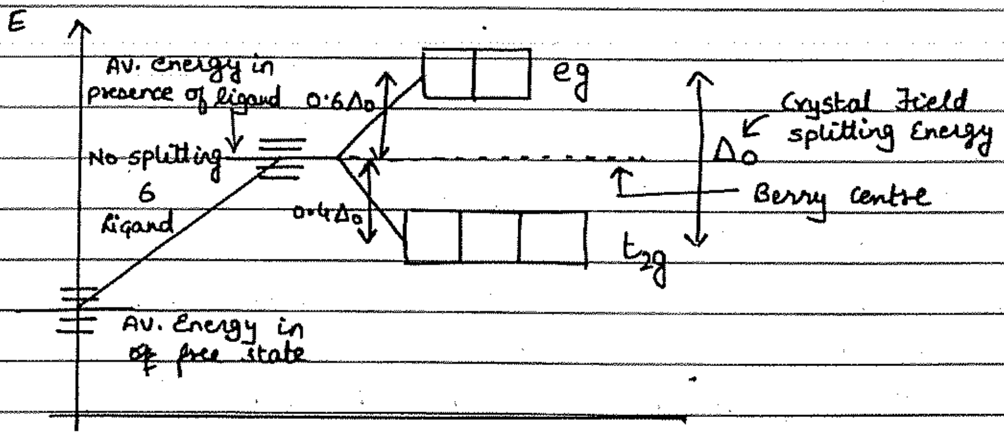
① CMA is considered as ~~anion~~ cation and ligands are considered as pt. charge or pt. dipole.

② Interaction b/w CMA and ligand is electrostatic in nature.

③ The degeneracy of (n-1)d orbitals of CMA is not maintained during the formation of complex. This is k/a crystal field splitting.

- **CFT for OCTAHEDRAL COMPLEX ⇒**

$d_{xy}, d_{yz}, d_{xz} \rightarrow t_{2g}$ $\quad$ $d_{x^2-y^2}, d_{z^2} \rightarrow e_g$



⇒ dⁿ system : $e^{\ominus}$ config. of $(n-1)d\ e^{\ominus}$ of CMA (after splitting) depends upon following types of energy *a) Δ_o b) pairing energy (P)

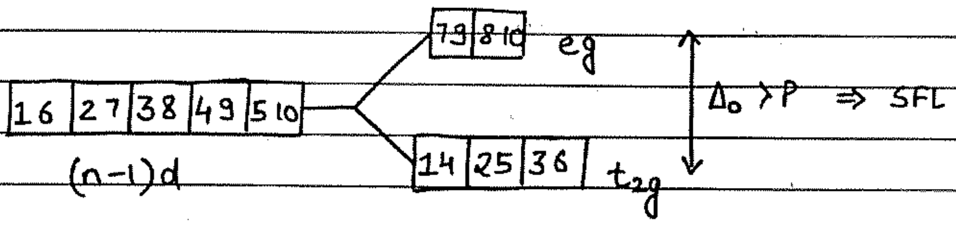
→ There are 2 conditions :-

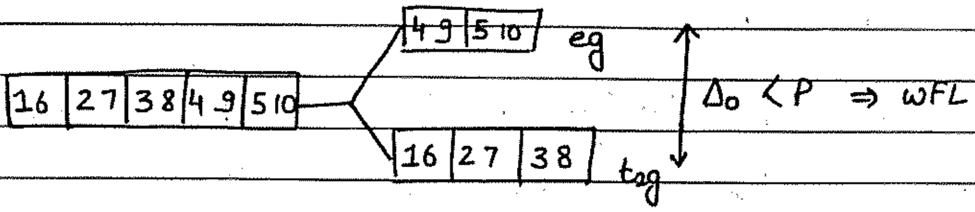
a) in presence of SFL :- $\Delta_o > P$

b) in presence of WFL :- $\Delta_o < P$

→

d^n	presence of SFL	presence of WFL
d^1	t_{2g}^1 e_g^0	t_{2g}^1 e_g^0
d^2	t_{2g}^2 e_g^0	t_{2g}^2 e_g^0
d^3	t_{2g}^3 e_g^0	t_{2g}^3 e_g^0
d^4	t_{2g}^4 e_g^0	t_{2g}^3 e_g^1
d^5	t_{2g}^5 e_g^0	t_{2g}^3 e_g^2
d^6	t_{2g}^6 e_g^0	t_{2g}^4 e_g^2
d^7	t_{2g}^6 e_g^1	t_{2g}^5 e_g^2
d^8	t_{2g}^6 e_g^2	t_{2g}^6 e_g^2
d^9	t_{2g}^6 e_g^3	t_{2g}^6 e_g^3
d^{10}	t_{2g}^6 e_g^4	t_{2g}^6 e_g^4





- ## FACTORS AFFECTING SPLITTING ENERGY –

a) $\Delta_o \propto$ charge of CMA

b) $\Delta_o \propto Z_{eff}$ of CMA

$$\underset{\text{series}}{3d} \xrightarrow[30-40\% \uparrow]{\Delta_o \uparrow} \underset{\text{series}}{4d} \xrightarrow[30-50\% \uparrow]{\Delta_o \uparrow} \underset{\text{series}}{5d} \;\Big|\; Z_{eff} \uparrow$$

c) $\Delta_o \propto$ strength of ligand $(\overline{X/S < O} < \overline{N < P < C})$ — WFL over $X/S < O$, SFL over $N < P < C$

d) Geometry :- $\Delta_{sp} > \Delta_o > \Delta_t$ $\quad \Delta_t = \frac{4}{9}\Delta_o$

$\Delta_{sp} = 1 \cdot 3\ \Delta_o$

→ $[Co(H_2O)_6]^{2+} < [Co(H_2O)_6]^{3+}$ (Δ_o)

d^7, WFL $\quad$ d^6, SFL

sp^3d^2, para. $\quad$ d^2sp^3, ~~para~~ dia.

→ $[Fe(H_2O)_6]^{3+} < [Ru(H_2O)_6]^{3+} < [Os(H_2O)_6]^{3+}$ (Δ_o)

d^5, WFL $\quad$ d^5, SFL $\quad$ ← same

sp^3d^2, para $\quad$ d^2sp^3, para

→ $[CrCl_6]^{3-} < [Cr(H_2O)_6]^{3+} < [Cr(NH_3)_6]^{3+}$ (Δ_o)

d^3, WFL

↓, always. $\quad$ same $\quad$ same.

d^2sp^3, para

→ $[Ni(CN)_4]^{2-} > [Ni(CN)_6]^{4-} > [Ni(Cl)_4]^{2-}$ (splitting E)

d^8, SFL → dsp^2 $\quad > \quad \Delta_o \quad > \quad$ d^8, WFL

CN=4 $\quad \Delta_{sp}$ $\quad$ CN=4 $\quad sp^3$

Δ_t

** STABILITY OF COMPLEX COMPOUND ⇒

a) Stability ∝ charge of CMA
∝ Z_{eff} of CMA (Top → Bottom)
∝ strength of ligand
∝ chelation effect

b) $\text{Stability} \propto \frac{1}{\text{size of CMA}}$ (Left → Right)

c) Synergic Bonding also increases stability of complex compound.

→ $[\overset{+2}{Fe}(CN)_6]^{4-} < [\overset{+3}{Fe}(CN)_6]^{3-}$

→ $[Co(H_2O)_6]^{3+} < [Rh(H_2O)_6]^{3+} < [Ir(H_2O)_6]^{3+}$ (Z_{eff} ↑)

→ $[\overset{+2}{Ni}Cl_6]^{4-} < [Ni(NH_3)_6]^{2+} < [\overset{+2}{Ni}(CN)_6]^{4-}$

→ $[\overset{+3}{Fe}(NH_3)_6]^{3+} < [\overset{+3}{Fe}(ox)_3]^{-3} < [\overset{+3}{Fe}(EDTA)]^{-}$
No chelation   3 chelation   5 chelation

- Generally chelation effect dominates over ligand strength.

EXCEPT :- $[Fe(ox)_3]^{3-} < [Fe(CN)_6]^{3-}$ due to synergic bond

→ Erving Williamson stability order

→ Most stable complexes

$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} \leq Cu^{2+} > Zn^{2+}$ complexes

$$M^{n+} + xL \underset{K'}{\overset{K}{\rightleftharpoons}} [ML_x]^{+n} \qquad K = \frac{[ML_x]}{[M^{n+}][L]^x}$$

- K = Stability / Formation constant.

$K\uparrow \Rightarrow$ Stability $\uparrow$ $\quad K = \frac{1}{K'}$ (K' = dissociation constant)

⇛ CRYSTAL FIELD STABILIZATION ENERGY (CFSE) –

→ Extra stabilization (released energy) due to splitting in comparison to no splitting.

→ $CFSE = -0.4\,\Delta_o(n_{t_{2g}}) + 0.6\,\Delta_o(n_{eg}) + xP$

(x = no. of new pairs)

Q. Calculate ≤ CFSE :-

① $[Fe(CN)_6]^{-4}$ O.S. = +2 CN = 6 ⇒ $3d^6$, SFL

$\boxed{\uparrow\downarrow|\uparrow|\uparrow|\uparrow|\uparrow} \Rightarrow t_{2g}^6\ e_g^0 \Rightarrow \boxed{\uparrow\downarrow|\uparrow\downarrow|\uparrow\downarrow}$

$CFSE = -0.4\,\Delta_o(6) + 0.6\,\Delta_o(0) + 2P$

$= -2.4\,\Delta_o + 2P$ (overall ⊖, as $\Delta_o > P$, SFL)

② $[\overset{+3}{Cu}F_6]^{-3}$ d^8, WFL

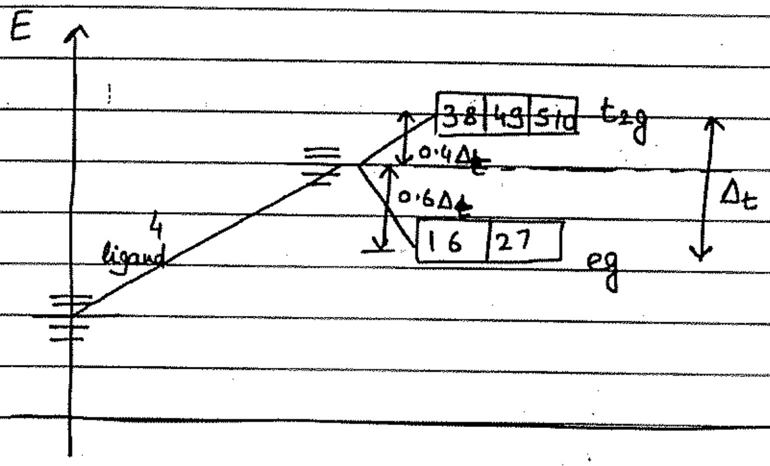
$\boxed{\uparrow\downarrow|\uparrow\downarrow|\uparrow\downarrow|\uparrow|\uparrow} \Rightarrow t_{2g}^6\ e_g^2$

$CFSE = -0.4\,\Delta_o(6) + 0.6\,\Delta_o(2) + 0P$

$= -2.4\,\Delta_o + 1.2\,\Delta_o = -1.2\,\Delta_o$

→ CFSE is released energy, so always ⊖, or max. 0.

CFT for TETRAHEDRAL COMPLEX ⇒



tetrahedral $\widehat{L-eg} = 55^\circ$ $\widehat{L-t_{2g}} = 35^\circ$ Diff $= 20^\circ$

octahedral $\widehat{L-eg} = 0^\circ$ $\widehat{L-t_{2g}} = 45^\circ$ Diff $= 45^\circ$

Due to difference in angle of contact of ligand (incoming) with own orbitals, there's a difference in repulsion, so difference in energy, so splitting occurs.

$\Delta_{sp} > \Delta_o > \Delta_t$ $\Delta_t = \frac{4}{9}\Delta_o$

$45^\circ \longrightarrow \Delta_o$
$1 \longrightarrow \Delta_o/45$
$20^\circ \longrightarrow \frac{4}{9}\Delta_o = \Delta_t$

Tetrahedral's CFT is reverse of that in octahedral.

Generally, $\Delta_t < P$, so all ligands act as WFL

- CFT for SQUARE PLANAR COMPLEX ⇒

⇒ $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{xz} = d_{yz}$ (divide into 4 orbitals)

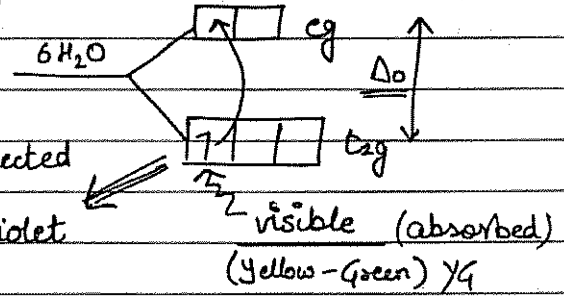
• COLOR :-

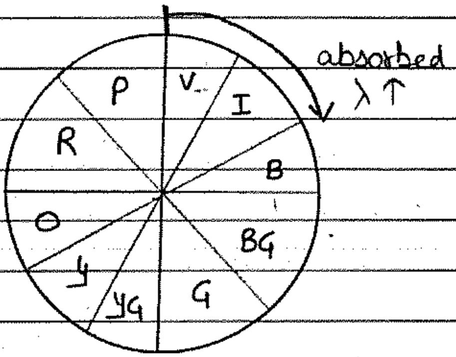
① d-d transition -

Color of complex compound is due to d-d transition.

e.g. aq. solⁿ of Ti^{3+} = violet

Ex $Ti^{3+} = 3d^1$





Color of complex compounds depend on splitting energy

Q. Which of these absorbs light of min. λ -

a) $[CrCl_6]^{3-}$ b) $[Cr(H_2O)_6]^{3+}$ c) $[Cr(NH_3)_6]^{3+}$ d) ✓ $[Cr(NO_2)_6]^{3-}$

⟶ ligand strength ↑ Δo ↑ req. energy E ↑ $\underline{\lambda \downarrow}$

ligand strength: $NO_2^- > NH_3$

Q. Color of $[MBr_6]^{-3}$, $[M(H_2O)_6]^{3+}$ and $[M(CN)_6]^{-3}$ are resp. →

a) O, G, V ✓~~b)~~ G, V, O c) V, O, G d) O, V, G

ligand strength ↑ Δ_o ↑ E ↑ λ ↓ (absorbed) ⇒ <u>ACW</u>

reflected color ⇒	Orange	Violet	Green
absorbed color ⇒	Blue	YG	Purple
	$\lambda\downarrow \Rightarrow$ lig ↑		$\lambda\uparrow \Rightarrow$ lig. ↓
	CN^-		Br^-

Q. ① $[Co(H_2O)(NH_3)_5]^{3+}$ = Red

② $[Co(NH_3)_6]^{3+}$ = ? a) B b) G ✓~~c)~~ O d) V

③ $[Co(CN)_6]^{3-}$ = YG.

Ans

lig. ⇒	~~③ < ① < ③~~	① <	② <	③
λ ⇒	~~③ > ① > ③~~	① >	② >	③ ($\lambda\downarrow$)
absorb	BG~~R~~	~~[illegible]~~ BG	⇒ B/I	V
reflect		R	O/Y	YG

Q. $[Ni(H_2O)_6]^{2+} \xrightarrow[-2H_2O]{+en} [Ni(en)(H_2O)_4]^{2+} \xrightarrow[-2H_2O]{+en} [Ni(en)_2(H_2O)_2]^{2+}$

Green BG ?

$\downarrow$ +en −2H_2O

Violet $[Ni(en)_3]^{2+}$

a) Y ✓~~c)~~ B
b) R d) YG

Δ_o = a < b < c < d

BG (बीच का) Violet
I / B

→ d-d transition is not possible for d^0 and d^{10} config.

Q. Which of these can absorb visible light?

a) $[Sc(H_2O)_6]Cl_3$ b) $[Ti(en)_3](SO_4)_2$

c) $[Zn(NH_3)_6]SO_4$ ✓d) $[Cr(NH_3)_6]Cl_3$

→ $[Ni(CN)_4]^{2-}$ is colorless due to high ~~Δ_o~~ splitting energy
$d^8 \rightarrow dsp^2$ = sq. p. $\Rightarrow \Delta_{sp} > \Delta_o$, so $E\uparrow\uparrow \Rightarrow \lambda \rightarrow \underline{UV}$

→ Red color of Ruby (Al_2O_3) and Green color of Emerald ($Be_3Al_2Si_6O_{18}$) is due to presence of some Cr^{+3} ions.

→ Complex becomes colorless in absence of ligand field.
e.g. a) $[Ti(H_2O)_6]^{3+}$ becomes colorless on heating due to removal of H_2O molecules.

b) Anhydrous $CuSO_4$ is colorless but hydrated $CuSO_4$ is blue.

$$CuSO_4 \xrightarrow[\text{test of moisture}]{+5H_2O} [Cu(H_2O)_4]SO_4 \cdot H_2O$$

~~$CuSO_4$~~

$\underline{H_2O = SFL}$
with Cu^{2+} (CN=4) $\Rightarrow dsp^2$

→ Color of f block elements is due to f-f transition.

→ Color of f^n configuration is generally similar to f^{14-n} configuration.

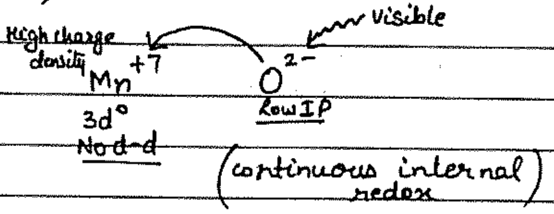
→ Color of G.I. of a complex compound may be different.

② Charge transition -

Color of some compounds is due to charge transfer ($e^{\ominus}$ transition) by absorption of visible light.

a) Charge transfer fm. anion (ligand) to metal ion :-

e.g. $KMnO_4$	purple	
K_2MnO_4	green	
$K_2Cr_2O_7$	orange	
Na_2CrO_4	yellow	
CrO_2Cl_2	Red orange	(CHROMYL CHLORIDE)
$[Fe(H_2O)_5(NO)]SO_4$	Brown	
$Na_4[Fe(CN)_5(NOS)]$	Brown / Violet	(NOS = Thionitrito-N)



b) Charge transfer fm. metal to metal ion :-

e.g. $\overset{+3}{Fe_4}[\overset{+2}{Fe}(CN)_6]_3$ dark blue ppt. (PRUSSIAN BLUE)
(d-d transition possible, but not reason of color)

$Fe_3[Fe(CN)_6]_2$ dark blue ppt. (TURN BULL BLUE)

③ Polarisation -

If polarisation ↑ then possibility of finding color ↑ and intensity of color ↑.

e.g. AgF = colorless, but AgI = yellow.

PbF_2 = colorless, but PbI_2 = yellow

* Ju NaI to life Colorless Hai.

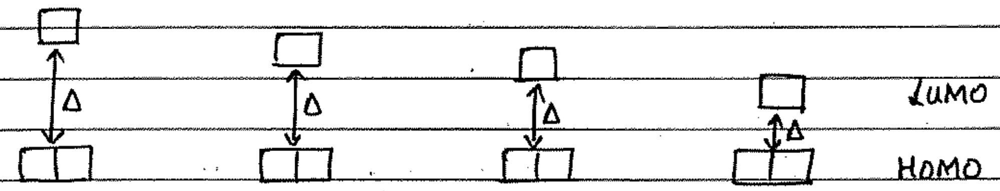
- HgF_2 = colorless, but HgI_2 = red

SnF_4 = colorless, but SnI_4 = red

ZnS = colorless, CdS = yellow, HgS = black

④ Color of halogens is due to $e^{\ominus}$ transition from HOMO to LUMO.

F_2	Cl_2	Br_2	I_2
Light yellow	Greenish Yellow	Reddish Brown	Violet



$\Delta \downarrow \Rightarrow$ Absorbed $|E| \downarrow \Rightarrow$ Absorbed $\lambda \uparrow \Rightarrow$ Absorbed color CW

- ISOMERISM :-

⇛ STRUCTURAL ISOMERISM - Same MF, diff. structural formula.

① COORDINATION ISOMERISM - It arises due to exchange of ligands between complex cation and complex anion.

→ $[Co(NH_3)_6][Cr(NO_2)_6]$ and $[Co(NH_3)_5(NO_2)][Cr(NH_3)(NO_2)_5]$

↳ possible coordination isomers = ?

Co^{+3} $NH_3 : NO_2^-$	Cr^{+3} $NH_3 : NO_2^-$
6 : 0	0 : 6
5 : 1	1 : 5
4 : 2	2 : 4
$\boxed{3 : 3}$	$\boxed{3 : 3}$

Neutral ⇒ Can't remain bonded.

Co^{+3}	Cr^{+3}
2 : 4	4 : 2
1 : 5	5 : 1
0 : 6	6 : 0

So, total coordination isomers = 6.

→ $[Pt(NH_3)_4][Pt(Cl)_4]$ possible isomers?

Pt^{+2}		Pt^{+2}	
$NH_3 : Cl^-$		$NH_3 : Cl^-$	
4 : 0		0 : 4	
3 : 1		1 : 3	
$\boxed{2 : 2}$	Neutral.	$\boxed{2 : 2}$	X
1 : 3		3 : 1	
0 : 4		4 : 0	→ same compd, when both CMAs are same.

⇒ ~~Ans ④~~

Ans = ②

→ $[Co(en)_3][Cr(NO_2)_6]$

→ $[Pt(NH_3)_4][ZnCl_4]$

→ $[Ag(NH_3)_2][Ag(CN)_2]$

→ $[Co(en)_3][Cr(NO_2)_6]$

Co^{+3}	Cr^{+3}
$en : NO_2^-$	$en : NO_2^-$
3 : 0	0 : 6
2 : 2	1 : 4
1 : 4	2 : 2
0 : 6	3 : 0

(Because en is bidentate)

Ans = ④

→ $[Pt(NH_3)_4][ZnCl_4]$

Pt^{2+}		Zn^{2+}	
$NH_3 : Cl^-$		$NH_3 : Cl^-$	
4 : 0		0 : 4	
3 : 1		1 : 3	
$\boxed{2 : 2}$	Neutral	$\boxed{2 : 2}$	X
1 : 3		3 : 1	
0 : 4		4 : 0	

Ans = $\underline{\underline{4}}$

→ $[Ag(NH_3)_2][Ag(CN)_2]$

Ag^{+}		Ag^{+}
$NH_3 : CN^-$		$NH_3 : CN^-$
2 : 0		0 : 2
$\boxed{1 : 1}$	Neutral	$\boxed{1 : 1}$
0 : 2		2 : 0

when CMA is same, they both are same compd.

Ans = $\underline{\underline{1}}$

② IONISATION ISOMERISM -

Structural isomers which give different ions in aq. sol^n.

→ $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$

→ $[Pt(NH_3)_4Cl_2]Br_2$; $[Pt(NH_3)_4(Cl)(Br)]BrCl$; $[Pt(NH_3)_4Br_2]Cl_2$

③ HYDRATE OR SOLVATE ISOMERISM :-

Special type of ionisation isomerism in which no. of water molecules or polar molecules differ in coordination sphere or outside region.

→ $[Cr(H_2O)_6]Cl_3$; $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$; $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$

→ $[Pt(NH_3)_6]Cl_4$; $[Pt(NH_3)_5Cl]Cl_3 \cdot NH_3$; $[Pt(NH_3)_4Cl_2]Cl_2 \cdot 2NH_3$;

$[Pt(NH_3)_{\cancel{4}3}Cl_3]Cl \cdot 3NH_3$ ⇒ Solvate isomerism

④ LINKAGE ISOMERISM -

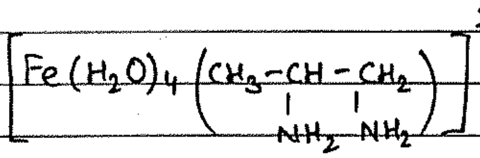
It arises due to presence of ambidentate ligand. For eg., ⇒

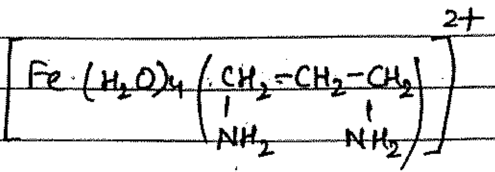
→ $[Co(NH_3)_5(CN)]SO_4$; $[Co(NH_3)_5(NC)]SO_4$ (linkage different)

→ $[Pd(NH_3)_2(SCN)_2]$; $[Pd(NH_3)_2(NCS)_2]$; $[Pd(NH_3)_2(NCS)(SCN)]$

⑤ LIGAND ISOMERISM -

It arises due to isomerism in ligands ~~it~~ themselves.

→ 

$\left[Fe(H_2O)_4\left(\underset{\quad\ NH_2\ \ NH_2}{CH_3-\overset{|}{C}H-\overset{|}{C}H_2}\right)\right]^{2+}$ and 

$\left[Fe(H_2O)_4\left(\underset{NH_2\qquad\ \ NH_2}{CH_2-CH_2-CH_2}\right)\right]^{2+}$

propane-1,2-diamine propane-1,3-diamine

⑥ POLYMERISATION ISOMERISM – Diff. MF, same empirical formula.

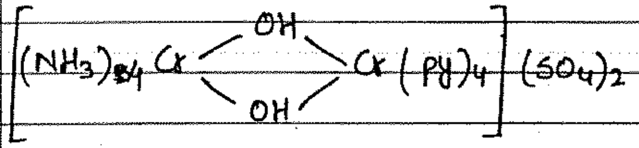
- Not true isomerism.

→ $[Pt(NH_3)_2Cl_2]$; $[Pt(NH_3)_4][PtCl_4]$; $[Pt(NH_3)_4][Pt(NH_3)Cl_3]_2$

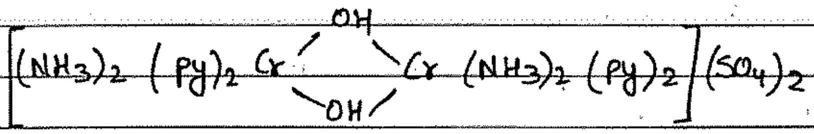
Pt : NH₃ : Cl 1:2:2 2:4:4 3:6:6

Different MF, same empirical formula.

⑦ COORDINATION POSITION ISOMERISM – Arises due to different position of ligands in polynuclear complexes.



$\left[(NH_3)_{\cancel{3}4}Cr\overset{OH}{\underset{OH}{\rightleftharpoons}}Cr(py)_4\right](SO_4)_2$ and



$\left[(NH_3)_2(py)_2Cr\overset{OH}{\underset{OH}{\rightleftharpoons}}Cr(NH_3)_2(py)_2\right](SO_4)_2$

⇛ GEOMETRICAL ISOMERISM in SQUARE PLANAR COMPLEX

→ Tetrahedral complexes do n't show G.I. but square planar complexes do.

→ Any two identical ligands @ 180° = trans

→ All identical ligands @ 90° = cis

→ $[Pt(NH_3)_4]Cl_2$ $Pt^{2+} = 5d^8 \xrightarrow{CN=4} dsp^2$ sq. planar.

$[M a_4]^{\pm}$ No. G.I.

→ $[Pt(NH_3)_3Cl]Cl$ $[Ma_3b]^{\pm}$ $\underset{180°}{(aa)}$ $\underset{180°}{(ab)}$ No G.I.

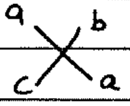
→ $[Pt(NH_3)_2Cl_2]$ Ma_2b_2 (aa) (bb) trans 2 G.I.
(ab) (ab) cis

→ cis $[Pt(NH_3)_2Cl_2]$ is also known as cis-platin and used as anti cancer agent.

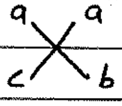
→ $[Pt(NH_3)_2 Cl Br]$

→ $[Pt(NH_3)(py)(Cl)(Br)]$.

→ $[Pt(NH_3)_2 Cl Br]$ $[Ma_2bc]^{\pm}$ (aa)(bc) 2 G.I.
(ab) (ac)



(trans)

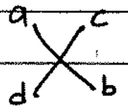


(cis)

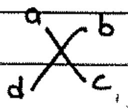
(For (aa) or (bc))

→ $[Pt(NH_3)(py)(Cl)(Br)]$ $[Mabcd]^{\pm}$ 3 G.I.

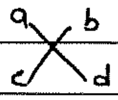
(a b) (cd)
(a c) (bd)
(ad) (bc)



(cis)



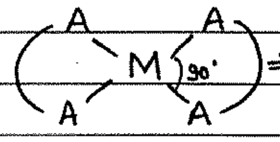
(cis)



(trans) For (ad)

For any 1 group, there'll be 2 cis and 1 trans.

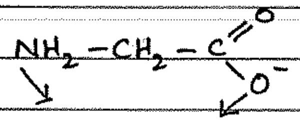
→ $[Pt(en)_2]Cl_2$ $[M(AA)_2]$ A = bidentate, AA = symmetric



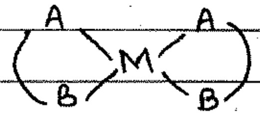
Bidentate donor atoms always @ 90°

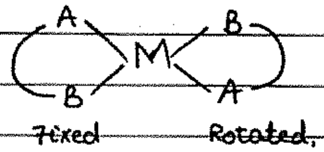
NO G.I.

→ $[Pt(gly)_2]$ $[M(AB)_2]$ glycenato =



$NH_2-CH_2-C(=O)O^-$

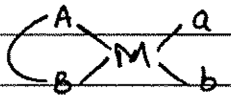


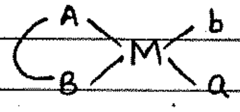


2 G.I.

cis   trans

→ $[Pt(gly)(NH_3)Br]$ $[M(AB)ab]$





2 G.I.

→ Ma_2b_2
Ma_2bc
$Mabcd$
$M(AB)_2$
$M(AB)ab$
] sq. planar compounds that show G.I.
Rest don't show G.I. (sq. planar)

Q. which of these shows G.I.?

a) $[Zn(NH_3)_2Cl_2]$ Ma_2b_2 ⇒ $Zn^{2+} = d^{10} = sp^3$ = Tetrahedral

b) $K[PtCl_3(\eta^2-C_2H_4)]$ Ma_3b X

c) $[Rh(PPh_3)_3Cl]$ Ma_3b X

✓d) $[Pd(gly)(py)Cl]$ $M(AB)ab$

Q. Which of these shows G.I.?

a) $[Pd(en)(gly)]^+$ $[M(AA)(AB)]$

b) $[Pd(gly)(NH_3)_2]^+$ $[M(AB)a_2]$

✓c) $[Pd(py)_2ClBr]$ $[Ma_2bc]$

d) $[Pd(en)ClBr]$ $[M(AA)ab]$

Q. Possible isomers of complex $[Pd(NH_3)_2(ONO)_2]$

a) 2 b) 4 ✓c) 6 d) 9

Ans 3 linkage $(ONO)_2$, $(ONO)(NO_2)$, $(NO_2)_2$

Then: Ma_2b_2 Ma_2bc Ma_2b_2 ⇒ Total = 6.

/\ /\ /\

GEOMETRICAL & OPTICAL ISOMERISM IN OCTAHEDRAL COMPLEX :-

→ $[Co(NH_3)_6]Cl_3$ $[Ma_6]^{\pm}$ (aa)(aa)(aa) No G.I.
optically inactive.

- Any 2 identical ligands @ 180° (aa) = O.I.
- Complex having 2 identical pairs (ab)(ab) = O.I.
- If 2 bidentate ligands are nonplanar (not @ 180°) = $\boxed{OA}$
- Complex having 3 bidentate ligands = Always $\boxed{OA}$

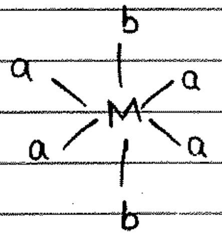
→ $[Co(NH_3)_5Cl]Cl_2$ Ma_5b $\underbrace{(aa)}_{O\cdot I\cdot}$ (aa) (ab) No G·I·

→ $[Pt(NH_3)_2Cl_2]Cl_2$ Ma_4b_2

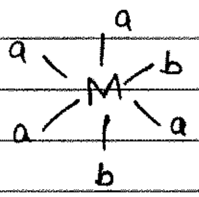
(aa) (aa) (bb) $\underline{(aa)}$ (ab) (ab) 2 G·I·

constant

(O·I·)



(O·I·)



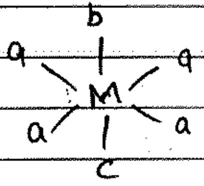
Acc. to aa trans (180°) trans(180°) So, not acc. to aa

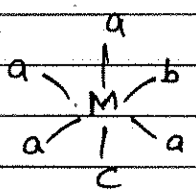
Acc. to bb trans (180°) cis (90°) ✓

→ $[Pt(NH_3)_4ClBr]Br_2$ Ma_4bc

(aa) (aa) (bc) (aa) (ab) (ac) 2 G·I·

O·I· O·I·





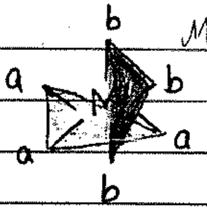
Acc. to <u>bc</u> trans (180°) cis (90°)

→ $[Co(NH_3)_3Cl_3]$ Ma_3b_3

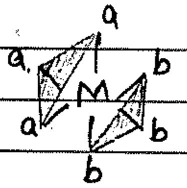
(aa) (ab) (bb) (ab) (ab) (ab) 2 G·I·

~~OA~~ O·I·

O·I·



Meridian पर



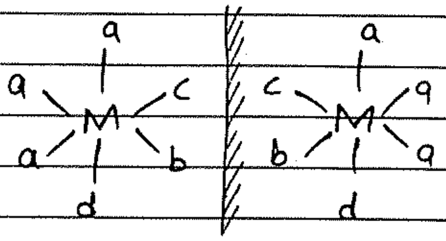
Face formation

(trans) Meridional (mer-)   Facial (fac-) (cis)

→ $[Ma_3b_2c]$ (aa) (ab) (bc) | (aa) (ac) (bb) | (ab) (ab) (ac) / 3 G.I.
all O.I.

→ $[Ma_3bcd]$

(ab) (ac) (ad) ⟶ $\boxed{OA}$ (cis)
(ab) (aa) (cd)
(aa) (ac) (bd)
(aa) (bc) (ad)
] O.I. (trans)



Enantiomer

G.I. = 4   O.A. = 2
Stereoisomers total = 5

→ $[Ma_2b_2c_2]$

(aa) (bb) (cc)
(aa) (bc) (bc)
(ac) (bb) (ac)
(ab) (ab) (cc)
] trans (O.I.)

(ab) (bc) (ac)   cis ; $\boxed{OA}$

G.I = 5
OA = 2   Total = 6

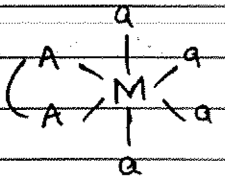
→ $[Ma_2b_2cd]$ G.I = 6   OA = 4   Total = 8

aa bb cd
aa bc bd
ac bb ad
ab ab cd

→? $[Ma_2bcde]$ G.I. = 9 OA = 12 Total = 15

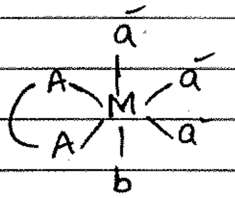
→ $(Mabcdef)$ G.I. = 15 OA = 30 Total = 30

→ $[Pt(en)(NH_3)_4]Cl_4$ $[M(AA)a_4]^{\pm}$

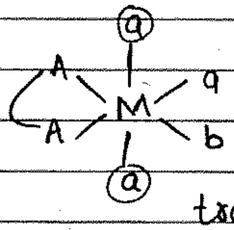


No G.I.
O.I.

→ $[Pt(en)(NH_3)_3Cl]Cl_3$ $M(AA)a_3b$



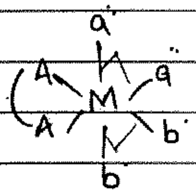
cis (90°)

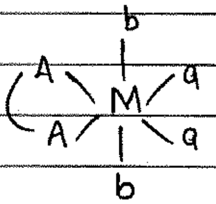


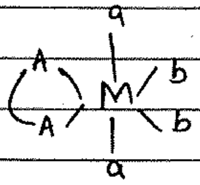
trans (180°), O.I.

$\underline{(Aa)\ (Aa)}\ (ab)$ = O.I.

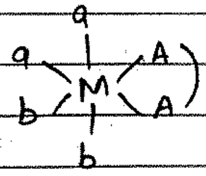
→ $[Pt(en)Cl_2Br_2]$ $[M(AA)\cancel{b_2}a_2b_2]$







(Ab) (Aa) (ab) (Aa)(Aa)(bb) (Ab)(Ab)(aa)
$\boxed{OA}$ cis O.I. trans O.I. trans



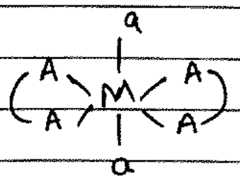
G.I. = 3 Total = 4
OA = 2

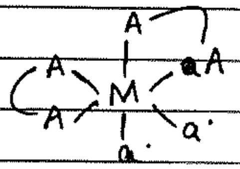
O I

OA

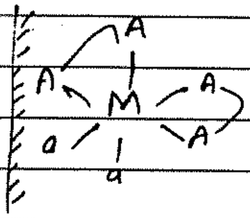
→ $[M(AA)abcd]$ G.I. = 6 OA = 12 Total = 12

→ $[Co(en)_2Cl_2]Cl$ $[M(AA)_2a_2]^{\pm}$





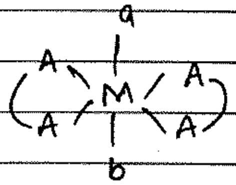
cis (90°)
2 AA rot@
180° ⇒ $\boxed{OA}$

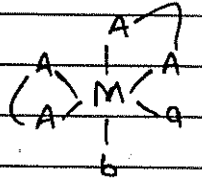


trans, optically inactive

G.I. = 2 OA = 2 Total = 3

→ $[Co(en)_2Cl\,Br]^+$ $M(AA)_2ab$



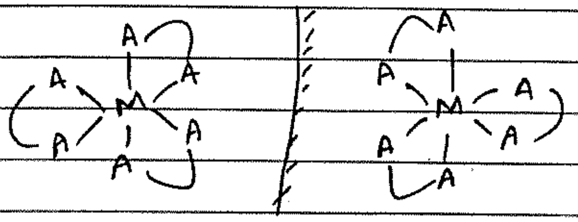


cis, $\boxed{OA}$

G.I. = 2 OA = 2 Total = 3

trans, O.I.

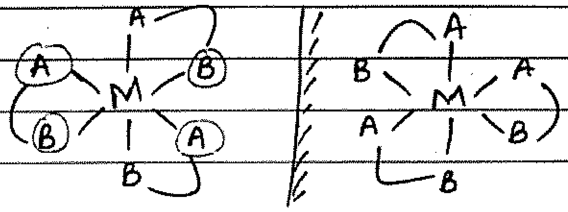
→ $K_3[Co(ox)_3]$ ~~Cl_3~~ $[M(AA)_3]$ No G.I. $\boxed{OA}$



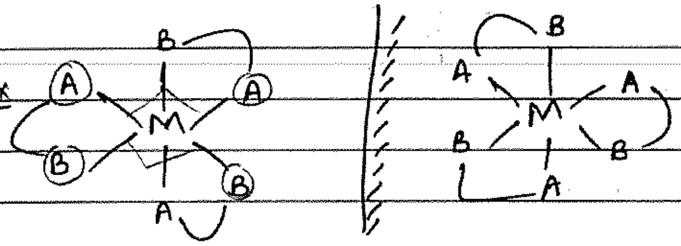
G.I. = 0
OA = 2
Total = 2.

→ $[Co(gly)_3]$ Inner Metallic Complex = Valency and CN both of CMA satisfied by ligands

$[M(AB)_3]$ where O.S. of CMA ≠ 0,
so, all rest neutral complexes.

- 

Trans $\boxed{OA}$



cis $\boxed{OA}$

G.I. = 2 $\boxed{OA}$ = 4 Total = 4

→ Tetrahedral complexes [Mabcd] and $[M(AB)_2]$ show optical isomerism.

→ Sq. planar complexes don't show optical isomerism

* APPLICATION OF COMPLEX COMPOUNDS :-

- TEST OF Ni^{2+} ⇒

Ni^{2+} + 2 dmg $\xrightarrow{NH_4OH}$ $[Ni^{\circ}(dmg)_2]$
salt
ROSY RED ppt

dsp^2, sq. planar, diamagnetic

- SEPARATION OF HYDROXIDE / OXIDE –

$$\underset{\text{Amphoteric}}{\overset{\text{Basic}}{Fe(OH)_3 \text{ ppt} + Al(OH)_3 \text{ ppt}}} \xrightarrow{NaOH \text{ sol}^n} Fe(OH)_3 \text{ insoluble (filter)} + Na^+[Al(OH)_4]^- \text{ OR}$$

$NaAlO_2 \cdot 2H_2O$
Sodium Aluminate

$$\downarrow \text{excess NaOH}$$

$Na_3[Al(OH)_6]$

- TEST OF Fe^{2+}, Fe^{3+}, Cu^{2+} –

→ $\underset{\text{salt}}{Fe^{2+}} \xrightarrow[\text{1-2 drop}]{K_3[\overset{+3}{Fe}(CN)_6]} Fe_3[Fe(CN)_6]$ dark blue ppt

Fe^{2+} $[Fe(CN)_6]^{3-}$ TURN BULL BLUE

$$\downarrow K_3[Fe(CN)_6]$$

$3\ \overset{+}{K}\overset{2+}{Fe}[Fe(CN)_6]^{3-}$ Blue Colloidal Sol^n

→ $\underset{\text{salt}}{Fe^{3+}} \xrightarrow[\text{1-2 drop}]{K_4[Fe(CN)_6]} Fe_4[Fe(CN)_6]$ dark blue ppt

PRUSSIAN BLUE

$$\downarrow K_4[Fe(CN)_6]$$

$4\ \overset{+}{K}\overset{+3}{Fe}[\overset{+2}{Fe}(CN)_6]^{-4}$ Blue Colloidal Sol^n

→ $KFe[Fe(CN)_6]$ w/o O.S. mentioning represents both Turn Bull Blue and Prussian Blue.

→ • $Cu^{2+} \xrightarrow{K_4[Fe(CN)_6]} Cu_2[Fe(CN)_6]$ chocolaty Brown ppt.
salt

- $K_4[Fe(CN)_6]$ gives CO gas when reacts with conc. H_2SO_4, but gives HCN when reacts with dil. H_2SO_4.

$$K_4[Fe(CN)_6] \xrightarrow{\text{conc. } H_2SO_4} K_2SO_4 + FeSO_4 + (NH_4)_2SO_4 + \underline{\underline{CO}}$$

$\downarrow$ dil. H_2SO_4

HCN

$\overset{\ominus}{C} \not\equiv N$ (bond break)

$\overset{+3}{=\textcircled{+2}}$ $\overset{-3}{\textcircled{-3}}$

$\overset{-}{C} \not\equiv \overset{+}{O}$

$\overset{+3}{\textcircled{+2}}$ $\overset{-3}{\textcircled{-2}}$

No redox

- **TEST OF S^{2-} –**

$$Na_2S + Na_2[Fe(CN)_5(\overset{+}{N}O)] \longrightarrow Na_4[Fe(CN)_5(NOS)]$$

Sodium Nitroprusside — Brown / Violet

$$\overset{2-}{S} + \overset{+}{N}O \longrightarrow NO\overset{-}{S}$$ = Thionitrito -N

- When excess amount of KCN is added to $CuSO_4$ solⁿ, then insoluble CuCN is formed which later turns into soluble complex.

$$CuSO_4\,(aq.) + 2KCN\,(aq.) \xrightarrow[K_2SO_4]{} Cu(CN)_2$$

salt — salt — doesn't exist

REDOX $\downarrow$ Cu^{+2} = OA (⊕ SRP)
CN^- = RA (pseudohalide)

$$\overset{+}{Cu}\overset{-}{CN} + \frac{1}{2}(CN)_2$$

$$\text{colorless soluble complex} \quad K_3[Cu(CN)_4] \xleftarrow[\text{(excess)}]{3\ KCN} CuCN$$

- CN^- acts both as complexing agent and reducing agent.
- AgCl or AgBr ppt. are soluble in NH_3 or NH_4OH (aq.). (But Not AgI)

$$AgCl \xrightarrow{2NH_3} [Ag(NH_3)_2]Cl$$ soluble complex.

- Undecomposed AgBr is removed from photographic film by using Hypo sol^n

$$AgBr \xrightarrow{h\nu} Ag + \frac{1}{2}Br_2$$

(negative)

$$AgBr + \underset{\text{Hypo } Sol^n}{2Na_2S_2O_3} \longrightarrow \underset{\text{soluble complex}}{Na_3[Ag(S_2O_3)_2]} + NaBr$$

- Light blue color of $CuSO_4$ sol^n turns into dark blue in presence of NH_3 or NH_4OH, but in presence of acid in above reaction, there's no color change.

$$\underset{\text{light blue}}{[Cu(H_2O)_4]SO_4} \xrightarrow[\text{stronger ligand (N-donor)}]{4NH_3} \underset{\text{dark blue}}{[Cu(NH_3)_4]SO_4} + [Cu(H_2O)_4]SO_4$$

conc. HCl ↓

$NH_3 + HCl \rightarrow NH_4Cl \Rightarrow NH_4^+ \neq$ ligand.

$[CuCl_4]^{2-} + [Cu(H_2O)_4]^{2+}$

yellow + blue = green. ($[CuCl_4]^{2-} \downarrow\downarrow$, as stability $\downarrow$)

- Oxalic acid is used to remove rusting spots of iron ($Fe_2O_3 \cdot xH_2O$) due to formation of soluble complex.

- $[Rh(PPh_3)_3Cl]$ Wilkinson's Catalyst is used in hydrogenation of alkene
- $[Ag(CN)_2]^-$ is used for electroplating of Ag
- $[EDTA]^{4-}$ is used for estimation and removal of hardness of water.

Ca^{2+} or Mg^{2+} ion + $EDTA^{4-} \longrightarrow [Ca(EDTA)]^{-2}$
not free ion.

- $[Ca(EDTA)]^{-2}$ is used to remove Pb poisoning.

$Pb^{2+} + [Ca(EDTA)]^{2-} \longrightarrow [Pb(EDTA)]^{2-} + Ca^{2+}$
pol. power ↑ $(18+2e^{\ominus})$, Z_{eff} ↑ (lanth.)
so more stable complex.

- BIOLOGICAL IMPORTANCE

→ Hb (Fe^{2+})
→ Myoglobin (Fe^{2+})
→ Vit. B_{12} (Co)
→ Plastocyanin (Cu)
→ Carboxy peptide (Zn)
→ Insulin (Zn)

* ORGANO METALLIC COMPOUND — Compounds in which C atom of hydrocarbon part is directly bonded with metal or metalloid

OMC	NOT OMC
$R-Mg-Cl$	$CH_3-COO^{\ominus}Na^{+}$
$CH_3-Zn-CH_3$ FRANKLAND'S REAGENT	$C_6H_5-O^{\ominus}Na^{\oplus}$
$R-Cd-R$	$CaCO_3$ (ionic)
$(CH_3)_3-As$	$NaCN$ (-"-)
$(R_2SiO)_n$	CaC_2 (-"-)
* $[Ni(CO)_4]$	$Ti-(OC_6H_5)_4$
$CH_3-Ti-(OC_6H_5)_3$	

- Types of OMC ⇒

1. σ bonded :- Only σ bond b/w metal and carbon.

$(C_2H_4)_4-Pb$ Tetraethyl Lead (TEL)
Used as :- Antiknocking agent

$TiCl_4 + (CH_3)_3-Al$ Ziegglar Natta Catalyst
Used :- in polymerisation of alkene.

2. π bonded :- Presence of π donor and π acceptor ligand.

$[Cr(\pi-C_6H_6)_2]$, $[Fe(\pi-C_5H_5)_2]$, $K[PtCl_3(\eta^2-C_2H_4)]$

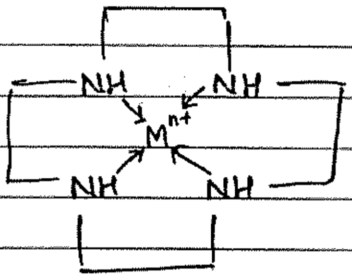
Cromocene Ferrocene Zeisel's Salt

3. **σ and π bonded :-** Synergic bonding with lp donor ligand. (Metal Carbonyl)

$[Ni(CO)_4]$, $[Fe(CO)_5]$, $[Cr(CO)_6]$

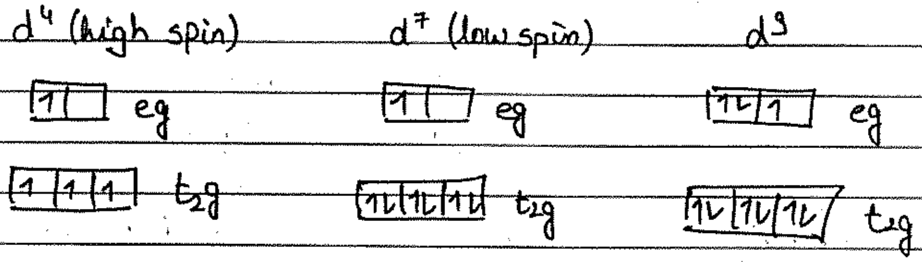
* **MACROCYCLIC LIGAND :-**

Ligand already in cyclic form. So, no. of chelate ring = denticity.
Also, these complexes are more stable, as no. of chelate rings ↑.

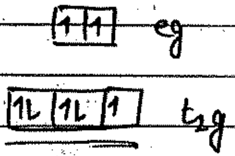


* **JOHN-TELLER EFFECT ⇒**

Distortion in octahedral geometry due to asymmetric $e^{\ominus}$ cloud in eg set of orbitals



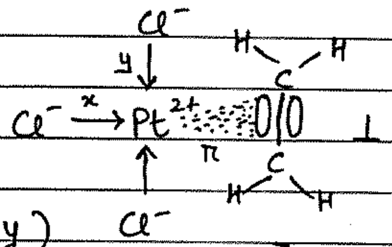
• **Weak John Teller Effect :-**



* **TRANS EFFECT ⇒**

$K[PtCl_3(\eta^2-C_2H_4)]$ $Pt^{+2} = 5d^8 \xrightarrow{CN=4} dsp^2$

sq. planar, dia.



No. of σ bonds = 8

Due to repulsion b/w H and ligand @ trans (180°) position, latter's BL ↑.

$(x > y)$

BL

$C \overset{z}{-} C$ $H_2C \overset{w}{=} CH_2$ $z > w$ (v. lil.)

- Strength order for ligands for trans effect

$F^-, OH^-, H_2O < NH_3 < py < Cl^- < Br^- < I^- < NO_2^- < CN^-, CO, C_2H_4$

classmate

Date ____________

Page ____________

d & f - blocks

★ **$KMnO_4$** :- POTASSIUM PERMAGNATE

• **METHOD OF PREPARATION** -

1. **INDUSTRIAL** :-

$$\underset{\text{PYROLUSITE}}{\overset{\text{Amphoteric}}{\overset{+4}{MnO_2}}} + KOH + \underset{\text{or } K_2CO_3 \ (OA)}{O_2} \xrightarrow[\Delta]{\text{OR } KNO_3 \ (OA)} \overset{+6}{K_2MnO_4} \text{ (green)}$$

potassium magnate

Cl_2 (OA) (OR) $H^+ \downarrow$ or $CO_2(g)$

$\overset{+7}{KMnO_4}$

$$\overset{+6}{MnO_4^{2-}} \xrightarrow{H^+} \overset{+7}{\underset{}{MnO_4^-}} + \overset{+4}{MnO_2} \text{ (disproportionation)}$$

(inert config.)

2. **LAB.** :- $\underset{(RA)}{Mn^{2+}} + \underset{(OA;\ peroxy)}{S_2O_8^{2-}} \longrightarrow \overset{+7}{MnO_4^-} + SO_4^{2-}$ (redox)

Q. $MnO_4^{2-} + H_2O \rightleftharpoons \underset{(O.A.)}{MnO_4^-} + OH^-$

Which of these reagents is used to increase production of MnO_4^- ?

a) KOH
$[OH^-]\uparrow\uparrow$ X

b) dil. HCl
R.A ⇒ Mn^{2+} X

c) SO_2
R.A. ⇒ Mn^{2+} X

✓d) CO_2 (g)
Acidic, not RA

→ Acidified $KMnO_4$ acts as strong O.A. and itself reduces to Mn^{2+}.

Q. $KMnO_4$ is acidified by :-

a) conc. $H_2SO_4 \xrightarrow{KMnO_4} 2\ HMnO_4 \xrightarrow[-2H_2O]{} Mn_2O_7$ (explosive)

✓b) dil. H_2SO_4 Not OA / RA, only an acid.

c) dil. HCl Acts as R.A. $\overset{+7}{KMnO_4} \longrightarrow Mn^{2+}$

d) conc. HNO_3 acts as O.A. itself [illegible]

OXIDISING NATURE →

Acidified $KMnO_4$ (purple)

H_2S	S
SO_2	SO_4^{2-}
NO_2^-	~~SO~~ NO_3^-
SO_3^{2-}	SO_4^{2-}
Fe^{2+}	Fe^{3+}
$Cl^-/Br^-/I^-$	$Cl_2/Br_2/I_2$
$HCOOH$	$H_2O + CO_2$
$H_2C_2O_4$	$H_2O + 2CO_2$
* $S_2O_3^{2-}$ Thiosulphate	$S_2O_6^{2-}$ Thionate

↓

Mn^{2+} or $MnSO_4$
(colorless)

→ $MnSO_4$ acts as auto catalyst; increases rate of reaction of which it is a product itself.

→ $KMnO_4$ acts as self-~~[illegible]~~ indicator for $KMnO_4$ v/s $H_2C_2O_4$ (oxalic acid) titration.

→ Neutral / weakly alkaline $KMnO_4$ also act as O.A.

- Neutral / Weak alkaline $KMnO_4$

I^-	IO_3^- ($I_2 \xrightarrow{OH^-} I^- + IO_3^-$)
* $S_2O_3^{-2}$	SO_4^{2-}
Mn^{2+}	Mn^{4+}

↓

MnO_2 (black solid)

→ K_2MnO_4 is paramagnetic, but $KMnO_4$ is diamagnetic.

→ $KMnO_4$ shows temperature dependent paramagnetism. (Band Theory; MOT for polyatomic species)

* $K_2Cr_2O_7$:- POTASSIUM DICHROMATE

- PREPARATION :-

$$\underset{\text{CHROMITE}}{FeO\cdot \overset{+3}{Cr_2}\overset{\text{amphoteric}}{O_3}} + \underset{\text{or } Na_2CO_3}{NaOH} + O_2 \xrightarrow{\Delta} \underset{\text{Sodium Chromate}}{Na_2\overset{+6}{Cr}O_4} \text{ (yellow)}$$

↓ dil. H_2SO_4

$\underset{\text{Sodium Dichromate}}{Na_2\overset{+6}{Cr_2}O_7} + Na_2SO_4$

Easy separation by crystallisation, as there's a major diff. in solubility as compared to ~~Na_2CrO_4~~ Na_2SO_4

↓ 2 KCl

$K_2Cr_2O_7$

$$\underset{\text{(yellow)}}{CrO_4^{2-}} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} \underset{\text{(orange)}}{Cr_2O_7^{2-}}$$

→ ~~$Na_2Cr_2O_7$ is more soluble in water than $K_2Cr_2O_7$~~

→ $K_2Cr_2O_7$ is used as standard solution in volumetric analysis, but $Na_2Cr_2O_7$ is not used, due to its hygroscopic nature.

– Standard Solⁿ – solⁿ of known concⁿ, acc. to which concⁿ of unknown solⁿ is checked in titration / volumetric analysis.

- OXIDISING NATURE –

Acidified $K_2Cr_2O_7$ (orange)

H_2S	S
SO_2	SO_4^{2-}
NO_2^-	NO_3^-
SO_3^{2-}	SO_4^{2-}
Fe^{2+}	Fe^{3+}
Sn^{2+}	Sn^{4+}
$HCl / Br^- / I^-$	$Cl_2 / Br_2 / I_2$
$HCOOH$	$H_2O + CO_2$
* C_2H_5-OH DRUNKEN DRIVER TEST	$CH_3-CHO \longrightarrow CH_3COOH$

Cr^{3+} or $Cr_2(SO_4)_3$ (green)

- CHROMYL CHLORIDE TEST ⇒

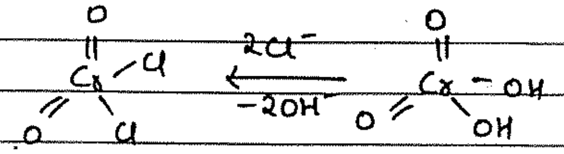
→ Test of only ionic chlorides

→ Not applicable for $AgCl$, Hg_2Cl_2, $HgCl_2$, $SnCl_2$, $PbCl_2$, $PbCl_4$, $AsCl_3$, etc. as they all are covalent chlorides

→ $Na^+Cl^- + K_2Cr_2O_7 + \text{conc. } H_2SO_4 \longrightarrow CrO_2Cl_2$ (Chromyl Chloride)
(red-orange vapor)
↓ NaOH solⁿ

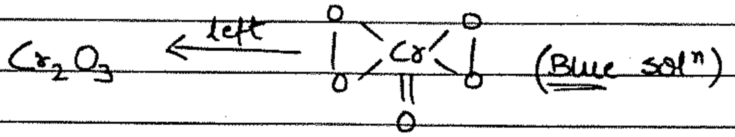
$PbCrO_4 \downarrow \xleftarrow{(CH_3-COO)_2Pb} Na_2CrO_4$ (aq.) (yellow)
(yellow)

$K_2Cr_2O_7 + \text{conc. } H_2SO_4 \longrightarrow H_2Cr_2O_7 \longrightarrow 2CrO_3 + H_2O$
↓
H_2CrO_4

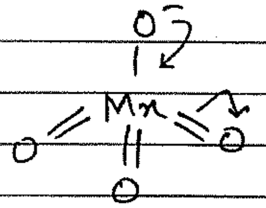


Q. Product formed when acidified $K_2Cr_2O_7$ reacts with H_2O_2 solⁿ

a) $Cr_2(SO_4)_3$ b) CrO_3 ✓ c) CrO_5 d) CrO

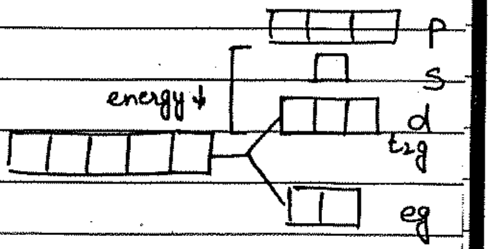


• MnO_4^- ⇒ tetrahedral; d^3s ($s + d_{xy} + d_{yz} + d_{xz}$)
All B.L. identical

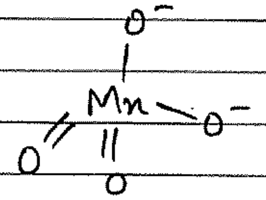


B.O. = ~~6~~ $\frac{7}{4}$

F.C. = $\frac{1}{4}$

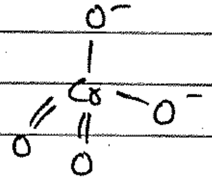


- MnO_4^{2-} Tetrahedral, d^3s, all B.L. identical



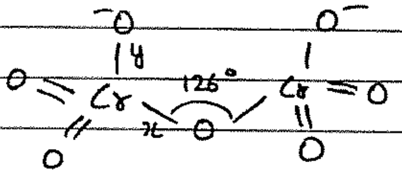
$B.O. = \frac{6}{4}$ $F.C. = \frac{2}{4}$

- CrO_4^{2-} Tetrahedral, d^3s, all B.L. identical



$B.O. = \frac{6}{4}$ $F.C. = \frac{2}{4}$

- $Cr_2O_7^{2-}$ Tetrahedral, d^3s, $x > y$ (B.L.)



Max. identical bonds = 6

- CATALYTIC PROPERTIES :-

d block metals, or their compounds are used as catalysts in many reactions due to:

a) possibility of variable O.S.

b) high adsorption power / presence of free valencies on surface.

→ $SO_2 + \frac{1}{2} O_2 \xrightleftharpoons{V_2O_5} SO_3$ Ea ↑ (w/o V_2O_5)

$$\left.\begin{array}{l} SO_2 + V_2O_5 \longrightarrow SO_3 + V_2O_4 \\ V_2O_4 + \frac{1}{2}O_2 \longrightarrow V_2O_5 \end{array}\right] \text{Ea} \downarrow$$

→ $2I^- + S_2O_8^{2-} \xrightarrow{Fe^{3+}} I_2 + 2\,SO_4^{2-}$ Ea ↑ (w/o Fe^{3+})
(RA) (OA)

$Fe^{3+} + 2I^- \longrightarrow Fe^{2+} + I_2$ O.A. R.A. $Fe^{2+} + S_2O_8^{2-} \longrightarrow Fe^{3+} + 2\,SO_4^{2-}$ (R.A.) (O.A.; peroxy.)	Ea ↓

→ $H_2C=CH_2 + H_2 \xrightarrow[\text{adsorbs } H_2]{Ni \downarrow} H_3C-CH_3$
so KE ↓↓, effective collision ↑↑.

→ Pt / PtO = Adam's Catalyst

$FeSO_4 + H_2O_2$ = Fenton's Reagent

* INTERSTITIAL COMPOUNDS :-

Smaller atoms like H, B, C, N, etc. are packed into crystal structure of ~~compounds~~ metals, called interstitial compounds.

e.g. Fe_3C, Cementite, Fe_3H, WC, $TiH_{1.7}$, etc.

- PROPERTIES :-

1. Non stoichiometric compounds.
2. Neither ionic nor covalent
3. Harder than pure metal

4. Higher MP than pure metal
5. Almost chemically inert.
6. Retain metallic conductivity
7. Malleability and ductility decrease.

- SPIN MAGNETIC MOMENT OF BIVALENT CATIONS OF 3d

Ti^{2+}	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$	$3d^{10}$

$\longrightarrow|$ spin mag. moment ↑ $\longrightarrow$ spin mag. moment ↓

→ spin mag. moment ⇒ $d^n = d^{10-n}$

- SPIN MAGNETIC MOMENT OF TRIVALENT LANTHANOIDS

Ce^{3+}	Pr^{3+}	Nd^{3+}	Pm^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}
$4f^1$	$4f^2$	$4f^3$	$4f^4$	$4f^5$	$4f^6$	$4f^7$	$4f^8$	$4f^9$	$4f^{10}$	$4f^{11}$	$4f^{12}$	$4f^{13}$	$4f^{14}$

$\longrightarrow|$ spin mag moment ↑ $\longrightarrow$ spin mag. moment ↓

→ Max. spin mag moment = Gd^{3+}
Only trivalent dia. lanthanoid = Lu^{3+}

→ spin mag. moment ⇒ $f^n = f^{14-n}$

Q. Which of these has max. magnetic moment :-

a) Gd → $4f^7\ 5d^1\ 6s^2$ ⇒ 8 unpaired ⇒ Max. spin mag moment
b) Tb
c) Eu
✓d) Nd

Mag. moment $\rightarrow$ spin, orbital

Mag. moment = $\sqrt{4s(s+1) + l(l+1)}$
s = sum of spin Q.N., l = sum of azimuthal Q.N.

Q. Which of these is diamagnetic ?

a) NO_2
b) ClO_2 } = odd $e^{\ominus}$ species.
c) KO_2
✓d) Na_2O_2 $O_2^{2-} = 18\ e^{\ominus}$ = dia.

* **MERCURY CHLORIDE & NH_3 rxn. ⇒**

$$\underset{\boxed{\text{CALOMEL}}}{Hg_2Cl_2} + NH_4OH \longrightarrow \underbrace{Hg + Hg<^{NH_2}_{Cl}}_{\text{Black ppt.}} + NH_4Cl + H_2O$$

$$HgCl_2 + NH_4OH \longrightarrow \underbrace{Hg<^{NH_2}_{Cl}}_{\text{white ppt.}} + NH_4Cl + H_2O$$

* **DENSITY** :- $\rho = \frac{m}{V}$

1. $3d < 4d << 5d$

2. $Sc \leq \leq \leq \leq Ni \simeq Cu \geq Zn$

3. $Li < K < Na < Rb < Cs$ $K < Na$ ⇒ K → 3d vacant; vol. ↑
   $Ca < Mg < Be < Sr < Ba$.
   ↳ extremely small size.

- Max. ρ of metals :- $Ir \geq Os$

* **ALLOYS** :-

Homogeneous mixture of 2 or more metals

- **CONDITIONS** ⇒ ① comparable size

→ Fe, Co, Ni don't form amalgam (alloy of Hg)

- **MISCH METAL** ⇒ Alloy of lanthanoid (mainly Ce) with Fe

95% lanth. + 5% Fe
mainly Ce

- **WHITE MECAL** ⇒ Li + Pb

- **SOME IMP. ALLOYS** ⇒

① BRONZE = Cu (75-90%) + Sn

② BRASS = Cu (60-80%) + Zn

③ GUN METAL = (Cu + Zn + Sn) (87 : 3 : 10)

④ GERMAN SILVER = (Cu + Zn + Ni) (2 : 1 : 1)

⑤ NICHROME = Ni + Cr + Fe

⑥ STEEL ⇒ CHROMIUM STEEL - Cr (2-4%)
NICKEL STEEL - Ni (3-5%)
STAINLESS STEEL - Cr (12-14%) + Ni (2-4%)
INVAR - Ni (36%)

s forms oxide layer and protects iron.

* COMPARISON B/W LANTHANOID & ACTINOID ⇒

- SAME IN BOTH :-

1. Both show dominant O.S. = +3

2. Both are electropositive, act as R.A.

3. Cations with unpaired $e^{\ominus}$ in both are paramagnetic.

4. Most of them are colored

5. Both show a steady decrease in ionic radius along L → R. So, lanthanoides show La contraction and Actinoids show Ac contraction.

- DIFFERENCE

	LANTHANOID	ACTINOID
1.	Besides common O.S. +3, these show +2 and +4 also in certain elements.	Besides common O.S. +3, these show +4, +5, +6 also in certain elements.
2.	Have less tendency towards complex formation.	Have high tendency for complex formation
3.	Except Pr, all are non radio.	All actinoids are radio.
4.	Oxides and hydroxides are less basic	Oxides and hydroxides are more basic

METALLURGY

* **MINERAL** :-

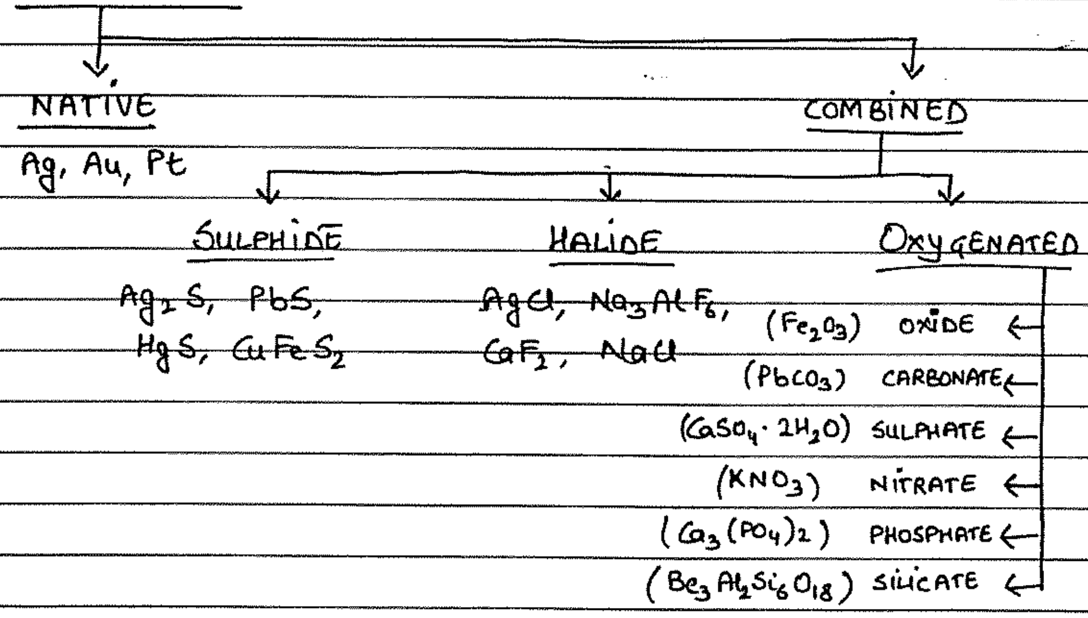
Metal compounds which are obtained fm. earth's crust by mining

* **ORE** :-

Minerals fm. which metal can be extracted easily and profitably.

- ABUNDANCE IN CRUST :- O > Si > Al > Fe.

- CLASSIFICATION :-



NATIVE

Ag, Au, Pt

COMBINED

SULPHIDE

Ag_2S, PbS, HgS, $CuFeS_2$

HALIDE

AgCl, Na_3AlF_6, CaF_2, NaCl

OXYGENATED

(Fe_2O_3) OXIDE
($PbCO_3$) CARBONATE
($CaSO_4 \cdot 2H_2O$) SULPHATE
(KNO_3) NITRATE
($Ca_3(PO_4)_2$) PHOSPHATE
($Be_3Al_2Si_6O_{18}$) SILICATE

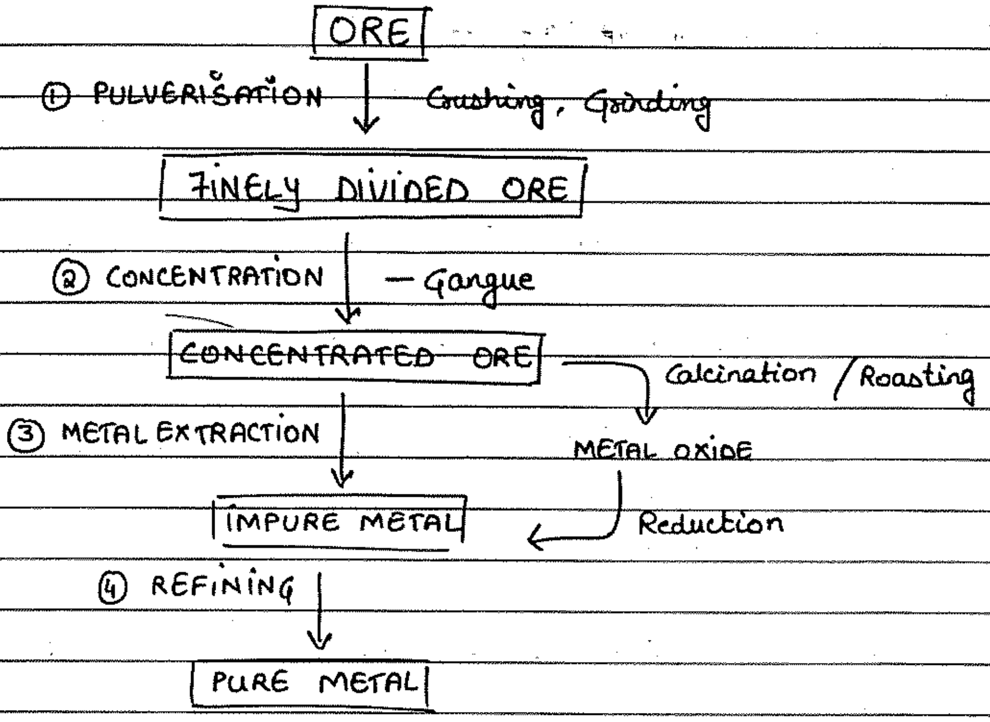
* **METALLURGICAL PROCESS** :-

Extraction of pure metal fm. ore.

APPENDIX

LIST OF ORES AND THEIR NAMES

TYPES OF ORES	S.N.	FORMULA OF THE ORE	NAME
Oxide Ore	1.	ZnO (Philosopher's Wool)	Zincite
	2.	MnO_2	Pyrolusite
	3.	SnO_2	Cassiterite (Tin stone)
	4.	Cu_2O	Cuprite (Ruby Copper)
	5.	Fe_2O_3	Haematite
	6.	$Al_2O_3.2H_2O$	Bauxite
	7.	$FeO.Cr_2O_3$	Chromite
	8.	Fe_3O_4	Magnetite
	9.	$Fe_2O_3.3H_2O$	Limonite
	10.	TiO_2	Illumanite
Sulphide Ore	1.	ZnS	Zinc Blende (Sphalerite)
	2.	HgS	Cinnabar
	3.	PbS	Galena
	4.	Ag_2S	Argentite or Silver glance
	5.	FeS_2	Iron pyrites (Fool's gold)
	6.	$CuFeS_2$, $CuS.FeS$	Copper pyrites (Chalcopyrities)
	7.	$Cu_2S.Ag_2S$	Copper silver glance
	8.	$Ag_2S.Sb_2S_3$	Pyrargirite (Ruby silver)
	9.	Cu_2S (Copper glance)	Chalcocite
Halide Ore	1.	$NaCl$	Rock Salt
	2.	$AgCl$	Horn Silver
	3.	CaF_2	Flourspar
	4.	$AlF_3.3NaF$	Cryolite
	5.	$KCl.MgCl_2.6H_2O$	Carnelite
Carbonate Ore	1.	$MgCO_3$	Magnesite
	2.	$CaCO_3$	Lime stone
	3.	$MgCO_3.CaCO_3$	Dolomite
	4.	$ZnCO_3$ (Smithosonite)	Calamine
	5.	$PbCO_3$	Cerrusite
	6.	$FeCO_3$	Siderite
	7.	$CuCO_3.Cu(OH)_2$	Malachite
	8.	$2CuCO_3.Cu(OH)_2$	Azurite
Sulphate Ore	1.	$CaSO_4.2H_2O$	Gypsum
	2.	$MgSO_4.7H_2O$	Epsomite Or Epsom salt
	3.	$K_2SO_4.Al_2(SO_4)_3.24H_2O$	Alum
Nitrate Ore	1.	$NaNO_3$	Chile- Salt Peter
	2.	KNO_3	Salt peter or Indian salt peter
Phosphate Ore	1.	$Ca_3(PO_4)_2$	Rock Phosphate



- Types :-

1. Pyro Metallurgy – Extraction of metal fm. ore by using Δ.
   Applicable for Cu, Zn, Sn, Pb, Fe, etc.

2. Electro Metallurgy – Extraction of metal fm. ore by using $e^{\ominus}$.
   Applicable for s-block metals and Al.
   (strong R.A.)

3. Hydro Metallurgy – Extraction of metal fm. ore by using H_2O as solvent.
   Applicable for Ag, Au and low grade ore of Cu.

$$\underset{\text{MALACHITE}}{CuCO_3 \cdot Cu(OH)_2} \xrightarrow{\text{dil. } H_2SO_4} CuSO_4\,(aq) \xrightarrow[\cancel{\text{faster}}]{\cancel{Zn}} ZnSO_4\,(aq) + Cu$$

✓ $\downarrow$ Fe slower

$$FeSO_4\,(aq) + Cu$$

- CONCENTRATION OF ORE – Separation of gangue /matrix frm. ore particles

1. GRAVITY SEPARATION / LEVITATION / HYDRAULIC WASHING –

→ Applicable for carbonate and oxide ores.

→ Based on density difference of ore and gangue particles

2. MAGNETIC SEPARATION –

→ Based on difference in magnetic properties of ore and gangue particles

→ Applicable for a) $FeO \cdot Cr_2O_3$ + silica
Chromite

b) SnO_2 + $[FeWO_4 + MnWO_4]$
Cassiterite / Tin Stone   Wolframite (magnetic)

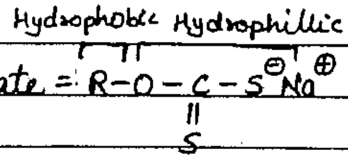
3. FROTH FLOATATION – (Metal sulphides insoluble in water)
(polar)

→ Applicable for sulphide ores

→ Sulphide ore particles are easily wetted by pine oil but gangue particles are easily wetted by water.

→ FROTHER : Pine oil or eucalyptus oil or mustard oil

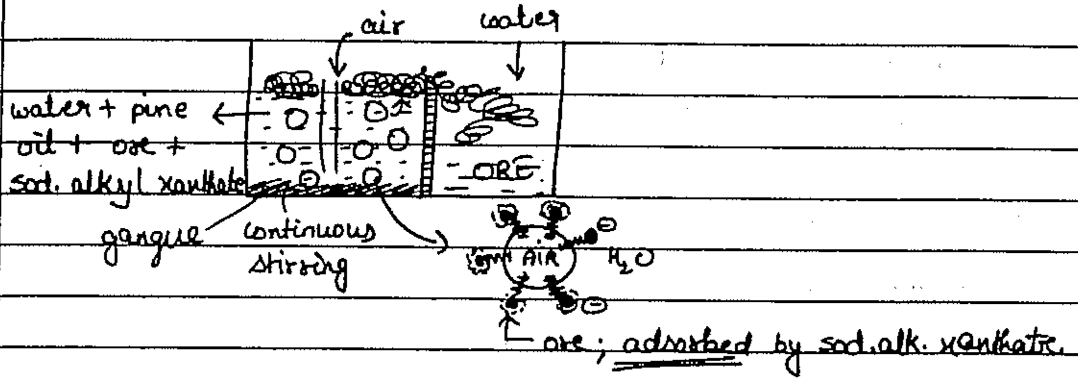
→ FLOATING AGENT : Sodium Alkyl Xanthate =



$R-O-\underset{\underset{S}{\|}}{C}-S^{\ominus}Na^{\oplus}$

→ Cresol or aniline are used to stabilise froth.

→



→ DEPRESSANT & ACTIVATOR – Used for separation of different sulphide ores.

$ZnS + PbS$
Zinc Blende Galena
NaCN ↓ → depressant; decreases floating property.

$Na_2[Zn(CN)_4]$ soluble complex

$\boxed{PbS}$ → froth

(~~Fool's Gold~~)
$ZnS + FeS_2$
Zinc Blende Iron Pyrite
$CuSO_4$ ↓ → activator; increases floating property

ZnS ore coated with CuS → froth

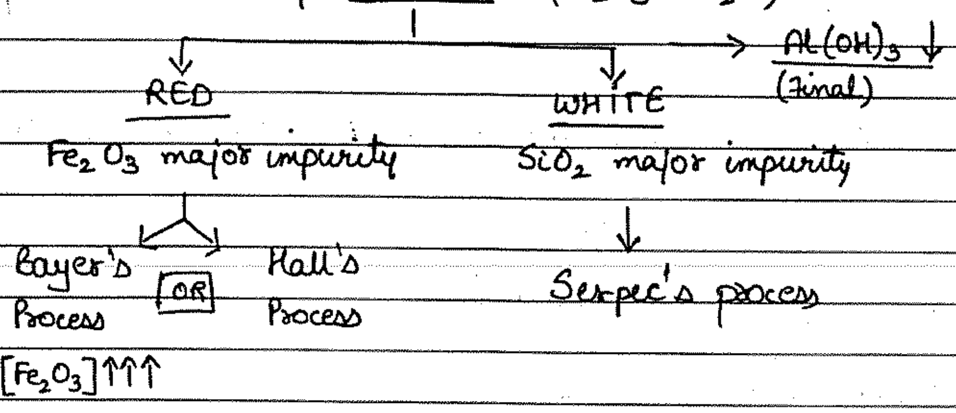
FeS_2 (no rxn)

solubility : $CuS < ZnS$ ← ZnS ore coated with CuS
CuS insoluble

4. CHEMICAL METHOD (LEACHING) –

→ Applicable for Ag, Au, Al.

Ⓠ) Concentration of Bauxite ($Al_2O_3 \cdot 2H_2O$)



BAYER'S PROCESS –

$$\underset{\text{amphoteric}}{Al_2O_3 \cdot 2H_2O} + \underset{\text{impurity}}{\overset{\text{basic}}{Fe_2O_3}} \xrightarrow{NaOH(aq)} Fe_2O_3 \text{ (insolube)} + NaAlO_2 \cdot 2H_2O$$

$$Na[Al(OH)_4] \text{ (soluble)}$$

$\curvearrowright CO_2(g)$ + excess H_2O (to neutralise NaOH)

$$\underset{\text{soluble}}{NaOH} + \underset{\text{insoluble (in } H_2O)}{Al(OH)_3 \downarrow}$$

$$NaOH \xrightarrow{CO_2(g)} Na_2CO_3$$

HALL'S PROCESS ⇒ Na_2CO_3 is used in place of NaOH

SERPEC'S PROCESS

$$Al_2O_3 \cdot 2H_2O + SiO_2 \xrightarrow[\substack{1800^\circ C \\ -CO\uparrow \\ -Si\uparrow}]{C + N_2} AlN \xrightarrow{3\ HOH} \underset{\text{(insoluble)}}{\downarrow Al(OH)_3} + NH_3$$

NH_3 → useful by product

b) Mac-Arthur Forest process / Extraction of Ag / Cyanide process / Complex Formation method / Metal displacement method / Hydrometallurgy / Leaching.

Ag_2S + impurity + $4\ NaCN_{(aq)}$ $\xrightleftharpoons{O_2}$ $\overset{+}{Na}[Ag(CN)_2]$ + Na_2S

SILVER GLASS ↳ insoluble soluble complex

$Na_2S \xrightarrow{O_2} Na_2SO_4$

$\downarrow Zn$

$Na_2[Zn(CN)_4]$ + $2\ Ag$

soluble

O_2 ⇒ makes rxn. irreversible

c) Extraction of Au –

Au + impurity + $4\ NaCN\ (aq)$ $\xrightarrow{O_2}$ $2\ Na[Au(CN)_2] + NaOH$

$\downarrow Zn$

$Na_2[Zn(CN)_4]$ + $2\ Au$

O_2 helps oxidise Au

- CALCINATION ⇒

→ Concentrated ore is heated below its fusion temperature in reverberatory furnace in absence of air.

→ Applicable for carbonates, hydroxides, ~~ox~~ oxides ore.

→ Impurities of P, S, As, etc. are removed as elemental vapour.

→ Ore becomes porous, anhydrous and S.A. ↑.

* Metal Sulphide $\xrightarrow[\Delta]{O_2}$ Metal oxide + $SO_2 \uparrow$
Metal Sulphide $\xrightarrow[\text{low temp.}]{O_2}$ Metal sulphate

→ $ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2 \uparrow$
Calamine

→ $PbCO_3 \xrightarrow{\Delta} PbO + CO_2 \uparrow$
Cerrusite

→ $MgCO_3 \cdot CaCO_3 \xrightarrow{\Delta} MgO + CaO + 2CO_2 \uparrow$
Dolomite

→ $Fe_2O_3 \cdot 3H_2O \xrightarrow{\Delta} Fe_2O_3 + 3H_2O \uparrow$
Limonite — anhydrous

→ $2Al(OH)_3 \xrightarrow[1100^\circ C]{} Al_2O_3 + 3H_2O \uparrow$
Alumina

- ROASTING –

1. Concentrated ore is heated below its fusion temperature in reverberatory furnace in presence of air.

2. Mainly applicable for sulphide ores which are converted to metal oxides

→ $ZnS \xrightarrow[\Delta]{O_2} ZnO + SO_2 \uparrow$
Zinc Blende
$ZnS + O_2 \longrightarrow ZnSO_4$ parallel rxn. (↓↓)

→ $PbS + O_2 \xrightarrow{\Delta} PbO + SO_2 \uparrow$
Galena
$PbS + O_2 \longrightarrow PbSO_4$ (minor)

Partial roasting in Cu metallurgy.

$$2\,CuFeS_2 + O_2 \xrightarrow{\Delta} \underbrace{Cu_2S + 2\,FeS}\ + SO_2\uparrow$$

Copper Pyrites
$[Cu_2S + FeS + FeS_2]$

$$\downarrow O_2$$

$$\underbrace{Cu_2O + FeO}_{\text{minor}} + SO_2\uparrow$$

Final $\rightarrow \underbrace{Cu_2S + FeS}_{\text{major}} + Cu_2O + FeO$

4. Roasting in Fe metallurgy → to prevent wastage of iron as slag, in reduction step.

$\overset{\text{ORE}}{Fe_2O_3} + \overset{\text{minor}}{FeO}$
Haematite

$$2\,FeO + \frac{1}{2}O_2 \xrightarrow[\Delta]{\text{limited supply of } O_2} Fe_2O_3 \longrightarrow \text{doesn't form slag with } SiO_2$$

High L.E.

otherwise in reduction, $FeO + \underset{\text{imp.}}{SiO_2} \longrightarrow FeSiO_3$ (slag)
ρ↓; Bahar; waste

5. Thermal Reduction

$$\underset{\text{Silver Glass}}{Ag_2S} + O_2 \xrightarrow[SO_2]{\Delta} Ag_2O \xrightarrow{300^\circ C} 2Ag + \frac{1}{2}O_2$$

$$\underset{\text{Cinnabar}}{HgS} + O_2 \xrightarrow[-SO_2]{\Delta} HgO \xrightarrow{400^\circ C} Hg + \frac{1}{2}O_2$$

6. In Sn metallurgy, some insoluble sulphide impurities are removed as soluble sulphates.

- $$\left.\begin{array}{l}SnO_2\\ +\ CuS\\ +\ FeS\end{array}\right. \xrightarrow[\text{low temp}]{O_2} \left.\begin{array}{l}SnO_2\\ +\ CuSO_4\\ +\ FeSO_4\end{array}\right]\begin{array}{l}\longrightarrow \text{insoluble.}\\ \xrightarrow{\text{hot water}} \text{soluble}\end{array}$$

7 Impurities of P, S, As, etc. are removed as volatile oxides

8\. Ore becomes porous, anhydrous and S.A. ↑.

- REDUCTION :-

1\. SMELTING / C Reduction —

$$MO + imp. + \underset{\swarrow\ \searrow}{Coke}\ \ + Flux \xrightarrow[\text{air, }\Delta\uparrow]{\text{Blast furnace}} Metal\ (l) + slag$$

fuel RA

a) $$MO + C \xrightarrow{\Delta} M + CO\uparrow$$

$$ZnO + C \xrightarrow{\Delta} Zn + CO\uparrow$$

$$SnO_2 + 2C \xrightarrow{\Delta} Sn + 2CO\uparrow$$

$$PbO + C \xrightarrow{\Delta} Pb + CO\uparrow$$

$$PbO + CO \longrightarrow Pb + CO_2\uparrow \text{ (minor)}$$

$$Fe_2O_3 + 3C \xrightarrow{\Delta} 2Fe + 3CO\uparrow \text{ (minor)}$$

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2\uparrow$$

b) imp + flux → slag → low MP
→ lighter than metal
→ prevents further oxidation of metal

Basic imp. + Acidic flux → Salt (slag)
Acidic imp. + Basic flux → Salt (slag)

→ iron metallurgy → main R.A = CO, otherwise C.

→ Borax, though has basic solⁿ, is an example of acidic flux, cuz due to pyrolysis, B_2O_3 (NMO → Acidic) forms.

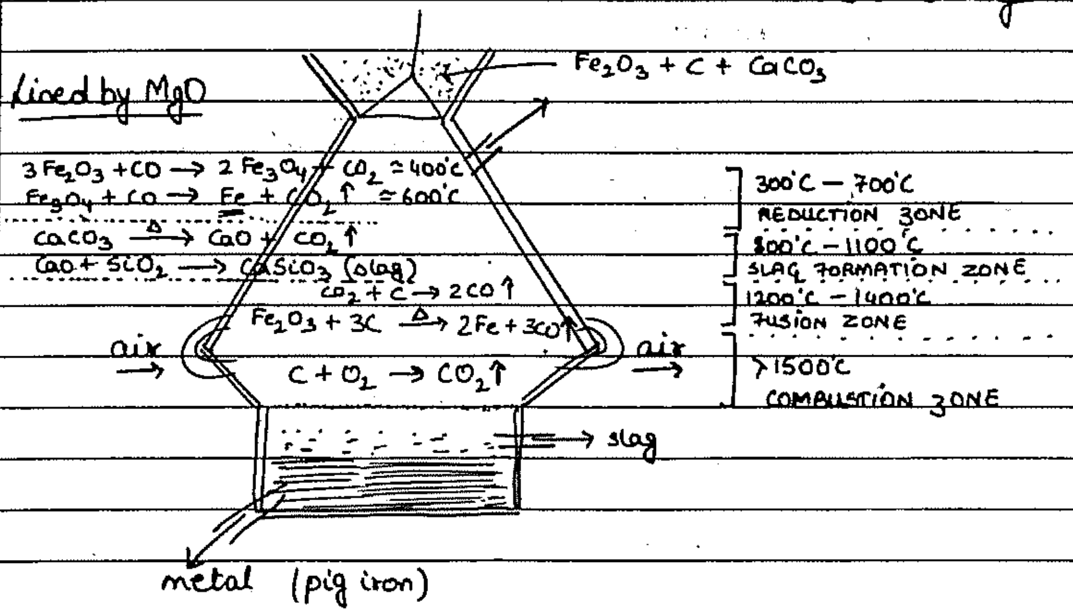
→ Fe metallurgy — Main imp = SiO_2, P_4O_{10}

$CaCO_3 \xrightarrow{\Delta} \underset{\text{(Basic)}}{CaO} + CO_2\uparrow$

$\underset{\text{Basic FLUX}}{CaO} + SiO_2 \longrightarrow CaSiO_3$ slag

$CaO + P_4O_{10} \longrightarrow Ca_3(PO_4)_2$ slag

Thomas Slag — used in cement ind, roads making



→ Smelting in Cu metallurgy

$Cu_2S + FeS + \underset{\substack{\Downarrow \\ \text{only fuel} \\ \text{NOT RA}}}{Coke} + \underset{\text{flux}}{SiO_2} \xrightarrow{\text{smelting}} \underbrace{Cu_2S + FeS}_{\text{COPPER METTE}} + \underset{\text{slag}}{FeSiO_3}$
$+ Cu_2O + FeO$

~~impurity~~

$MS + C \longrightarrow M + CS_2$ $\Delta G = \oplus$, so roasting done for $MS \rightarrow MO$; then C redⁿ ✓.

- Oxides Cu_2O + FeO aren't C reduced, as C is R.A. @ high temp, before which

$$Cu_2O + FeS \longrightarrow Cu_2S + FeO$$

Now, $FeO + SiO_2 \longrightarrow FeSiO_3$ (slag)

So, only sulphides remain

2. SELF REDUCTION ⇒ Applicable for Cu, Pb, ~~Ag~~, Hg

$\underset{\text{Galena}}{PbS} \longrightarrow \underset{\text{floatation}}{\text{froth}} \longrightarrow$ Roasting $PbS + O_2 \longrightarrow \underset{\downarrow\ \text{C reduction}}{PbO} + SO_2\uparrow$

Or In roasting, close O_2 supply after some time and increase Temp.

$$PbS + 2PbO \longrightarrow \underline{\underline{3Pb}} + \cancel{2}\,SO_2\uparrow$$

⇒ Cu Metallurgy = Bessemerisation

more reactive

$$Cu_2S + FeS + \underset{\text{flux}}{SiO_2} \xrightarrow[\text{Air Blasting }\Delta\uparrow\uparrow]{\text{Bessemer Convertor}} \underset{\text{BLISTER Cu}}{\underline{\underline{Cu}}} + \underset{\text{slag}}{FeSiO_3}$$

$FeS + O_2 \longrightarrow FeO + SO_2\uparrow$

$FeO + SiO_2 \longrightarrow FeSiO_3$ (slag)

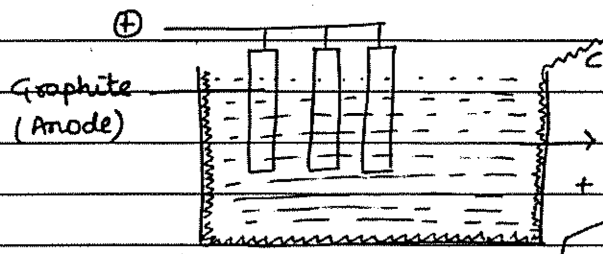
Till slag formation continues, green flames on mouth appear. After no green flame visible, slag is removed.

$Cu_2S + 2Cu_2O \xrightarrow{\Delta} 6Cu + SO_2\uparrow$

$Cu_2S + O_2 \longrightarrow Cu_2O + SO_2$ (minor than FeS)

3. ELECTROLYTIC REDUCTION – Applicable for s block metals + Al (strong R.A.)

a) Extraction of Al from Alumina = Hall Heroult Process



→ molten ~~Fe~~ Al_2O_3 (12-13%)
+ Na_3AlF_6 + CaF_2
Cryolite (85%) Fluorospar ~~15%~~ (2-3%)

main electrolyte ← Cryolite

Neutral Flux (2250°C → 950°C)
→ ① decreases MP of Alumina
② increases conductivity

economic ✓ ; decreases energy consumption

Cryolite → increases decomposition of Alumina

जो SRP में जितना नीचे आएगा, Cathode पर पहले जाएगा।

$$2AlF_3 \longrightarrow 2Al^{+3} + 6F^-$$

$$6F^- \xrightarrow{-6e^\ominus \text{ oxidation}} \boxed{3F_2}$$

$$3F_2 + Al_2O_3 \xrightarrow{-3/2\, O_2} 2AlF_3$$

(F_2 displaces O_2
$F_2 > Cl_2 > O_2 > N_2$)

$$2Al^{+3} \xrightarrow{6e^\ominus \text{ Red}^n} 2Al \text{ (Cathode)}$$

$$Al_2O_3 \longrightarrow 2Al^{+3} + 3O^{-2}$$

$$3O^{-2} \xrightarrow{-6e^\ominus} \frac{3}{2}O_2 \xrightarrow{C} CO + CO_2$$

(anode)

↓ corrosion of anode

If, on surface, powdered coke is put, SA↑, reactivity ↑, so graphite anode is less corroded.
Coke layer also reduces excessive metal shining.

b) Extraction of Na from NaCl = DOWN'S PROCESS

Cathode = Fe   Anode = Graphite

Electrolyte = Molten NaCl + $\underbrace{CaCl_2 + KF}_{\text{Neutral Flux}}$ (900°C → 600°C)

$$\begin{array}{ccccc} NaCl & \longrightarrow & Na^+ & + & Cl^- \\ & & \downarrow e^{\ominus} & & \downarrow -e^{\ominus} \\ & & \underset{\text{Cathode}}{\underline{Na}} & & \underset{\text{Anode}}{\underline{\frac{1}{2}Cl_2}} \end{array}$$

c) Preparation of NaOH by Nelson's Cell / Diaphragm ~~Ste~~ Cell

C = Fe / steel $NaCl \rightarrow Na^+ + Cl^-$
A = Graphite $H_2O \rightarrow H^+ + OH^-$
E = NaCl (aq.)

$$H^+ \xrightarrow{e^{\ominus}} \frac{1}{2}H_2 \text{ (Cathode)}$$

$$Cl^- \xrightarrow{-e^{\ominus}} \frac{1}{2}Cl_2 \text{ (anode)}$$

Parallel rxn. (minor)

① $Cl_2 + NaOH \longrightarrow NaCl + NaOCl + H_2O$

② $4OH^- \xrightarrow{\text{anode}} 4OH + 4e^{\ominus}$

$$\begin{array}{c} 4OH \\ \downarrow \\ 2H_2O + O_2 \end{array}$$

3) NaOH preparation by Castner – Kellner Cell.

→ C = Hg
A = Graphite
E = Brine solⁿ of NaCl (saturated) $[Na^+ + Cl^-]\uparrow\uparrow$, so H_2O dissociation ↓.

C and E taken such as to reduce Na^+ instead of H^+

$$\begin{tikzcd}
\mathrm{NaCl} \arrow[r] & \mathrm{Na^+} \arrow[d, "+e^{\ominus}", "\text{cathode}"'] & +\ \mathrm{Cl^-} \arrow[r, "-e^{\ominus}"] & \frac{1}{2}\mathrm{Cl_2}\ (\text{anode}) \\
& \mathrm{NaHg} \arrow[r, "H_2O", "-Hg"'] \arrow[loop left, "Hg"] & \mathrm{NaOH} + \frac{1}{2}\mathrm{H_2}\ (\text{not explosive})
\end{tikzcd}$$

$Na + H_2O$ can be controlled by adding Hg

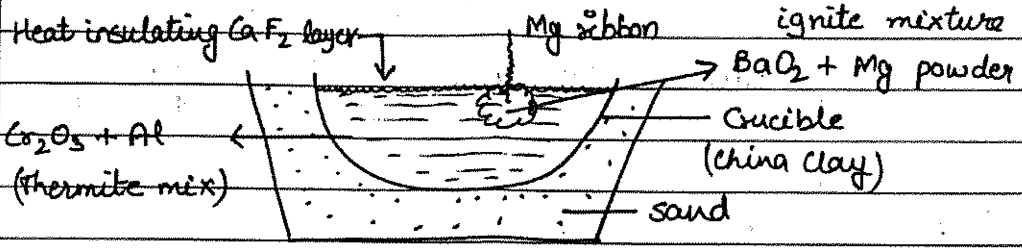
4. ALUMINO - THERMITE PROCESS = GOLD SCHMIDT METHOD

→ Some MO can't be reduced by C, even at high temperature.

→ $CaO + 3C \xrightarrow{\Delta} CaC_2 + CO\uparrow$

→ Applicable for Cr_2O_3, MnO_2, TiO_2, B_2O_3, etc.

→ Al is used as R.A. as it has strong affinity with O_2 and formation of Al_2O_3 is highly exothermic



$$Cr_2O_3 + 2Al \xrightarrow[\text{ignition}]{3300^\circ C} 2Cr + Al_2O_3 \quad (\Delta H = \ominus)$$

→ $Fe_2O_3 + 2Al \xrightarrow{\Delta} Al_2O_3 + 2Fe$

This reaction is used in thermite welding, usually in joints in railway track.

5. REDUCTION By H_2 – Applicable for GeO_2, WO_3, MoO_3.

$MoO_3 + 3H_2 \longrightarrow 3H_2O + Mo.$

→ Generally H_2 is not used as R.A due to –

a) explosive nature.
b) expensive process
c) it can form metal hydride

6. REDUCTION By Na, Mg or Ca –

→ Applicable for $TiCl_4$, VCl_3, B_2O_3

$TiCl_4 + 2Mg \longrightarrow 2MgCl_2 + Ti$ KROLL'S PROCESS.

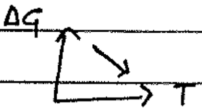
ELLINGHAM DIAGRAM :- ΔG v/s T for oxides formⁿ.

→ $\Delta G = \Delta H - \Delta S\ T$ slope = M = $-\Delta S$

$y = +C - M\ X$

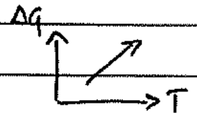
→ $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$

$\Delta S = \oplus \Rightarrow$ slope $= \ominus \Rightarrow$



→ $M(s) + \frac{1}{2}O_2(g) \longrightarrow MO(s)$

$\Delta S = \ominus$; slope $= \oplus \Rightarrow$



① $2Ag(s) + \frac{1}{2}O_2(g) \longrightarrow Ag_2O(s)$

$\Delta G = \oplus$ above 300°C ⇒ non spontaneous.

Decomposition temp. for Ag_2O = 300°C

Temp > Decomp. temp ⇒ only decomposition

Temp < ——"—— ⇒ only formation

② Decomposition temp. for HgO = 400°C

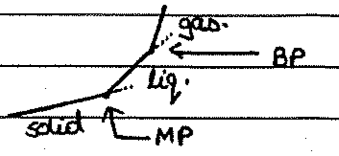
——"—— $Cu_2O < \cancel{\geq} FeO$ (same for T.S.)

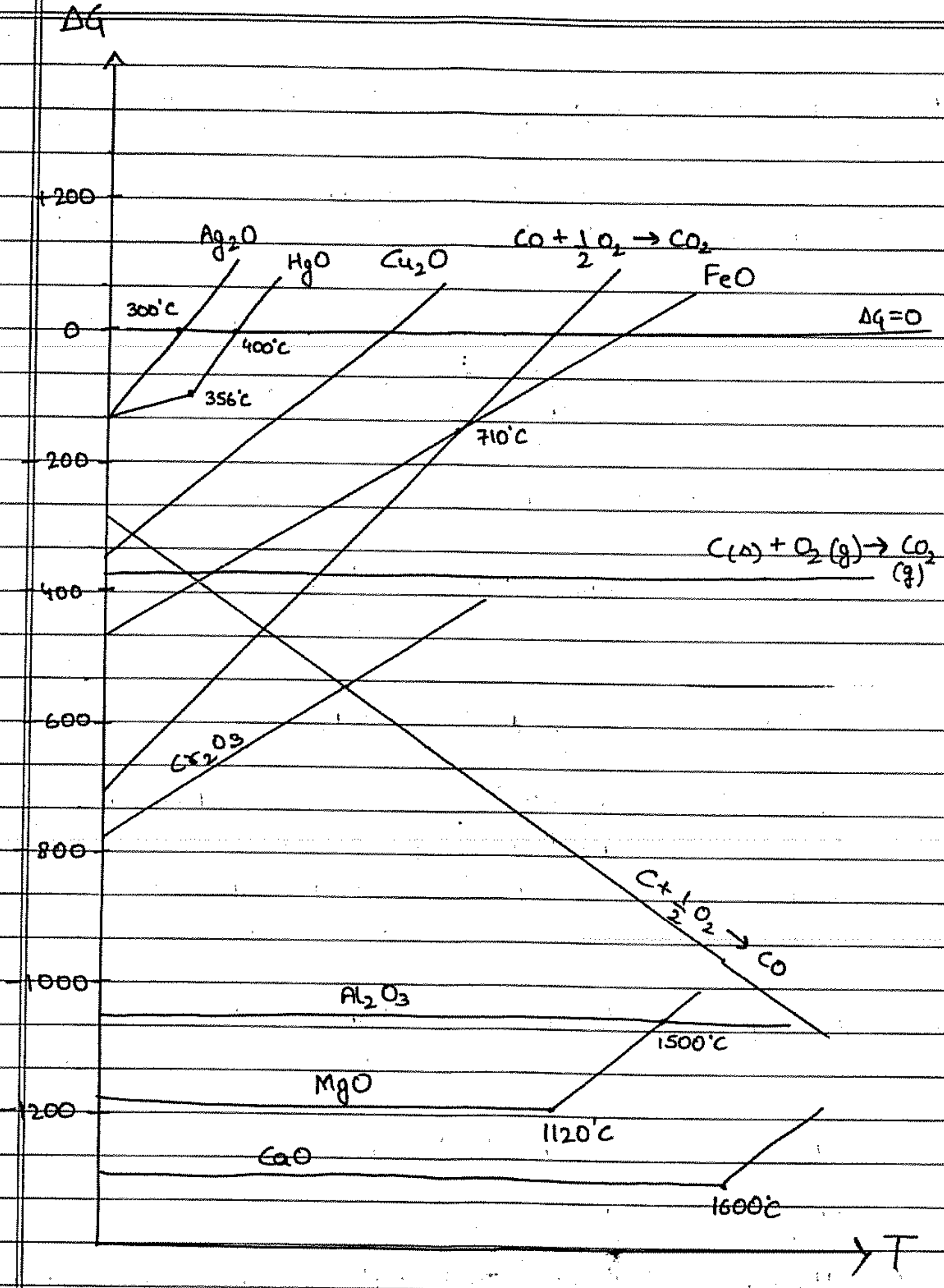
③ $Hg(l) + \frac{1}{2}O_2(g) \longrightarrow HgO(s)$ $\Delta S = \ominus$ slope $\oplus$ ↗

BP ↓ 356°C

$Hg(g) + \frac{1}{2}O_2(g) \longrightarrow HgO(s)$ $\Delta S = \ominus \uparrow$ slope $\oplus \uparrow$ ↗

* Metal :-




ΔG
+200
Ag_2O
HgO
Cu_2O
$CO + \frac{1}{2}O_2 \rightarrow CO_2$
FeO
300°C
0
400°C
ΔG=0
356°C
710°C
200
$C(s) + O_2(g) \rightarrow CO_2(g)$
400
600
Cr_2O_3
800
$C + \frac{1}{2}O_2 \rightarrow CO$
1000
Al_2O_3
1500°C
MgO
1200
1120°C
CaO
1600°C
T

(a) $2Al(s) + \frac{3}{2}O_2(g) \longrightarrow Al_2O_3(s)$ $\Delta G = -1000$ kJ/mol.

$Cr_2O_3(s) \longrightarrow 2Cr(s) + \frac{3}{2}O_2(g)$ $\Delta G = +550$ kJ/mol.

(b) $2Al + Cr_2O_3 \longrightarrow Al_2O_3 + 2Cr$ $\Delta G = \ominus$ spontaneous

Cr_2O_3 का reduction Al से possible hai; reverse not true.

* ऊपर आने वाली Metal oxide को नीचे आने वाली Metal reduce कर सकता है। Reverse not true.

* जिस Temp पर कोई Metal oxide $\Delta G = 0$ line cross करता है, वो उसका Thermal decomposition temp. है।

→ Cr_2O_3 can be reduced by Al; But Al_2O_3 can't be reduced by Cr.

→ CO is better R.A. for FeO @ low temperature. (< 710°C) But C is better R.A for FeO @ high temp.

→ Below 1500°C, Al_2O_3 can be reduced by Mg.
Above 1500°C, MgO can be reduced by Al.

→ @ 1500°C, net ΔG for formation of Al_2O_3 and that for decomposition for MgO = 0. (eqⁿ).

- **REFINING** :-

1. **LIQUATION** – Applicable for Sn, Pb, Sb, Bi.

→ These metals have low MP in comparison to their impurities.

2. <u>FRACTIONAL DISTILLATION</u> – Applicable for Zn, Cd, Hg

→ Based on difference in BP of metal and impurities.

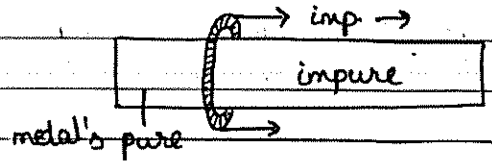
$$\underset{+\,Fe,\,Cu,\,Cd}{Zn} \xrightarrow[-Cd\uparrow]{>767^\circ C} \underset{+\,Fe,\,Cu}{Zn} \xrightarrow{>920^\circ C} \begin{cases} Zn\uparrow \xrightarrow{cool} Zn(s) \\ Fe + Cu \text{ (as residue)} \end{cases}$$

3. <u>ZONE REFINING</u> – Applicable for Si, Ge, Ga.

→ This method is used to obtain highly pure form of metal.

→ Impurities are more soluble in molten metal than in ~~pure~~ solid metal,

→ Pure metal is easily solidified, impure is difficult.

→ 

4. <u>VAPOUR PHASE REFINING</u> –

a) <u>MOND'S PROCESS</u> – Applicable for <u>Ni</u>

$$\underset{\hookrightarrow \text{Non-volatile}}{Ni + imp} + 4\,CO \xrightarrow{50^\circ - 60^\circ C} [Ni(CO)_4] \text{ volatile}$$

$$\downarrow 150 - 170^\circ C$$

$$\text{(pure) } Ni + 4CO\uparrow$$

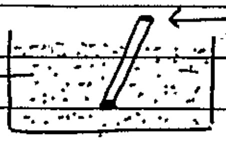
4) VAN-ARKEL PROCESS - Applicable for Ti, Zr.

$$\underset{\text{non volatile}}{Ti + imp. + 2I_2} \xrightarrow{\Delta} \underset{\text{volatile}}{TiI_4} \xrightarrow{1700 K} \underset{\text{pure}}{Ti} + 2I_2$$

5. POLING METHOD -

→ Used when metal has impurity of its own oxide.

→ $Cu + Cu_2O$
$Sn + SnO_2$
$Pb + PbO_2$


molten Cu + Cu_2O

stirred by GREENWOOD, full of hydrocarbon that undergo pyrolysis to give small hydroc., CH_4 → R.A.

$$Cu_2O \longrightarrow Cu$$
$$\downarrow$$
$$CO_2 + H_2O$$

Upon stirring, impurities also reach surface, when they come in contact with air which form 2 kinds of oxides → volatile (↑), and non volatile (form scum on surface, can be removed).

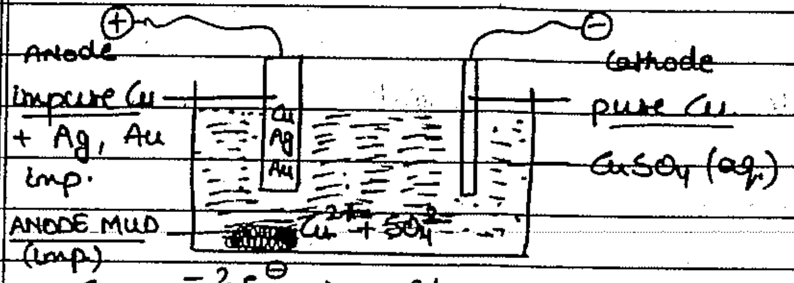
6. CUPELLATION METHOD - Applicable for Ag or Au (Pb imp)

→ When impurities are easily oxidised by air, but oxidation of metal is not possible.

→ Cupell is made of bone ash, can absorb Pb dissolved refining, and rest come in contact with air, form volatile PbO.

7. ELECTROLYTIC REFINING - Applicable for Cu, Ag, Au, Al, Sn, Pb, Zn, etc.

a) Cu Refining –

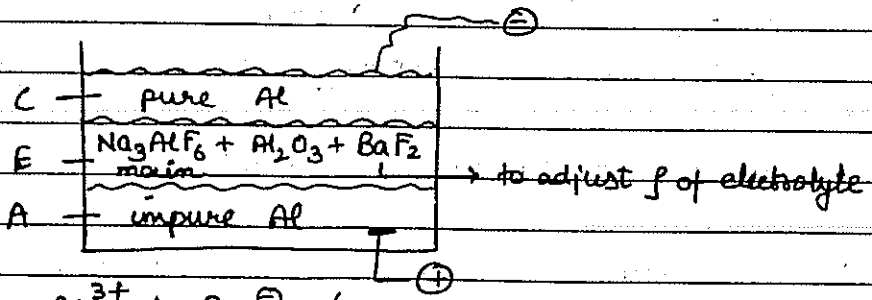


$Cu \xrightarrow[oxid^n]{-2e^{\ominus}} Cu^{2+}$ (Anode)

$Cu^{2+} \xrightarrow[red^n]{+2e^{\ominus}} Cu$ (cathode)

If there are Fe, Zn imp, they come in sol^n but can't deposit on Anode as they have ⊖ SRP.

b) Al Refining – HOOP'S PROCESS



$Al \longrightarrow Al^{3+} + 3e^{\ominus}$ (anode → electrolyte)
$Al^{3+} \longrightarrow Al +$ [illegible] (electrolyte → cathode)

c) Ag Refining
C = pure Ag
A = impure Ag
E = $AgNO_3$ sol^n

d) Au Refining
C = pure Au
A = impure Au
E = $AuCl_3$ sol^n

e) **Pb Refining** C = pure Pb
BETT'S PROCESS A = impure Pb
E = $PbSiF_6$ sol^n + dil. H_2SiF_6
(to increase overvoltage of H^+)

f) **Zn Refining** C = Al
A = impure Zn
E = $ZnSO_4$ sol^n + dil. H_2SO_4

8. **Fe - Refining** -

$$\underset{\substack{93\%\ Fe\ +\ 4\%\ C\ +\\ S,\ P,\ Mn,\ Si}}{\text{PIG IRON}} \xrightarrow[\text{air}]{\text{Fe strips}} \underset{3\%\ C\ +\ P, S, Si, Mn}{\text{CAST IRON}}$$

a) **Bessemerisation** :-

$$\underset{+\ C, P, S, Si, Mn}{\text{Cast iron}} \xrightarrow[\text{air}]{\text{in Reverberatory furnace, lined by CaO}} \underset{(0.5 - 1.5\%\ C)}{\text{Steel}}$$

$$C + O_2 \longrightarrow CO_2 \uparrow$$

$$\left.\begin{array}{l} S + O_2 \longrightarrow SO_2 \uparrow \\ Mn + \frac{1}{2} O_2 \longrightarrow MnO \\ \\ Si + O_2 \longrightarrow SiO_2 \end{array}\right] \longrightarrow \underset{\text{slag } (P\downarrow)}{MnSiO_3}$$

$$P_4 + 5O_2 \longrightarrow P_4O_{10}\ (\text{acidic}) \xrightarrow{CaO} Ca_3(PO_4)_2 \quad \text{Thomas slag}$$

b) **Pudding Process**

$$\text{Cast iron} \xrightarrow[\text{air}]{\text{in Reverberatory Furnace lined by } Fe_2O_3} \text{Wrought iron}$$

Purest Form.

+ C, P, S, Si, Mn

0.15 – 0.25 % C

Fe_2O_3

$$C + O_2 \longrightarrow CO_2 \uparrow$$

$$S + O_2 \longrightarrow SO_2 \uparrow$$

$$Mn + \frac{1}{2}O_2 \longrightarrow MnO$$

$$Si + O_2 \longrightarrow SiO_2$$

MnO, SiO_2] $MnSiO_3$ slag

$$P_4 + 5O_2 \longrightarrow P_4O_{10} \xrightarrow{Fe_2O_3} FePO_4 \text{ slag}$$

$Fe_2O_3 \downarrow$ Fe

9. **CHROMATOGRAPHY** –

→ Different components of a mixture are adsorbed in different entents on adsorbent.

10. **PERK'S PROCESS** – Applicable for Pb refining (Ag imp.)

$$\text{Molten Pb} + \text{Ag imp.} \xrightarrow{\text{Molten Zn}} \boxed{\begin{array}{c}\text{Molten Zn + Ag} \\ \hline \text{Molten Pb}\end{array}} \xrightarrow{\text{cooling}} \begin{cases}\text{Molten Pb} \\ \text{Solid Zn + Ag alloy}\end{cases}$$

$$\text{Solid Zn + Ag alloy} \xrightarrow{\Delta} Zn \uparrow + Ag.$$

s - block

* **FLAME TEST :-**

s-block metals give characteristic flame color due to excitation of $e^{\ominus}$ by absorption of heat. When these $e^{\ominus}$ come back to G.S., they emit absorbed energy in form of visible light.

- Be and Mg do not give flame test due to high I.P.

- Li = Crimson Red
  Na = Golden Yellow
  ~~Ca~~K = Violet
  Rb = Red - Violet
  Cs = Blue

- Ca = Brick Red
  Sr = Dark / Crimson Red
  Ba = Apple Green.

O^{2-} O_2^{-2} O_2^{-}

* **MONOXIDE / PEROXIDE / SUPEROXIDE -**

- All s-block metals form monoxide.

- Be, Mg, Li mainly form monoxide.

- Na, Ca, Sr, Ba can form peroxides in presence of excess O_2.

- K, Rb, Cs can form superoxides in presence of excess O_2.

- On the basis of IP values and Thermal Stability.

- Stability: Metal oxide > Metal peroxide > Metal superoxide
  (I.E.) O^{2-} O_2^{2-} O_2^{-}

- Oxidising Nature: Metal oxide < Metal peroxide < Metal superoxide.

- Peroxides are colorless and diamagnetic but superoxides are colored and paramagnetic.

- Some peroxides are also colored due to some impurities of superoxide ions
  e.g. Na_2O_2 = yellow

- Metal oxide + $H_2O \longrightarrow$ Metal Hydroxide

  —"— Peroxide + $H_2O \longrightarrow$ —"— + H_2O_2

  —"— Superoxide + $H_2O \longrightarrow$ —"— + H_2O_2 + O_2

- Peroxides or superoxides are useful for respiration in submarines, as they absorb CO_2 (g) and produce O_2 (g).

Q. Product formed when Na reacts with moist air

a) Na_2O
b) Na_2O_2
c) $NaOH$
[✓ d)] Na_2CO_3

$$2Na + \frac{1}{2}O_2 \longrightarrow Na_2O \xrightarrow{H_2O} 2NaOH \xrightarrow{CO_2} Na_2CO_3$$

- This is not exhibited by Be (IP ↑↑). Rest all s block ✓

- Except Be, all s block metals form Metal carbonates when reacts with moist air.

- Except Be, all s block metal surfaces become tarnished in presence of air due to oxide formation.

- Be is the least reactive s-block metal due to highest IP.

- Alkali metals are kept in kerosene, except Li (in wax).

* COMPOSITION OF CEMENT → CaO (50% - 60%)

SiO_2 (20 - 25%)
Al_2O_3 (5 - 10 %)
] Ratio 4 to 2.5

Fe_2O_3, MgO, SO_3, etc.

- $\text{Limestone + Silica + Alumine} \xrightarrow[\text{powder}]{\Delta} \text{Cement Clinker} \xrightarrow{\text{Gypsum}} \text{Cement}$

- Gypsum is used to slow down setting of cement, to increase hardness.

Q. Important ingredients of Portland Cement -

a) Dicalcium Silicate Ca_2SiO_4 (28 %)
b) Tricalcium Silicate Ca_3SiO_5 (51 %)
c) Tricalcium Aluminate $Ca_3Al_2O_6$ (11 %)
✓ d) All.

Q. Which of these is not a diagonal property of Li and Mg

a) Both LiCl and $MgCl_2$ are soluble in ethanol (C_2H_5OH)
b) Both LiCl and $MgCl_2$ are deliquescent
($LiCl \cdot 2H_2O$ and $MgCl_2 \cdot 8H_2O$)
c) Both Li_2O and MgO don't form superoxide
[✓ d)] Both Li and Mg vigorously react with cold water.

Q. Which of these is not an anomalous property of Li:

a) High MP and BP than any other alkali metal
b) Highest IP, but strongest R.A. due to highest H.E.
[✓ c)] All Li salts are water insoluble.
d) Li doesn't form ethynide with ethyne

Q. Which of these is not a diagonal property of Be and Al

a) Both Be and Al become inert in presence of conc. HNO_3.
b) Both $BeCl_2$ and $AlCl_3$ have bridged chloride structure
c) Both $Be(OH)_2$ and $Al(OH)_3$ are soluble in NaOH.
[✓ d)] Both Be and Al have max. C.N. = 6.

- Except LiCl, other alkali metal chlorides are not hygroscopic (due to larger size).

Q. A : Table salt is hygroscopic in nature
R : Table salt contains impurity of $MgCl_2$ and $CaCl_2$
(A)

Q. A: Impure NaCl sol^n is saturated by HCl(g)

R: Pure NaCl crystals separate out in presence of high conc^n. of Cl^- ions.

Ans (A)

$$NaCl + \underbrace{MgCl_2 + CaCl_2}_{\rightarrow \text{High } K_{sp}}$$
$$\downarrow HCl(g)$$
$$[Na^+][Cl^-] > K_{sp(NaCl)} \Rightarrow NaCl \text{ ppt.}$$

Q. A: Cs is used in photoelectric cell
R: Cs has least IP in PT.

Ans (A)

Q. A: $NaHCO_3$ is used as baking soda and fire extinguisher.
R: $NaHCO_3$ gives bubbles of $CO_2(g)$ on heating.

Ans (A)

Q. Which of these is incorrectly matched:

a) NaOH - deliquescent
b) Na(l) - used as coolant in nuclear reactor
c) KOH - best absorbent of CO_2
✓d) White Metal - Na + Sn (Li + Pb)

Q. A suspension of $Ca(OH)_2$ is k/a

a) Quick Lime (CaO) b) Lime Water aq. sol^n of Ca(OH
c) Slaked Lime ($Ca(OH)_2$) ✓d) Milk of Lime

- $CaO + H_2O \rightarrow Ca(OH)_2$ slaking of lime.

• Q. A suspension of $Mg(OH)_2$ = Milk of magnesia
= Antacid.

Q. Which of these metal hydrides is not obtained by direct reaction of metal and H_2

a) NaH b) CaH_2 (Hydrolith)
✓c) BeH_2 (least Be reactive) d) KH

$$2\,BeCl_2 + LiAlH_4 \longrightarrow 2\,BeH_2 + LiCl + AlCl_3$$

Q. Which of these is not correctly matched?

a) $NaHCO_3$ – amphoteric; used as antacid
b) NaCl – for making freezing mixture with ice
✓c) $CaCl_2$ (anhydrous) – drying agent for NH_3
d) $(NH_4)_2SO_4$ – fertiliser which increases acidity of soil

Q. Which of these is wrong – (7CUK)

a) CaO is used for purification of sugar.
b) NaOH is used in petroleum refining.
c) Mg is used in flashlight
d) Ra is used in treatment of cancer
e) Be is used for making windows of X-Ray Tubes
f) Mortar is a mixture of cement, sand and water.
g) $BeCl_2$ is obtained by Reductive chlorination of BeO
h) BeF_2 is obtained by thermal decomposition of

$$(NH_4)_2BeF_4 \longrightarrow 2NH_3 + 2HF + BeF_2$$

i) Tendency to form hydrated salts decreases down a group.

HYDROGEN & COMPD

HARDNESS OF WATER -

Due to Ca or Mg salts

- Ca^{2+} salt or Mg^{2+} salt + $2\ C_{17}H_{35}COO^{-}Na^{+}$ (soap) $\longrightarrow [(C_{17}H_{35}COO^{-})_2Ca^{2+}] \downarrow$ (scum)

- Types -

1. **TEMPORARY** - Due to presence of $Ca(HCO_3)_2$ or $Mg(HCO_3)_2$

Removal: a) By boiling : $Ca(HCO_3)_2 \xrightarrow{\Delta} \underset{ppt}{CaCO_3} + H_2O + CO_2$

$$Mg(HCO_3)_2\ (aq.) \xrightarrow{\Delta} \underset{(less\ K_{sp})}{Mg(OH)_2} \downarrow + H_2O + CO_2$$

b) **CLARK Method** - By using $Ca(OH)_2$

$$\underset{Amphoteric}{Ca(HCO_3)_2} + \underset{Base}{Ca(OH)_2} \longrightarrow 2\ CaCO_3 \downarrow + 2\ H_2O$$

2. **PERMANENT** - Due to chlorides or sulphates of Mg^{2+} or Ca^{2+}

Removal: a) By using Na_2CO_3

$$CaCl_2 + Na_2CO_3 \longrightarrow 2\ NaCl + CaCO_3 \downarrow$$

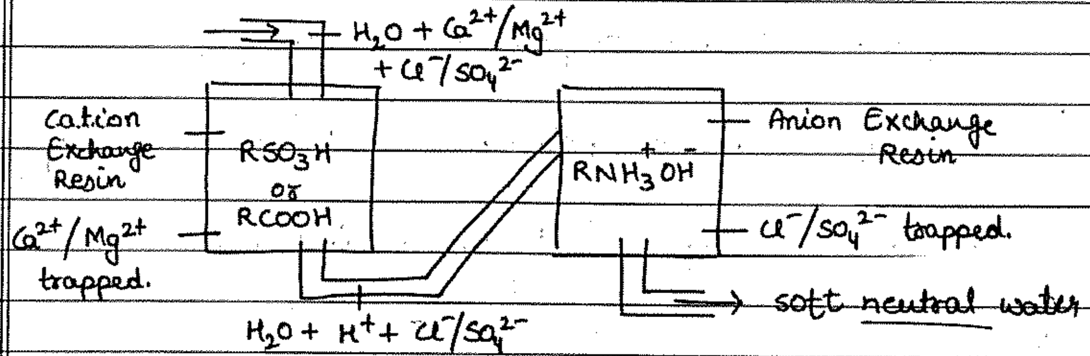
b) **PERMUTIT Method** - By using Sodium Zeolite ($Na_2Al_2Si_2O_8$)

$$Na_2Z + MgSO_4 \longrightarrow MgZ \downarrow + Na_2SO_4$$

c) By using Calgon ($Na_6P_6O_{18}$) (not a complex)

$$2CaSO_4 + Na_2[Na_4(PO_3)_6] \longrightarrow \underset{\text{soluble complex}}{Na_2[Ca_2(PO_3)_6]} + 2Na_2SO_4$$

d) Ion- Exchange Method



* HYDRIDES :-

IONIC / SALINE / SALT LIKE

s-block metal hydrides.

EXCEPT : BeH_2, MgH_2 (covalent)

ionic hydrides
molten; electrolysis
Anode → $H_2(g)$
aq. solⁿ; electrolysis
Cathode → $H_2(g)$
Anode → $H_2(g)$

COVALENT / MOLECULAR

p-block hydrides.

ⓐ $e^\ominus$ deficient
e.g. B_2H_6, $(AlH_3)_n$

ⓑ $e^\ominus$ precise; complete octet, 0 lp.
eg. CH_4, SiH_4

ⓒ $e^\ominus$ rich hydride
complete octet + lp
eg. $\ddot{N}H_3$, $H_2\ddot{S}$:

INTERSTITIAL

d- block metal Hydride

- Only possible hydride of group 6 is CrH.
- Metals of group 7, 8, 9 do not form any hydride. This is k/a "hydride gap".

* H_2O_2 :- HYDROGEN PEROXIDE

- PREPARATION :-

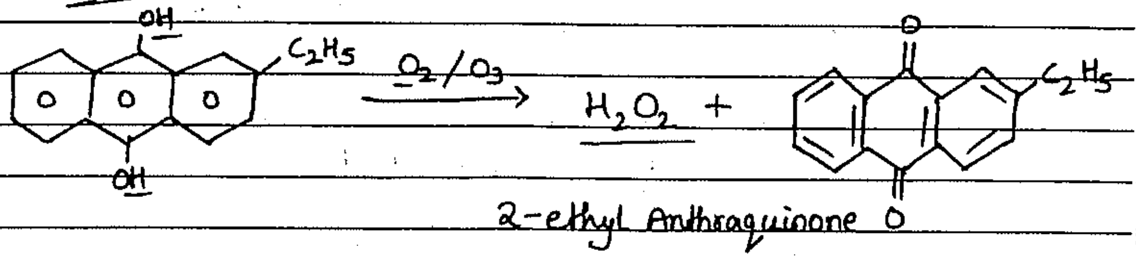
1. LAB – $Na_2O_2 + dil.\ H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$

2. MERCK'S PROCESS

$$BaO_2\cdot 8H_2O + \underset{\text{or } H_3PO_4}{dil.\ H_2CO_3} \longrightarrow H_2O_2 + \underset{\text{or } Ba_3(PO_4)_2}{BaCO_3}$$

dil. H_2SO_4 is not used here, as $Ba(HSO_4)_2$ catalyses decomposition of H_2O_2.

3. By OXIDATION OF 2-ethyl anthraquinol



2-ethyl Anthraquinone O

4. By ELECTROLYSIS OF 50% H_2SO_4 solⁿ –

$$2H_2SO_4 \longrightarrow 2H^+ + 2HSO_4^- \xrightarrow{2e^\ominus} H_2S_2O_8$$

$$2H^+ \xrightarrow{e^\ominus} H_2 \ \text{(cathode)} \qquad H_2S_2O_8 \xrightarrow{2H_2O} 2H_2SO_4 + H_2O_2$$

$\overset{-1}{O} \to \overset{-2}{O}$ $\overset{-1}{O} \to \overset{0}{O}$

- H_2O_2 can act as O.A. and R.A. both.

→ $\boxed{H_2O_2}$ (O.A.)

Fe^{2+} → Fe^{3+}
Mn^{2+} → Mn^{3+}
PbS (Black ↓) → $PbSO_4$ Colorless (Black spots on old oil paintings are removed)

$\boxed{H_2O}$

→ $\boxed{H_2O_2}$ (R.A.)

Acidified $KMnO_4$ → Mn^{+2}
$HOCl$ → Cl^-
$I_2 + OH^-$ → I^-

$\boxed{O_2}$

- 30% aq. sol^n of H_2O_2 = PERHYDROL
- H_2O_2 easily decomposes in presence of light, so it is stored in dark bottles
- Liq. H_2 is used as cryogenic agent
- Liq. H_2 + Liq. O_2 is used as rocket fuel.
- D_2O is used as neutron moderator.

Q. Highly pure (> 99.95 %) H_2 is obtained by:

a) Amphoteric metal + NaOH
b) Electrolysis of pure water — not possible; insulator
[✓ c)] Electrolysis of $Ba(OH)_2$ solⁿ
d) Bosch's Process

Ans a) $Al + NaOH \rightarrow NaAlO_2 + H_2$ (UNOXI METHOD)

c)
$$\begin{tikzcd} H_2O \arrow[r] & H^+ \arrow[d] & + & OH^- \arrow[r, "-e^{\ominus}"] & OH + OH \arrow[d] \\ & \text{(cathode)}\ \frac{1}{2}H_2 & & & H_2O + \frac{1}{2}O_2\ \text{(anode)} \end{tikzcd}$$

d)
$$\begin{tikzcd} C(s) + H_2O \arrow[r, "1270\ K", "\text{coal gassificaⁿ}"'] & {[CO + H_2]}\ \text{WATER GAS} \arrow[d, "H_2O\ \text{Water Gas shift rxn.}"] \\ & CO_2 + \underline{2H_2} \end{tikzcd}$$

whole : Bosch's process

$CO + H_2$ = Water gas
$CO + 3H_2$ = Syn gas.

* ISOTOPIC EFFECT ⇒ If different ~~isomers~~ isotopes of an element show different properties (mainly physical).
Due to – appropriate difference in atomic mass

- Applicable only for H.

* **NUCLEAR ISOMERS OF H** – On basis of spin of nucleus.

ORTHO H_2

PARA H_2

@ 0 K, 100% para H_2 exists

At room temp. ⇒ 75% ortho H_2 + 25% para H_2.

* **HEAT TREATMENT OF STEEL** –

1. **ANILING** :- $\text{Hard Steel} \xrightarrow[\downarrow \text{ Slow cooling}]{\text{Red Hot}} \underline{\text{Soft Steel}}$

Malleability ↑
Ductility ↑
Tensile Strength ↑

2. **TAMPERING / HARDENING** :-

$\text{Soft Steel} \xrightarrow[\downarrow \text{ Sudden cooling}]{\text{Red Hot}} \underline{\text{Hard steel}}$

Hard; Brittle.

3. **QUENCHING** :-

$\text{Hard Steel} \xrightarrow[\downarrow \text{ slow cooling}]{200^\circ C - 500^\circ C} \underline{\text{Hard steel}}$

Not brittle anymore.

4. **CASE HARDENING** :-

$\text{Iron} \xrightarrow[\Delta]{\text{Hydrocarbon}} \text{Layer of Fe Carbide}$

5. **NITRIDING** :-

$\text{Steel} \xrightarrow[\Delta]{NH_3} \text{Layer of Fe Nitride}$